ISOTOPIC COMPOSITION OF NITRATE AND AMMONIUM IN SÃO PAULO WET DEPOSITION

A Thesis

by

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This thesis meets the standards for scope and quality of Texas A&M University-Corpus Christi and is hereby approved.

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December 2021

ABSTRACT

Humans have altered the nitrogen cycle by emitting excess reactive nitrogen into the atmosphere causing ammonia (NH₃) and nitrogen oxides (NO_x) concentrations to increase exponentially over the last century. This excess nitrogen causes negative environmental and health effects by contributing to acid rain, decreased air quality, soil acidification, eutrophication, and a change in biodiversity. To better understand the nitrogen cycle, emission sources, and mitigation strategies, regional emissions of NH₃ and NO_x should be quantified. This study measured the stable nitrogen and oxygen isotope composition of nitrate (NO_3) and ammonium (NH^+) in wet deposition to estimate NH₃ and NO_x emission sources in the Ribeirão Preto region of São Paulo, Brazil from October 2018 through February 2020. The average NO₅ and N H⁺ concentrations throughout the sampling period were $13.1 \pm 10.0 \ \mu\text{M}$ and $31.0 \pm 24.2 \ \mu\text{M}$, respectively. The average δ^{15} N-NO₃, δ^{18} O-NO₃ and δ^{15} N-NH ⁺ values were -2.2 ± 4.5‰, 55.7 ± 7.8‰ and -4.0 ± 8.8‰, respectively. The δ^{15} N-NO₃ values were corrected for isotope f ractionation which occurs during the NO_x oxidation to HNO 3. The δ^{15} N-NO₃ and δ^{15} N-NH ⁺ values in wet deposition and δ^{15} N values of NO_x and NH ₃ emission sources were applied to the Stable Isotope Analysis in R (SIAR) mixing model to estimate source contributions. The NO_x emissions in Ribeirão Preto during the dry season were primarily from biogenic $(9.8 \pm 1.4\%)$, biomass burning $(49.8 \pm 1.8\%)$ and vehicle sources (40.4 \pm 2.5%). During the wet season, percent contributions for biogenic and vehicular sources were $18.6 \pm 5.3\%$ and $81.5 \pm 5.3\%$, respectively. NH₃ emissions in the dry season were primarily from agriculture (i.e. livestock waste, fertilizers) ($26.1 \pm 9.5\%$, $26.4 \pm$ 14.0%), vehicles $(21.6 \pm 8.2\%)$, and biomass burning sources $(25.9 \pm 18.8\%)$. In the wet season, livestock waste, fertilizers, and vehicles contributed $26.6 \pm 14.4\%$, $16.2 \pm 11.2\%$ and $57.2 \pm$ 23.3% of the NH₃ emissions, respectively. Lower summer δ^{18} O-NO₃⁻ values (55.6 ± 7.5‰)

indicate NO_x oxidation predominately through the OH radical pathway while increased winter δ^{18} O-NO₃⁻ values (69.9 ± 1.7‰) imply increased influence of the ozone oxidation pathway. Results of this study aid in understanding the NO_x and NH₃ emission sources and atmospheric processes affecting air quality in São Paulo, Brazil.

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TABLE OF CONTENTS

ABSTRACTiv
ACKNOWLEDGEMENTS vi
TABLE OF CONTENTS
LIST OF FIGURESix
LIST OF TABLES
CHAPTER I: INTRODUCTION
CHAPTER II: METHODS
2.1 Collection Site – Ribeirão Preto, São Paulo, Brazil
2.2 Rainwater Collection
$2.3\ NO_3{}^-$ and $NH_4{}^+$ Concentration – USP-RP
2.4 Ammonium Oxidation to Nitrite for Subsequent Isotope Analysis
2.5 NO_2^- Concentration Analysis to Check for NH_4^+ Conversion
2.6 Sample pH adjustment
2.7 Isotope Analysis (University of California - Davis & University of Pittsburgh)10
2.8 Air Mass Back Trajectory
2.9 Isotope Mixing Models
2.9.1 Mixing Model Endmember Selection: NO _x
2.9.2 Mixing Model Endmember Selection: NH ₃ 15

2.9.3 Mixing Model Endmember Eliminations	17
2.10 Calculation of nitrogen isotope fractionation associated with HNO ₃ formation	18
CHAPTER III: RESULTS & DISCUSSION	20
3.1 Nitrate concentration & N isotopic composition	20
3.2 Temporal Variation of NO_3^- concentrations and $\delta^{15}N-NO_3^-$ values	25
3.3 Spatial Variation of NO _{3⁻} concentrations and δ^{15} N-NO _{3⁻} values	31
3.4 Nitrate Oxygen Isotopic Composition	33
3.5 Temporal Variation of δ^{18} O-NO ₃ ⁻	33
3.6 Ammonium Concentration & N Isotopic Composition	36
3.7 Temporal Variation of NH_4^+ concentrations and $\delta^{15}N-NH_4^+$ values	39
3.8 Spatial Variation of NH_4^+ concentrations and $\delta^{15}N-NH_4^+$ values	44
3.9 NO _x source apportionment	45
3.10 NH ₃ source apportionment	49
CHAPTER IV: CONCLUSION / IMPLICATIONS	53
REFERENCES	55
APPENDIX A Overall data table including date, precipitation (mm), $[NO_3^-] \mu M$, $[NH_4^+] \mu$	М,
δ^{15} N-NH ₄ ⁺ , δ^{15} N- NO ₃ ⁻ , δ^{18} O-NO ₃ ⁻ , pH, back trajectory	68

LIST OF FIGURES

Page
Figure 1: Location of collection site (yellow circle) in Ribeirão Preto, São Paulo, Brazil7
Figure 2: Boxplots of average NO_3^- concentrations during a) wet and dry seasons and during b)
fall, spring, summer, and winter25
Figure 3: Box plots summarizing seasonal distribution of δ^{15} N-NO ₃ averages during a) wet and
dry seasons and during b) fall, spring, summer, winter27
Figure 4: Wet deposition mean concentration of NO_3^- by month from October 2018 – February
2020 sampling period. Shaded area representing dry season27
Figure 5: Comparison of results of δ^{15} N-NO ₃ ⁻ and δ^{18} O-NO ₃ ⁻ monthly average values over time
from October 2018 – February 2020. Shaded area representing dry season28
Figure 6: Comparison of results of δ^{15} N-NO ₃ ⁻ and NO ₃ ⁻ concentrations for each wet deposition
sample collected during the sampling period28
Figure 7: 24-hour air mass back trajectories for all sampling days in Ribeirão Preto, São Paulo,
Brazil, based on NOAA HYSPLIT model back trajectories. a) green lines represent dry season
and red lines represent wet season b) Blue tone lines represent dry seasons (light blue, fall; dark
blue, winter) and red tones represent wet seasons (red, spring; orange, summer)32
Figure 8: Box plots summarizing seasonal distribution of δ^{18} O-NO ₃ averages during a) wet and
dry seasons and during b) fall, spring, summer, winter36
Figure 9: Comparison of results of δ^{18} O-NO ₃ ⁻ and NO ₃ ⁻ concentrations for each wet deposition
sample collected during the sampling period36
Figure 10: Wet deposition mean concentration of NH_{4^+} by month from October 2018 – February
2020 sampling period. Shaded area representing dry season40

Figure 11: Box plots of average NH_{4^+} concentrations during a) wet and dry seasons and during b)
four weather seasons of sampling41
Figure 12: δ^{15} N-NH ₄ ⁺ values over time from October 2018 – February 2020. Shaded area
representing dry season43
Figure 13: Box plots summarizing seasonal distribution of δ^{15} N-NH ₄ ⁺ averages during a) wet and
dry seasons and during b) fall, spring, summer, and winter43
Figure 14: Linear regression of δ^{15} N-NH ₄ ⁺ and NH ₄ ⁺ concentrations for each wet deposition
sample collected during the sampling period44
Figure 15: δ^{15} N-NO _x source apportionments for biogenic, biomass burning, and vehicles over
time from October 2018 – February 2020. Shaded area representing dry season48
Figure 16: Average NO_x and NH_3 source apportionments for dry and wet seasons. Samples from
October 2018 – February 202049
Figure 17: Monthly average δ^{15} N-NH ₄ ⁺ source apportionments for agriculture, biomass, and
vehicles over time from October 2018 – February 2020. Shaded area represents the dry season 50
Figure 18: Fires detected in the state of São Paulo by satellite systems corresponding to the
biomass contributions51

LIST OF TABLES

Table 1. Known isotopic signature ranges for atmospheric NO _x sources (Elliott et al., and
references therein)17
Table 2. Known isotopic signature ranges for atmospheric NH ₃ sources (Chang 2016, Felix et al.,
2013, Freyer 1978, Walters et al., 2020, Kawashima and Kurahashi, 2011)18
Table 3. Seasonal mean [NO ₃ ⁻] (μ M), mean δ^{15} N-NO ₃ ⁻ , weighted mean δ^{15} N-NO ₃ ⁻ values, mean
δ^{18} O-NO ₃ ⁻ (‰), and weighted mean δ^{18} O- NO ₃ ⁻ values (‰) 22
Table 4. Average concentration of $NO_{3}^{-}(\mu M)$ and $NH_{4}^{+}(\mu M)$ in rainwater in Ribeirão Preto,
Brazil (this study) and various locations across the globe 23
Table 5. Range and average of δ^{15} N-NO ₃ ⁻ , δ^{18} O-NO ₃ ⁻ , and δ^{15} N-NH ₄ ⁺ in rainwater in Ribeirão
Preto, Brazil (this study) and other various locations across the globe24
Table 6. Seasonal mean [NH ₄ ⁺] (μ M), mean δ^{15} N-NH ₄ ⁺ (‰), and weighted mean δ^{15} N-NH ₄ ⁺
values (‰). (Note: 44 wet deposition samples were collected for analysis, 2 samples were unable
to undergo proper analysis and were eliminated from the results interpretation therefore, $n = 42$)
40
Table 7. Average NO_x and NH_3 source apportionments for dry and wet seasons. Samples from
October 2018 – February 2020 48

CHAPTER I: INTRODUCTION

Humans convert significant amounts of natural occurring atmospheric nitrogen (N₂) to reactive nitrogen (N_r) compounds (e.g. NO, NO₂, NO₃⁻, NH₃, and NH₄⁺) and have greatly altered the nitrogen cycle by emitting this excess N_r to the environment. Nitrogen as N₂ comprises 78% of the Earth's atmosphere by volume and can react with other elements through natural (e.g. microorganisms, lightning) or anthropogenic processes (e.g. fertilizer production, fossil fuel combustion) to produce N_r (Manahan, 2017). The elevated amounts of N_r result in negative impacts including acid rain, decreased air quality, eutrophication, soil acidification, and changes in biodiversity (Davidson et al., 2012). Globally, anthropogenic NO_x (i.e. NO + NO₂) emissions (e.g. vehicles and power plants) have increased exponentially since the industrial revolution far exceeding naturally occurring emissions from soil biomes, biomass burning and lightning (Fang et al., 2011; Galloway et al., 2004).

In comparison to the United States and other developed countries, Brazil is lagging behind in implementing current NO_x emission regulations needed to prevent environmental pollution. The United States enacted the Clean Air Act Amendments and ratified the NO_x Cap and Allowance Trading Programs to mitigate adverse NO_x effects. These laws helped reduce the NO_x from stationary sources by > 50% of the unregulated 1990 levels (U.S. EPA, 2019). Brazil's program mimics the United States Tier 3 regulations to guide and improve their own standards. In 1986, Brazil implemented PROCONVE (Programa de Controle de Poluição do Ar por Veículos Automotores), a regulatory program to improve emission performance on new vehicles (Dallman & Facanha, 2017). This program regulates some passenger vehicles and light commercial vehicles under its LD (light duty) regulatory program however, PROCONVE falls behind other international regulatory practices. In Brazil diesel vehicles account for 40% of the

total LD vehicle NO_x emissions (Dallmann & Facanha, 2017). To improve this, Brazil plans to strengthen emission standards implemented in the latest version of PROCONVE (Dallmann & Facanha, 2017).

Metropolitan areas in Brazil, including the São Paulo region, experience atmospheric N pollution from both anthropogenic and natural sources. Previous studies in the state of São Paulo, estimated a total of 1080 tons of NO_x emissions per year in the southern region and 19,440 tons in the central region of the state (Allen et al. 2011). Biomass burning influences the NO_x emissions in Brazil and varies from wet to dry seasons. The climate in Brazil is defined by two seasons, wet (October – March), and the dry, winter season (April - September) (Godoy-Silva, 2017). During dry seasons, shrubs, grasslands, and forests are susceptible to burning from natural and man-made fires, causing local air pollution in Brazil, while during the wet season, the tropical rain belt pours constant rain preventing any form of fire ignition (de Souza et al., 2015; Chang et al., 2021).

South America is home to the Amazon, the largest rainforest in the world, with most of it located in Brazil. From July 2019 to January 2020, intense fires in the Amazon rainforest along the Bolivia-Paraguay border sent smoke clouds as far as São Paulo, 2,700 km away. Satellites from NOAA and NASA monitored the spread of the wildfires during this time and captured smaller fires which burned daily (Voiland, 2020). Brazil's National Space Research Institute (INPE) detected more than 9,500 forest fires, mostly in the Amazon, between August 15 - 20, 2019 (Yao, 2020). By the end of 2019, 17.9 million acres of Brazil's Amazon burned, which is almost the size of West Virginia in the United States (Rainforest Foundation, 2020). These forest fires contributed to NO_x emissions in the region.

Contrary to NO_x regulation, in most countries outside the European Union, there are no regulations for ammonia (NH₃) emissions despite known environmental and health effects associated with direct emissions, transformation products and deposition. NH₃ emissions are influenced by climatic interactions, nearly doubling every 5°C with the warming of Earth's atmosphere (Sutton et al., 2013). Emissions world-wide will potentially increase 43% by the year 2100 if the global temperature increases 5°C (Sutton et al., 2013).

The agriculture industry is the largest source of global NH₃ emissions, (e.g. volatized livestock waste and fertilizer), contributing about 85% of the total emissions (Zhu et al., 2015). Agriculture cultivation, the process relating to the care and growth of plants and soil alone, is responsible for about 30% of the total NH₃ emissions (Allen et al., 2011). Other studies have estimated that domestic livestock, fertilizers, and agricultural crops contribute 40%, 17% and 7%, respectively to global NH₃ emissions (Erisman et al., 2007, Asman et al. 1998, Bouwman et al., 1997). This significant agricultural source is apparent in Brazil where anthropogenic N_r emissions have doubled from 1995 to 2002 due to activities related to the production of food and energy (Filoso et al. 2006). In Brazil's tropical areas, an increase of N_r in the atmosphere is emitted primarily due to land-use change (deforestation and afforestation), agriculture expansion, and installation of new industries (Allen et al., 2011, Smith et al., 2014). As primary contributors to the economy, sugarcane cultivation and livestock pose great influence and perpetuates São Paulo's atmospheric emissions (Allen et al., 2011, CETESB, 2008).

Ammonia and NO_x emissions can be deposited as ammonium (NH₄⁺) and nitrate (NO₃⁻) in wet deposition (rain, snow, and fog). NH₃ atmospheric lifetime is short, 24 hours or less, however once converted to aerosol NH₄⁺ it can remain in the atmosphere for several days to a week, therefore having the capability to be transported over long ranges (Zhu et al., 2015). NO_x

atmospheric lifetime is less than 24 hours due to being lost in HNO₃ formation and aerosol uptake. The acidic HNO₃ product formed can survive up to 5 days in the atmosphere (Aneja et al., 2001). The longer the lifetime of atmospheric gases, the further the distance it travels downwind, while experiencing an exponential concentration decrease further from the emission source (Aneja et al., 2001; Asman et al., 1998; Berner & Felix, 2020). Atmospheric NO_x and NH₃ deposited downwind can be incorporated into the environment (such as deposited to the soil and bodies of water) or released back into the atmosphere.

Continued advancements in isotope investigation techniques provide the ability to trace source emissions and estimate NO_x and NH₃ source contribution to NO₃⁻ and NH₄⁺ deposition. NO_x and NH₃ emission sources have varying δ^{15} N "source signatures," (Tables 1 and 2) which allow for differentiation among sources. However once released to the atmosphere, the δ^{15} N values of NO_x and NH₃ can change over time due to fractionation processes associated with physical and chemical pathways (Elliot et al. 2019). The isotopic fractionation of NO_x during equilibrium exchange and photochemical pathways influences the δ^{15} N values (Li et al., 2020). The ¹⁵N fractionation varies depending on the oxidation pathway undergone in either the daytime or nighttime, described in reactions 1 – 6 (R1- R6). NO and NO₂ cycling is the primary first fractionation pathway during the day and night. During the daytime "OH" pathway" (R1 to R3), NO₂ is then oxidized to HNO₃ via OH radical (Fang et al., 2011). During the nighttime "N₂O₅ pathway" (R4 to R6), NO₃ radical is produced and combined with NO₂ to form N₂O₅. Hydrolysis of N₂O₅ yields HNO₃ (Elliot et al., 2019).

The extent of these HNO_3 formation pathways can be modeled using ¹⁸O-NO₃⁻ and allow for prediction of the ¹⁵N fractionation associated with the formation (Chang et al., 2019, Walters and Michalski, 2016). Ozone and OH contributes 2/3 and 1/3 of the oxygen to the formation of HNO₃ through the OH pathway whereas, the N₂O₅ pathway forms HNO₃ with 5/6 O₃ and 1/6 H₂O oxygen contributions (Hastings et al., 2003, Fang et al., 2011). Due to less oxygen contribution from ozone with relatively high δ^{18} O, the HNO₃ formed during the OH pathway will have lower δ^{18} O values than those formed during the N₂O₅ pathway (Fang et al., 2011). The δ^{18} O value fluctuates with seasonal variations due to an increase and decrease of sunlight present during the summer months and winter months, respectively. The oxidation of NO₂ to HNO₃ with the OH radical is prevalent in summer months when the OH radical concentration is the highest. However, during winter months the N₂O₅ is thermally stable, therefore it is more widespread during this time. The δ^{18} O-NO₃⁻ can be applied to determine the percent contribution of each oxidation pathway and the associated ¹⁵N fractionation with the pathways can be used to determine the original δ^{15} N-NO_x value contributing to δ^{15} N-NO₃⁻ in rain (Felix & Murgulet, 2020).

Daytime	
$NO + O_3 \rightarrow NO_2 + O_2$	R (1)
$NO_2 + h\nu \rightarrow NO + O(^3P)$	R (2)
$NO_2 + OH \rightarrow HNO_3$	R (3)
Nighttime	
$NO_2 + O_3 \rightarrow NO_3 + O_2$	R (4)
$NO_2 + NO_3 + M \rightarrow N_2O_5$	R (5)
$N_2O_5 + H_2O aerosol \rightarrow 2HNO_{3(aq)}$	R (6)

An alternative approach to determining the ¹⁵N fractionation associated with the equilibrium and photochemical reactions is presented by Li et al., 2020. The Li study measured the NO and NO₂ in a simulation chamber. Simulations with known NO and O₃ levels were coupled with the measured δ^{15} N value of NO₂ to model the fractionation effect associated with both equilibrium exchange and the NO_x photochemical cycle. This study ultimately uses rate constants, O₃ concentration and the NO₂/NO_x ratio to determine the ¹⁵N fractionation effect during NO_x oxidation. Before utilizing isotope mixing models to determine NO_x sources

contributing to the δ^{15} N of NO₃⁻ in rainwater, the potential fractionation occurring during HNO₃ formation must be determined. While NH₃ can also undergo fractionation during equilibrium and kinetic conversion to NH₄⁺, it is often assumed that rainwater scavenges both species, resulting in both sourcing to rainwater δ^{15} N-NH₄⁺ thus the fractionation effect is considered negligible.

In this study, isotopic techniques are used to investigate NO_3^- and NH_4^+ in wet deposition samples collected in Ribeirão Preto, São Paulo, Brazil. The major objectives were to determine dominant NO_x and NH_3 emissions sources in the region, determine how these sources change seasonally, and provide a better understanding of NO_x and NH_3 transportation and processing in the atmosphere. Assessing N_r emission source contributions empowers people to adapt their behavior and policies and create informed air quality mitigation strategies to protect the environment and their health.

CHAPTER II: METHODS

2.1 Collection site – Ribeirão Preto, São Paulo, Brazil

The rainwater collection site was located on the University of São Paulo – Ribeirão Preto (USP-RP) campus in Ribeirão Preto, São Paulo, Brazil ($21^{\circ}09^{\circ}58.64S$, $47^{\circ}50^{\circ}42.960$ W), Figure 1. São Paulo is the largest state in Brazil, located in the southeast subtropical region bordering the Atlantic Ocean. The state has an area of $248 \times 10^8 \text{ km}^2$ (Allen et al., 2011). São Paulo has important agricultural and industrial economic sectors as well as defined wet and dry seasons (Allen et al., 2011). The wet and dry seasons typically occur from October – March and April – September, respectively (Godoy-Silva, 2017).

The city of Ribeirão Preto is a municipality located in the northeast region of the state. Therefore, its economy is based primarily on the agro-industries. The city's population is ~600,000 and the distance to the South Atlantic Ocean is ~338 kilometers (Coelho et al., 2011).



Figure 1. Location of collection site (yellow circle) in Ribeirão Preto, São Paulo, Brazil

2.2 Rainwater collection

Rainwater samples (n = 44) were collected from October 2018 – February 2020 using a wet-only automatic collector. The automatic collector remains covered in the field. During rain events, a constant flow of rainwater passes through the sensor initiating the lid on the collector to open. Rainwater flowed through a glass funnel and into a glass bottle. When the event culminated, the lid closed. Samples were collected immediately after every rain event. The glass funnel and bottle from the collection device was replaced with a clean set of glassware after each rain event. Rain samples were filtered immediately after collection using 0.2 μ m polyethersulfone membranes then stored at -22°C until analysis (Crispim et al., 2018).

2.3 NO_3^- and NH_4^+ Concentration – USP-RP

The concentrations were measured in the filtered rain samples at USP-RP by using a Metrohm 761 Compact ion chromatograph equipped with a conductivity detector (Coelho et al., 2011) before shipment to Texas A&M University – Corpus Christi (TAMU-CC) to be processed for subsequent isotope analysis. The concentration measurement is further described in Leal et al., 2004.

2.4 Ammonium oxidation to nitrite for subsequent isotope analysis

Samples were prepared for NH_4^+ oxidation by first diluting the NH_4^+ concentration to 10 μ M using 18.2 M Ω -cm water. Samples with concentrations lower than 10 μ M did not require a change in concentration. Ammonium in the samples was converted to nitrite (NO_2^-) via bromate oxidation (Zhang et al., 2007) before analysis so the isotopic composition can be measured via the bacteria denitrifier method (Sigman et al. 2001). The oxidation was performed at TAMU-CC, then samples were shipped to isotope laboratories (University of California, Davis, and the University of Pittsburgh Stable Isotope Laboratories) to complete the bacterial denitrifier method

and isotope analysis. The bromate/bromide stock solution was prepared by mixing 0.6 grams of sodium bromate (NaBrO₃) and 5 grams of sodium bromide (NaBr) to 250 mL of 18.2 MΩ-cm water. Next, the bromate/bromide working solution was prepared by mixing 1 mL bromate/bromide stock solution with 50 mL of 18.2 MΩ-cm water, and 3 mL of 6 N hydrochloric acid. The mixture was left in the dark for 5 minutes to react, following an addition of 50 mL 6 N sodium hydroxide (NaOH). 10 mL of the rain samples were placed in 15 mL centrifuge tubes and labeled NH_4^+ . 1 mL of the bromate/bromide working solution was added to each sample and shaken vigorously for about 30 seconds to allow the solution to mix. All samples were then placed on a shaker table for 90 minutes at 100-125 excursions/minute.

2.5 NO₂-Concentration Analysis to Check for NH₄+ Conversion

After NH_4^+ oxidation to NO_2^- , the concentration of NO_2^- was measured following the NO_3^- colorimetric method protocol (U.S. EPA, 1971). Nitrite standards were created by adding 0.6899 grams of NaNO₂ to 100 mL of HPLC grade water resulting in a 100 mM stock solution. The stock solution was diluted to make nitrite standards with concentrations of 1 μ M, 2.5 μ M, 5 μ M and 10 μ M. 1 mL of each sample of NO_2^- standards and of the oxidized sample were placed in individual cuvettes.

Reagents were prepared including sulfanilamide solution and N-(1-Naphthyl)ethylenediamine dichloride (NEDA). Sulfanilamide solution was prepared by dissolving 8 g sulfanilamide in 70 mL phosphoric acid then diluting it to 100 mL with MQ water. NEDA was prepared by dissolving 0.56 g of NEDA into 100 mL of MQ water. A color producing reagent was prepared immediately before using it by mixing the sulfanilamide and NEDA solution in a 10:1 ratio (sulfanilamide:NEDA).

0.250 mL of the color producing reagent was added to each cuvette then shaken on a shaker table to ensure that the reagent was well mixed. The samples were then placed in the refrigerator for 30 minutes then removed and allowed to equilibrate for 20 minutes. A Trilogy laboratory fluorometer was used to measure the absorbance of each sample. By using the absorbance values of the prepared standards with a known concentration, a NO₂⁻ standard calibration curve was created by plotting absorbance versus concentration. The equation of the line was then used to calculate the NO₂⁻ concentration.

The percent conversion of NH_{4^+} to NO_{2^-} in the rain samples was obtained by dividing the calculated NO_{2^-} concentration by the original sample NH_{4^+} concentration then multiplied by 100. If NH_{4^+} was not over 90% converted, then fractionation is a concern due to an incomplete oxidation process, and the sample was unable to undergo isotope analysis.

2.6 Sample pH adjustment

After conversion, the pH of the samples was too high for the bacteria denitrifier isotope analysis to be applied. The pH for all the samples were adjusted and lowered to range between 3-9 by using 6 N hydrochloric acid and 6 N sodium hydroxide.

2.7 Isotope analysis (University of California – Davis & University of Pittsburgh)

The NH_4^+ and NO_3^- samples were shipped to an isotope lab for analysis. Nitrate samples did not require an alteration for analysis, as the denitrification pathway consists of the reduction of NO_3^- to N_2O . The denitrifier bacterial method is performed using *Pseudomonas aureofaciens*, which lacks the enzyme to reduce NO_3^- beyond N_2O in the sample. Bacteria were first cultivated in soy broth using potassium nitrate, ammonium sulfate, and an antifoaming agent. After bacterial growth, the culture was purged with N_2 gas, then added to rainwater samples to undergo denitrification, converting NO_3^- to N_2O . The N_2O gas was removed using an automated

headspace analyzer, purified, and analyzed for δ^{15} N using an isotope ratio mass spectrometer (IRMS) coupled to a gas bench (Kendall et al., 2007; Sigman et al., 2001).

Isotope ratio values are reported in parts per thousand relative to atmospheric N_2 as follows:

$$\delta^{15}N(\%) = \frac{(({}^{15}N/{}^{14}N) \text{ sample}) - (({}^{15}N/{}^{14}N) \text{ standard})}{(({}^{15}N/{}^{14}N) \text{ standard})} X 1000$$
E1

International reference standards for δ^{15} N-NH₄⁺ and δ^{15} N-NO₃⁻ were used for data normalization. The standards used for δ^{15} N-NH₄⁺ correction were USGS25, ammonium sulfate (-30.4‰), and USGS 26, ammonium sulfate (+53.7‰). The standards for δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ correction were USGS 32, potassium nitrate (+180‰), USGS 34, potassium nitrate (-1.8‰; -27.9‰), IAEA N3 (+4.7‰; +25.6‰) and USGS 35, sodium nitrate (+2.7‰; +57.7‰).

When NH_{4^+} is oxidized to NO_2^- , NO_3^- still exists within the rain sample. $\delta^{15}N-NO_3^-$ is initially determined then $\delta^{15}N-NO_2^-$ (e.g. oxidized NH_{4^+}) + $\delta^{15}N-NO_3^-$ is determined using the denitrifier method. The $\delta^{15}N-NH_{4^+}$ value is back calculated using the mixing equation below (Felix et al. 2013).

$$(\delta^{15}N - NO_3 + \delta^{15}N - NO_2) = f^* \delta^{15}N - NO_3 + (1-f)^* \delta^{15}N - NH_4 + E2$$

Where *f* represents (NO₃^{-/}(NH₄⁺ + NO₃⁻)) in each rain sample. Standard deviations for $\delta^{15}N - NO_3^-$, $\delta^{18}O-NO_3^-$ and $\delta^{15}-NH_4^+$ values were 0.2‰, 0.5‰, and 0.9‰, respectively.

2.8 Air mass back trajectories

NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) on-line transport model was used to determine the 24-hour air mass back trajectory for each sampling event (Stein et al., 2015, Draxler, 1999, Draxler & Hess, 1997 & 1998). The time frame was selected because both NO_x and NH₃ have a short lifespan in the atmosphere of about 24 hours or less (Zhu et al., 2015). By using NOAA's HYSPLIT model on each collection event, air mass sectors can be categorized by air mass direction, Figure 7.

2.9 Isotope mixing models

SIAR (Stable Isotope Analysis in R) is an isotope mixing model that uses a Bayesian framework to calculate the apportionment of emissions from available sources. The simmr package installed within R_{Studio} version 3.6.1 was used to estimate the NO_x and NH₃ source emissions contributing to NO₃⁻ and NH₄⁺ in the Brazilian wet deposition samples. Three NO_x sources (biogenic, biomass burning, and vehicles emissions) and four NH₃ sources (livestock, volatized fertilizer, vehicles, and biomass burning) were used in the mixing models for this project. Two mixing equations were used for both δ^{15} N-NO_x and δ^{15} N-NH₃, one for the dry season and one for the wet season. Biomass burning was eliminated from the wet season mixing model because high levels of precipitation diminish the biomass burning events.

The δ^{15} N-NO_x mixing equation developed for this study and used with the SIAR software during the dry season was:

E3

δ^{15} N-NO₃⁻rain, dry season =

 $f_{\text{biogenic}} (\delta^{15}\text{NO}_x)_{\text{biogenic}} + f_{\text{biomass burning}} (\delta^{15}\text{NO}_x)_{\text{biomass burning}} + f_{\text{vehicles}} (\delta^{15}\text{NO}_x)_{\text{vehicles}}$ The mixing equation used for δ^{15} N-NO_x during the wet season was:

E4

δ^{15} N-NO₃⁻rain, wet season =

$$f_{\text{biogenic}} (\delta^{15} \text{NO}_{\text{x}})_{\text{biogenic}} + f_{\text{vehicles}} (\delta^{15} \text{NO}_{\text{x}})_{\text{vehicles}}$$

The mixing equation used for δ^{15} N-NH₃ in this study during the dry season was:

E5

 $f_{\text{livestock waste}} (\delta^{15}\text{NH}_3)_{\text{livestock waste}} + f_{\text{volatized fertilizer}} (\delta^{15}\text{NH}_3)_{\text{volatized fertilizer}} + f_{\text{vehicles}} (\delta^{15}\text{NH}_3)_{\text{vehicles}} + f_{\text{biomass burning}} (\delta^{15}\text{NH}_3)_{\text{biomass burning}}$

The mixing equation used for δ^{15} N-NH₃ during the wet season was:

E6

δ^{15} N-NH₄⁺ rain, wet season =

 $f_{\text{livestock waste}} (\delta^{15}\text{NH}_3)_{\text{livestock waste}} + f_{\text{volatized fertilizer}} (\delta^{15}\text{NH}_3)_{\text{volatized fertilizer}} + f_{\text{vehicles}} (\delta^{15}\text{NH}_3)_{\text{vehicles}}$ f_{xxx} represents the fraction of each source contributing to the NO₃⁻ and NH₄⁺ wet deposition samples. The endmember values are the δ^{15} N values associated with each emission source (i.e. biogenic, biomass burning, vehicles, volatized fertilizer and livestock waste) (Table 1 and 2). The δ^{15} N-NO_x endmember values for biogenic, biomass burning, and vehicles are -35 ± 10‰, 1 \pm 4‰, and -3 \pm 6‰ respectively (Elliot et al., 2019). The endmember δ^{15} N-NH₃ values for volatized livestock waste, volatized fertilizer, biomass burning, and vehicles are $-15.0 \pm 7.7\%$, - $30.6 \pm 5.0\%$, 12‰, and $6.6 \pm 2.1\%$ respectively (Felix et al., 2013, Walters et al., 2020, & Chang et al., 2016, Freyer, 1978). It should be noted that the δ^{15} N-NH₃ biomass burning endmember is inferred by Kawashima and Kurahashi 2011 and future work should focus on constraining the δ^{15} N-NH₃ values of biomass burning to increase the efficacy of this source apportionment approach. The δ^{15} N-NH₃ endmember values that are used in this study were corrected for sampling fractionation if needed. A portion of the source δ^{15} N-NH₃ values of livestock waste and volatilized fertilizer were obtained from studies that used passive samplers which causes fractionation as an artifact of the sampling processes thus altering the true δ^{15} N-NH₃ (Chang 2016, Felix et al., 2013). To correct these passively collected agricultural δ^{15} N-NH₃ endmember values, a 15.4‰ fractionation effect recorded as the difference between passive and active samplers observed in previous field studies was used (Pan et al., 2020 & Walters et al., 2020). These corrected passively sampled endmembers were averaged with available actively sampled endmembers to create NH₃ volatized livestock waste and fertilizer endmembers. It should be noted that only δ^{15} N values from samples collected in the field (as opposed to laboratory) were used for these NH₃ endmembers.

2.9.1 Mixing model endmember selection: NO_x

Biomass burning emissions originate from sources such as agricultural waste burning, forest fires, grassland fires, and combustion of biofuels for energy purposes (Behera et al., 2013). The Moderate Resolution Imaging Spectroradiometer and the Visible Infrared Imaging Radiometer Suite instruments on NASA and NOAA satellites provide burning maps from small everyday fires to large brush and forest fires across Brazil (Amazon wildfires) (Voiland, 2020). Observations from these satellite programs and previous literature provide evidence that extreme wildfires in the Amazon rainforest along with local fires, are a key emission source and are included as an endmember for NO_x, having a δ^{15} N-NO_x value of 1 ± 4‰ (Elliott et al., 2019).

Globally, fossil fuel combustion via electricity generating units (EGU) and vehicles is listed as the primary source of NO_x emissions, with the δ^{15} N-NO_x value for vehicles being -3 ± 6‰ (Denman et al., 2007, Elliott et al., 2019). In Brazil, the demand for personal vehicles have increased due to the shortage of infrastructure for public transportation. Many incentives within the country including tax exemptions and fuel efficiency have increased the sales of personal vehicles. The state of São Paulo has the largest vehicular fleet in Brazil, with 28.6 million units that emitted 180 Gg of NO_x in 2016, most emissions originating in municipalities around the metropolitan area of São Paulo city (Targino et al., 2019). With the lenient vehicle standards in

the country and incentives to vehicle purchasing as well as the study site city, Ribeirão Preto, being urbanized, the vehicular emissions are considered as an NO_x endmember.

In comparison to vehicle and biomass burning δ^{15} N-NO_x value, NO_x produced biogenically in soils has a lower δ^{15} N-NO_x value, with an average of $-35 \pm 10\%$ (Elliot et al., 2019). In Brazil, and the study area Ribeirão Preto, the biogenic NO_x emissions originate from both agriculture soils and soils within the Amazon rainforest, giving reason to include biogenic as an endmember of NO_x emissions. More evidence for the inclusion of agricultural soils is further explained in section 2.9.2 regarding NH₃ agricultural emissions.

2.9.2 Mixing model endmember selection: NH₃

Volatilized livestock waste $(-15.0 \pm 7.0\%)$ and fertilizer $(-30.6 \pm 5.0\%)$ are primary sources of global NH₃ emissions (Berner & Felix, 2020) and were chosen as endmembers due to agriculture being a significant economic sector in the state of São Paulo (Felix et al., 2013; Chang 2016; Freyer 1978). The central, northern, and western regions of the state's economy is based on agro-industries: sugar/alcohol, orange, livestock and meat packaging (Allen et al., 2011). The southern regions of the state rely more heavily on metallurgical and food industries and the agriculture industry (i.e tea and banana) for its region's economy (Allen et al., 2011). Of the various agricultural activities, cattle farming for beef production is one of the most important activities in Brazil and has the second largest cattle herd in the world (de Souza et al., 2019). The state of Mato Grosso (NW of São Paulo) is known to be the leading beef producer state in Brazil, containing 15% of the Brazilian cattle herd, and it is one of the largest and most productive agricultural locations in the world (Cerri et al. 2016, dos Reis et al., 2021). The four states of São Paulo, Mato Grasso, Gioas, and Mato Grosso do Sul account for 73% of feedlots in Brazil (Silva, 2019). The number of head in feedlots are constantly increasing due to the higher cattle prices and lower feed costs (Silva, 2019). NH_3 is directly emitted from livestock waste and from the degradation of urea and uric acid found in animal feces (Behera et al., 2013). The emission mechanism is similar for NH_3 and urea fertilizer emission. As one of the primary sources of the region's economy, the demand for fertilizers and its application is great. Various factors affect NH_3 emissions from fertilizers including the type of fertilizer, the soil properties, and meteorological conditions (Behera et al., 2013).

Biomass burning will also be used as an endmember for NH₃ having a δ^{15} N-NH₃ value of 12‰ (Kawashima & Kurahashi 2011). The primary influence for choosing biomass burning as an emission source, as stated in previous sections, is the massive wildfires that occurred in the Amazon rainforest and smaller ag-related fires surrounding the sampling site. Nitrogen is present in all biomasses and when burned, it can be released as NH₃. NH₃ is the dominant nitrogen product released in smoldering combustion, which is part of the visible glowing combustion (Yokelson et al. 1997).

As mentioned with NO_x emission endmember selection, the demand for personal vehicle ownership in Brazil is increasing due to a shortage of public transportation and little to no regulations of vehicle manufacturing to comply with limits of the fuel economy. Since Brazil implemented PROCONVE, three-way catalytic converters have been placed in vehicles to address vehicular emissions (Dallmann & Facanha, 2017). In three-way catalytic converters, the formation of NH₃ occurs as a by-product of the catalytic reduction of NO_x to N₂. Also, within a catalytic system, NH₃ increases in vehicle exhaust from high CO and low H₂ conditions (Oh & Trilpett, 2014). Due to the presence of concentrated vehicles in the urban setting, vehicle emissions are considered an endmember and have a δ^{15} N-NH₃ value of $6.6 \pm 2.1\%$ (Walters et al., 2020).

2.9.3 Mixing model endmember eliminations

Natural gas and coal-fired power plants were not included as NH₃ and NO_x endmembers because Brazil uses hydroelectric energy as its primary energy source. It is one of the largest producers of hydroelectricity in the world and is still seeking to expand its hydroelectric power throughout the country (Ruffato-Ferreira et al., 2007). In 2005, it was recorded that 83.4% of generated electricity and 76.06% of installed power came from hydroelectric power plants in Brazil. The installed hydroelectric power, potential, and utilization rate in the state of São Paulo is 10,229 MW, 15,226 MW, and 67.18%, respectively (Caentano de Souza, 2008). Since most of Brazil energy is produced from hydroelectric power; coal, petroleum, and natural gas burning power plant percent contribution is minimal to Brazil power supply and therefore not used as a potential source of emissions.

NOAA's HYSPLIT models helped to eliminate marine emissions as an endmember. Ribeirão Preto's geographical location puts it free from significant influence by the Atlantic – as indicated by air mass projections being almost entirely landlocked, with few samples originating from the Atlantic Ocean. Therefore, marine emissions are not used as an endmember since they have little to no contribution in the area.

Source	δ^{15} N-NO _x (‰)	Reference
Biogenic	-35 ± 10	Elliott et al., 2019
Biomass burning	1 ± 4	Elliott et al., 2019
Vehicles	-3 ± 6	Elliott et al., 2019

Table 1. Known isotopic signature ranges for atmospheric NO_x sources (Elliott et al., and references therein).

Source	δ^{15} N-NH ₃ (‰)	Reference
Volatized Fertilizer	-30.6 ± 5	Chang 2016, Felix et al., 2013
Livestock	-15.0 ± 7	Felix et al., 2013, Chang 2016, Freyer 1978
Vehicles	6.6 ± 2.1	Walters et al., 2020
Biomass burning	12	Kawashima and Kurahashi, 2011
	Source Volatized Fertilizer Livestock Vehicles Biomass burning	Source δ^{15} N-NH3 (‰)Volatized Fertilizer -30.6 ± 5 Livestock -15.0 ± 7 Vehicles 6.6 ± 2.1 Biomass burning12

Table 2. Known isotopic signature ranges for atmospheric NH₃ sources (Chang 2016, Felix et al., 2013, Freyer 1978, Walters et al., 2020, Kawashima and Kurahashi, 2011).

2.10 Calculation of nitrogen isotope fractionation associated with HNO₃ formation

After emission, NO_x can undergo fractionation during atmospheric transformations potentially altering the resulting δ^{15} N-NO₃⁻ value. To calculate the nitrogen isotope fractionation, the overall equation (7) below was used and the equations underlying this general equation will be followed as outlined by Li et al. 2020:

$$\delta(NO2) - \delta(NOx) = \frac{(\alpha 2 - \alpha 1)xA + (\alpha NO2 - NO - 1)}{A + 1} X \ 1000\%$$

To evaluate equation 7, the A factor was calculated using equation 8. Rate constants of isotopic exchange, k_5 and k_1 were previously determined. k_5 is the rate constant for NO + O₃ reaction (1.73 x 10⁻¹⁴ cm³ s⁻¹) and k_1 is the rate constant for NO + NO₂ reaction (8.14 x 10⁻¹⁴ cm³ s⁻¹) (Atkinson et al., 2004 & Sharma et al., 1970).

E8

$$A = \frac{(k5)(\delta 15N - HNO3)}{k1[NO2]}$$

 α_1 and α_2 are isotopic fractionation factors for the NO + O₃ and NO + NO₂ reactions. The factor ($\alpha_1 - \alpha_2$) was theoretically predicted as -0.010 and α (NO₂ – NO) was experimentally determined as 1.0289 from Li et al., 2020.

 NO_2/NO_x ratio was determined using values reported by Targino et al., 2019. Targino et al., 2019 monitored air quality in 25 cities, 24 cities across São Paulo, Brazil and one city in Parana, Brazil. The study used cluster analysis to minimize the amount of data points/ cities and consequently observed a total of four clusters. The air quality data for all cities were presented together within the clusters for both episode and non-episode periods. Episode periods referring to a pollution outbreak (an increase in regional fires) and non-episode period referring to before the pollution outbreak. The non-episode values from the cluster closet in location to the study site, Ribeirão Preto were used to help determine the NO_2/NO_x ratio. The NO_2/O_x ratio, 0.20, and O_3 values, 41.2, provided within the study were viewed initially to solve for NO_2 while $O_x = O_3 + NO_2$. Therefore, NO_2/O_x ratio is equivalent to $NO_2/(O_3+NO_2)$, resulting in NO_2 value to be 10.3. From the study, NO_x value is 11.1, which was used to determine the NO_2/NO_x ratio, 0.9279. This was the only local NO_2/NO_x ratio literature or monitoring data available so was used to calculate ¹⁵N fractionation for each sample.

 δ HNO₃ – δ NO_x from equation 1 represents the fractionation corrected δ ¹⁵N-NO₃⁻ values. The calculated fractionation effect used to correct each δ ¹⁵N-NO₃⁻ value was 1.09‰. As with other current studies the fractionation during conversion of NO₂ to HNO₃/NO₃⁻ was considered negligible but does need future characterization in future studies.

CHAPTER III: RESULTS & DISCUSSION

3.1 Nitrate concentration & N isotopic composition

Results represent measurements of rain samples (n = 42) collected from October 2018 – February 2020 on an event basis in Ribeirão Preto, São Paulo, Brazil. The NO₃⁻ concentrations for the samples ranged from 1.7 μ M to 42.3 μ M with an average of 13.1 ± 10.0 μ M. The overall NO₃⁻ concentration corresponds to 29.6% of the dissolved inorganic nitrogen present in the rain samples.

The NO₃⁻ concentrations in wet deposition samples from Ribeirão Preto are lower compared to other developed cities (i.e. urbanized and industrialized), such as Guangzhou, China (average 70 μ M), one of China's most polluted cities due to its rapid development and high population (Fang et al., 2011), Providence, RI, USA, which is highly influenced by vehicular traffic (average 27.22 µM) (Fibiger, 2014), and Pataling Jaya, Malayasia, an urban-industrial location (average 38.5 µM). The concentrations in this study are also lower than values in Shinjuku, Tokyo, the largest industrial area in Japan, during normal rain events (average, 31.6 μ M) and urban heavy rains (average 38.7 μ M) (Uchiyama et al., 2017). However, the NO₃⁻ concentrations in this study are higher than those associated with "clean" marine rains like heavy typhoon rains $(3.62 \,\mu\text{M})$ in Shinjuku, or hurricane rains in the Eastern or Gulf Coast US (e.g., 9.5 μ M and 9.3 μ M) (Felix et al., 2015, Felix & Murgulet, 2020). NO₃-concentrations are generally lower in rural areas and this can be seen in Tanah Rate, Nakhon Pathom Province, and Puding with averages of 4.80 µM, 15.2 µM, and 16.99 µM respectively (Khan et al., 2018, Mallika & Rattapon, 2008, & Wu et al., 2012). Although rural areas tend to have lower NO₃⁻ concentrations than urbanized locations, the concentration values in rural Yanging District,

Beijing are averaged at 59.6 μ M, higher than values in this study and other cities compared to in Table 4 (Xu et al., 2020).

The NO₃⁻ concentrations in this study are comparable to recently reported values within the state of São Paulo, Brazil. NO₃⁻ concentrations from Rio de Janeiro region, Brazil and Serra dos Órgãos National Park, Brazil averaged 17.58 μ M, slightly higher than reported values from this study (de Souza et al., 2015). Urbanized cities throughout the state of São Paulo including, Cubatão, São Paulo city, and Limeira, (listed starting from on the coast to deeper inland), all have higher average NO₃⁻ concentrations than Ribeirão Preto, Table 4. The NO₃⁻ concentrations presented in this study are similar to concentrations from Ribeirão Preto reported in 2011 (12.8 ± 1.4 μ M) (Coelho et al., 2011) suggesting the magnitude of NO_x emissions may have been consistent over the last decade.

 δ^{15} N-NO₃⁻ values ranged from -10.6‰ to 13.1‰. Mean and concentration/ isotope weighted mean δ^{15} N- NO₃⁻ are reported in Table 3 as (δ^{18} N- NO₃⁻ = $\sum [NO_3^{--}] * \delta^{15}$ N- NO₃⁻ / $\sum [NO_3^{--}]]$). The seasonal weighted mean δ^{15} N-NO₃⁻ values ranged from -4.6‰ to -0.8‰. The overall average for δ^{15} N-NO₃⁻ values was 2.2 ± 4.6‰. A simple linear regression analysis comparing the δ^{15} N-NO₃⁻ values and the NO₃⁻ concentrations for each wet deposition sample collected during the sampling period revealed no significant relationship (n = 42, R² = 0.0762, pvalue = 0.07679), Figure 6.

 δ^{15} N-NO₃⁻ values determined in this study have a wider range than some urbanized cities such as Nanyang Technological University, Singapore; Guangzhou, China; Universidad Nacional, Costa Rica; and Guiyang, China (Table 5). When comparing average δ^{15} N-NO₃⁻ values, this study has higher values than Zhanjiang, China (0.8‰); Providence, Rhode Island, USA (-5.1‰); Geestacht, Germany (0.4‰); and Guiyang, China (-1.9 ± 3.0‰) and lower average values than Universidad Nacional, Costa Rica (7 \pm 2.2‰). All locations listed, with the exception of Geestacht, Germany, are rapidly developing or highly developed cities around the world, some with severe pollution situations. Singapore has haze pollution due to biomass burning, industrialization, and having an urbanization rate of 100% (Li et al., 2020). Zhanjiang has N pollution due to the rapidly developing and increasing economy, industries, agriculture production, and coal combustion for power (Chen et al., 2019). Guiyang has severe acid deposition from urbanization (Liu et al., 2017) and Guangzhou has high pollution levels due to rapid development and high population, as previously mentioned (Fang et al., 2011). Geesthacht, Germany is a forested area surrounded by grassland, however, it has slight exposure from nearby industrial and agricultural sites, influencing the δ^{15} N-NO₃⁻ values in the area (Beyn et al., 2014).

Analyte	n	Spring	n	Summer	n	Fall	n	Winter
NO3 ⁻ (μM)	15	2.9 to 22.7	15	2.1 to 42.3	10	1.7 to 36.8	2	13.9 to 33.6
NO ₃ -mean (µM)		12.5 ± 5.9		11.5 ± 11.6		14.1 ± 11.8		23.7 ± 13.9
δ^{15} N-NO ₃ - range (‰)		-10.6 to 13.1		8.9 to 4.3		-2.3 to 6.7		-2.8 to 0.1
δ ¹⁵ N-NO ₃ - mean (‰)		-3 ± 5.9		-3.5 ± 3.3		0.9 ± 3.2		-1.4 ± 2.1
δ^{15} N-NO ₃ - weighted mean		-4.6		-3.8		-1.0		-0.8
δ ¹⁸ O-NO ₃ - range (‰)		39.3 to 65.2		41.4 to 63.7		38.0 to 59.5		68.7 to 71.1
δ^{18} O-NO ₃ - mean (‰)		55.9 ± 7.4		55.6 ± 7.5		52.7 ± 7.0		69.9 ± 1.7
$\delta^{18}\text{O-NO}_3^-$ weighted mean		58.2		57.9		56.4		69.4

Table 3. Seasonal mean $[NO_3^-]$ (μM), mean $\delta^{15}N$ -NO₃⁻, weighted mean $\delta^{15}N$ -NO₃⁻ values, mean $\delta^{18}O$ -NO₃⁻ (‰), and weighted mean $\delta^{18}O$ - NO₃⁻ values (‰)

Location	n	NO ₃ -	\mathbf{NH}_{4}^{+}	Source
Ribeirão Preto, São Paulo, Brazil	42	13.1 ± 10.0	31.0 ± 24.2	This Study
Limeira, São Paulo, Brazil	38	14.73*	34.36*	Martins et al., 2019
Cubatão, Brazil	95	17.8*	23.5*	Vieira-Filho et al., 2015
São Paulo, Brazil	58	16.3*	25.5*	Vieira-Filho et al., 2015
Providence, Rhode Island, USA	61		21.0 ± 22.5	Le Roy et al., 2021
Providence, Rhode Island, USA	7	27.2 ± 11.4		Fibiger, 2014
Beijing, China	58	59.6*	76.3*	Xu et al., 2020
Shinjuku, Tokyo (normal rain)	55	31.6*	27.0*	Uchiyama et al., 2017
Shinjuku, Tokyo (urban heavy rain)	12	38.7*	28.0*	Uchiyama et al., 2017
Shinjuku, Tokyo (Typhoon heavy rain)	5	3.62*	12.0*	Uchiyama et al., 2017
Nanyang Technological University, Singapore	247	5.56 ± 4.69		Li et al., 2020
Guangzhou, China	113	70		Fang et al., 2011
Petaling Jaya, Klang Valley, Malaysia	168	38.5 ± 16.1	18.7 ± 21.5	Khan et al., 2018
Tanah Rata, Pahang, Malaysia (rural)	168	4.80 ± 3.87	8.80 ± 24.9	Khan et al., 2018
Nakhon Pathom Province, Thailand (rural)	319	15.2*	36.6*	Mallika & Rattapon, 2008
Puding, China (rural)	24	16.99*	33.14*	Wu et al., 2012

Table 4. Average concentration of $NO_{3}^{-}(\mu M)$ and $NH_{4}^{+}(\mu M)$ in rainwater in Ribeirão Preto, Brazil (this study) and various locations across the globe.

n = Number of samples * = Volume weighted mean

Location	n	δ ¹⁵ N-NO ₃ -	δ ¹⁸ O-NO ₃ -	δ^{15} N-NH4 ⁺	Source
Ribeirão Preto, São Paulo, Brazil	42	-10.6 to 13.1, avg 2.2 ± 4.6	38 to 71.1, avg 55.7 ± 7.8	-19.8 to 14.6, avg -4.0 \pm 8.8	This Study
150 sites across USA	883		63 to 94		Kendall et al., 2007
Nanyang Technological University, Singapore	247	-6.5 to 8.2	38.9 to 71.1		Li et al., 2020
Guangzhou, China	113	-4.9 to 10.1	33.4 to 86.2		Fang et al., 2011
Guangzhou, China	11	-4.2 to 4.4		-12.4 to 0.4	Jia & Chen, 2010
Geestacht, Germany	92	-6.0 to 11.6, avg 0.4			Beyn et al., 2014
Bermuda	98			-5.5 ± 2.9	Altieri et al., 2014
Zhamjiang, China	208	avg 0.8	52.4		Chen et al., 2019
Universidad Nacional, Costa Rica	76	-3.8 to 7.1, $avg7 \pm 2.2$	33.7 to 65.3, avg 51.7 ± 6.5		Villalobos – Forbes et al., 2021
Guiyang, China	44	-8.3 to 3.0, avg -1.9 \pm 3.0		-28.7 to 6.6, avg -10.6 ± 7.7	Liu et al., 2017
Providence, Rhode Island, USA	7	-5.1			Fibiger, 2014
Guiyang, China	1235			-19.8 to -10.4, avg-15.9	Xiao et al., 2012
Mtn Yahiko, Niigatu Platin, Japan (top, warm)	Х	avg -3.4		avg-5.5	Fukuzaki & Hayasaka, 2009
Mtn Yahiko, Niigatu Platin, Japan (top, cold)	Х	avg -2.8		avg-1.7	Fukuzaki & Hayasaka, 2009
Mtn Yahiko, Niigatu Platin, Japan (foot, warm)	Х	avg -4.5		avg-5.3	Fukuzaki & Hayasaka, 2009
Mtn Yahiko, Niigatu Platin, Japan (foot, cold)	Х	avg-3.7		avg-2.1	Fukuzaki & Hayasaka, 2009
Beijing, China	78			-16 to 22	Xie et al., 2008

Table 5. Range and average of δ^{15} N-NO₃⁻, δ^{18} O-NO₃⁻, and δ^{15} N-NH₄⁺ in rainwater in Ribeirão Preto, Brazil (this study) and other various locations across the globe.



Figure 2. Box plots of average NO_3^- concentrations during a) fall, spring, summer, and winter and during b) wet and dry seasons

3.2 Temporal variation of NO₃⁻ concentrations and δ^{15} N-NO₃⁻ values

The NO₃⁻ concentrations ranged from 2.1 μ M to 42.3 μ M and 1.7 μ M to 36.8 μ M during the wet and dry season, respectively (Figure 2a). The average NO₃⁻ concentration in the wet season (11.6 ± 8.9 μ M) was lower than that of the dry season (15.7 ± 12.0 μ M), but not significantly (ANOVA; p-value = 0.286) (Figure 2).

The seasonal distribution of NO_3^- concentration (higher values in the dry season, lower values in the wet season) can be influenced by the dilution of the differing amounts of precipitation occurring in the dry and wet seasons (Chen et al., 2019). This is true for this study data because in Ribeirão Preto about 80% of the total rainfall volume deposited throughout the study period occurs during the rainy season in Ribeirão Preto and as previously mentioned lower NO_3^- concentrations occurred in the wet season.

To further isolate the results, Table 3 presents the range and mean NO_3^- concentrations and isotopic composition by seasons (spring = October - December, summer = January - March,
fall = April - June, and winter = July - September). During the summer, the NO₃⁻ mean concentration is at its lowest, $12.5 \pm 5.9 \,\mu$ M and is at its highest during the winter, $23.7 \pm 13.9 \,\mu$ M, however, the concentrations in the two seasons are not significantly different (ANOVA; p-value = 0.1852). The NO₃⁻ concentrations throughout the year do not show a significant difference when viewing the spring, fall, summer, and winter seasons (ANOVA; p-value = 0.433). The average NO₃⁻ concentrations by month are shown in Figure 4, with the highest NO₃⁻ concentration value observed during the month of September (33.57 μ M) and the lowest during the month of April (8.04 μ M).

During the wet and dry seasons, the δ^{15} N-NO₃⁻ values ranged from -10.6‰ to 13.1‰ and -2.8‰ to 6.7‰ respectively. Lower weighted mean δ^{15} N-NO₃⁻ values were observed in the wet season (averaging -4.2‰) and higher values were observed in the dry season (averaging -0.9‰) Figure 3a. The simple average δ^{15} N-NO₃⁻ values for the wet and dry season were -3.2 ± 4.7‰ and 0.5 ± 3.1‰, respectively. A one-way ANOVA was applied to determine that the δ^{15} N-NO₃⁻ values during the wet and dry seasons were significantly different (p-value = 0.0143). This significant difference among wet/dry seasons can be due to changing NO_x oxidation pathways and/or changing NO_x sources, following the same trend as previous studies which is discussed further below (Fang et al., 2011, Chen et al., 2019). High overall δ^{15} N-NO₃⁻ values occur during fall, 0.9‰, and the lowest mean values occurred during the summer, -3.5‰ however, they were not significantly lower (ANOVA; p-value =0.0945). Figure 5 shows the highest δ^{15} N-NO₃⁻ values during the month of April (3.5‰) and the lowest during the month of November (-7.2‰).



a) b) Figure 3. Box plots summarizing seasonal distribution of δ^{15} N-NO₃⁻ averages during a) wet and dry seasons and during b) fall, spring, summer, winter



Figure 4. Wet deposition mean concentration of NO_3 - by month from October 2018 – February 2020 sampling period. Shaded area representing dry season.



Figure 5. Comparison of results of δ^{15} N-NO₃⁻ and δ^{18} O-NO₃⁻ monthly average values over time from October 2018 – February 2020. Shaded area representing dry season.



Figure 6. Comparison of results of δ^{15} N-NO₃⁻ and NO₃⁻ concentrations for each wet deposition sample collected during the sampling period

Seasonal variation in NO_x emissions is common and differs from site to site worldwide. δ^{15} N-NO₃⁻ values for the various study sites result from different sources present in their locations and the temporal variation in source magnitude. Highly populated regions are known to produce more anthropogenic NO₃⁻ emissions with relatively higher δ^{15} N-NO₃⁻ values. For instance, δ^{15} N-NO₃ values are significantly higher in urban areas with dense vehicle traffic and in regions such as East Asia where coal combustion is highly active (Song et al., 2021). In a study performed in Guangzhou, China, high δ^{15} N-NO₃-values were coincident with temperature in 2009 versus 2008, mainly due to an increase fossil fuel demand during the preparations for the Asian Games that summer. δ^{15} N-NO₃ values were not determined months prior to summer 2009 due to a drought causing an underestimated amount of precipitation. In preparation for the Asian games an increase of construction took place in the area. An increase of coal combustion occurred during the summer, as it is commonly used to generate electricity, showing evidence for higher δ^{15} N-NO₃ values. During the warm season in Guangzhou in 2009 and 2008 the δ^{15} N-NO₃ values were 4.1‰ and 3.8‰, respectively (Fang et al., 2011). In the present study, δ^{15} N-NO₃values followed the trend from Guangzhou in 2008, Geestacht, Germany, and Zhamjiang, China which showed lower values in the warm summer months and higher values in the cool, dry months (Li et al., 2011; Beyn et al., 2014, & Chen et al., 2019). The higher δ^{15} N values in winter are related to both the change in source and N isotope exchange between NO and NO₂. Previous studies find trends of higher δ^{15} N values in winter due to isotope exchange effect between NO and NO₂, which is more pronounced in seasons with low NO₂/NO_x ratio and O₃ concentration (i.e. winter) (Chen et al. 2019). However, the change in δ^{15} N values between the seasons more likely corresponds to a change in source activities in the present study as the seasonal changes in physical atmospheric characteristics are more moderate in the region. Additionally, while higher δ^{15} N-NO₃⁻ values in the study can be explained by N isotope exchange between NO and NO₂, previous studies found higher values with low NO₂/NO_x ratio, and the present study found higher δ^{15} N-NO₃-values while having a high NO₂/NO_x ratio (0.9279). The present study shows lower

 δ^{15} N-NO₃-values during the wet seasons likely due to a decrease activity of biomass burning occurring and an increase of biogenic activity during summer months.

Given the cropland and urban characteristics of the study site, biogenic emissions and anthropogenic sources including vehicular traffic and biomass burning may be driving the temporal δ^{15} N-NO₃⁻ trends. Higher NO₃⁻ concentrations and δ^{15} N-NO₃⁻ values occur during the dry season and can be in part due to more biomass burning occurrence. The large magnification of biomass burning occurrence in the study area can be shown by the number of detected fires in the State of São Paulo. Rural areas throughout the state of São Paulo and Brazil such as the savanna biome are commonly known to burn fire for agriculture and pasture expansion, removal of waste and renewal of agricultural areas, or sugarcane harvesting coinciding with the dry season (Godoy-Silva et al. 2017). During the sampling period, 3,362 fires were detected through a reference satellite; 2,456 fires were detected during the dry season alone in the state of São Paulo (INPE, 2021). Therefore, seasonal fires provide an explanation of NO₃⁻ concentrations increase from May 2019 to September 2019, with the highest number of detected fires in September 2019, 872 fires (INPE, 2021).

During the winter season, less biogenic activity and an increase in biomass burning activity occur. Biogenic emissions, having a low $\delta^{15}N$ value of $-35 \pm 10\%$, is expected to decrease during the wintertime and increase during the summer due to greater water availability and increasing temperatures. This lack of low $\delta^{15}N$ value contribution during wintertime would decrease the $\delta^{15}N$ -NO₃⁻ while the increase in biogenic NO_x emissions during summer would explain the significantly lower $\delta^{15}N$ -NO₃⁻ observed in this study. The increase in biomass burning, which has a higher $\delta^{15}N$ value than biogenic of $1 \pm 4\%$, occurs during the wintertime

30

(dry season) due to the change precipitation patterns. The seasonal variations in these two sources likely contribute to the observed higher $\delta^{15}N$ in the winter vs summer.

3.3 Spatial variation of NO₃⁻ concentrations and δ^{15} N-NO₃⁻ values

The dominant air mass back trajectory in the study area is northeast followed by northwest, making the wet deposition in Ribeirão Preto mainly influenced by continental air mass, Figure 7. The average nitrate concentration for NE, SE, SW, and NW air mass directions are $11.07 \pm 8.65 \,\mu$ M, $14.51 \pm 7.64 \,\mu$ M, $22.18 \pm 28.47 \,\mu$ M and $13.79 \pm 10.12 \,\mu$ M, respectively. The average δ^{15} N-NO₃⁻ values for NE, SE, SW and NW air mass directions are -2.05 ± 3.94‰, $0.01 \pm 7.71\%$, $1.36 \pm 7.52\%$, and $-3.62 \pm 3.89\%$. Although the NE and NW direction were dominant, the least dominant air mass, occurring from the SW direction, had the highest NO₃concentration and average δ^{15} N-NO₃⁻ values. The high NO₃⁻ concentrations associated with air masses originating in the SW or Pontal do Paranapanema region of the state may be due to the frequent sugarcane burning occurrences emitting substantial NO_x (Lara et al., 2001). The δ^{15} N-NO₃- values are lowest in air masses originating from the NW suggesting significant contribution from biogenic emissions ($\delta^{15}N = 35 \pm 10\%$) of the Amazon rainforest located NW of the collection site. However, it could also indicate ag-related biogenic emissions from Brazilian states Goias & Mato Grosso de Sul which are located NW of the study area and are characterized mainly by agriculture.



Figure 7. 24 hour air mass back trajectories for all sampling days in Ribeirão Preto, São Paulo, Brazil, based on NOAA HYSPLIT model back trajectories. a) green lines represent dry season and red lines represent wet season b) Blue tone lines represent dry seasons (light blue, fall; dark blue, winter) and red tones represent wet seasons (red, spring; orange, summer).

3.4 Nitrate oxygen isotopic composition

The δ^{18} O-NO₃⁻ mean and range values are present in Table 6 for all four seasons. The average δ^{18} O-NO₃⁻ value was 55.7 ± 7.8‰ with a range of 38.0‰ to 71.1‰. The concentration/ isotope weighted mean δ^{18} O-NO₃⁻ values are reported in table 3 as (δ^{18} O-NO₃⁻ = $\sum [NO_3^-] * \delta^{18}$ O-NO₃⁻/ $\sum [NO_3^-]$]) and ranged from 56.4 to 69.4‰. A simple linear regression analysis comparing the δ^{18} O-NO₃⁻ values and the NO₃⁻ concentrations revealed a significant relationship based on the p-value determined (n = 42, R² = 0.2507, p-value = 0.0143), Figure 9.

The overall δ^{18} O-NO₃⁻ values in this study were low compared to reported δ^{18} O-NO₃⁻ values ranging 63‰ to 94‰ across ~150 sites in the U.S. (n = 883) (Kendall et al. 2007) but had an identical range from values at Nanyang Technological University, Singapore (+38.9‰ to +71.1‰) (Li et al., 2020). Although Singapore land use dominates to cropland, urbanization, and forest as like the study area, the similarities in δ^{18} O-NO₃⁻ despite high contrast in source emission settings, reiterate evidence from previous studies that he δ^{18} O-NO₃⁻ values are primarily controlled by seasonal/diurnal oxidation chemistry that also can be related to latitude (as further referenced below). Singapore and the study site both being low-latitude locations and having similar "low end" range in δ^{18} O-NO₃⁻, indicates that they may share similar NO_x oxidation scenarios.

3.5 Temporal variation of $\delta^{18}O$ -NO₃-

The average δ^{18} O-NO₃⁻ values for the wet and dry season are very similar, 55.8 ± 7.3‰ and 55.6 ± 9.2‰ respectively. The concentration/ isotope weighted mean δ^{18} O-NO₃⁻ values were slightly lower in the wet season (averaging 58.0‰) than the dry season (averaging 62.9‰). A one-way ANOVA clarified the δ^{18} O-NO₃⁻ values during the wet and dry season were not significantly different (p-value = 0.947). The temporal patterns also show an increase of δ^{18} O-NO₃⁻ values during the dry seasons (April - September) from 45.66‰ to 68.68‰.

Previous studies show higher δ^{18} O-NO₃⁻ values in the dry season and lower values in the wet season, directly following the trend of δ^{15} N-NO₃⁻ values (Fang et al., 2011, Chen et al., 2019). δ^{18} O-NO₃⁻ values are determined by formation pathways which are affected by temperature and solar radiation (Elliot et al., 2009). Hasting et al, 2003 determined the δ^{18} O-NO₃⁻ values are higher in the winter due to ozone contributing more to the N₂O₅ pathway than the OH pathway. Due to lower OH concentrations in the winter, the N₂O₅ pathway is favored. The NO₃⁻ values due to relatively high δ^{18} O associated with O₃ (Fang et al., 2011). HNO₃ formed via the OH pathway is formed with 2/3 O₃ and 1/3 OH, the substantial oxygen contribution from OH, creates lower δ^{18} O-NO₃⁻ values. Therefore, the δ^{18} O-NO₃⁻ values should be lower in warmer seasons than cooler seasons due to longer daytimes, sunshine hours in the warmer seasons. This will produce lower δ^{18} O-NO₃⁻ values during the summertime where more solar radiation is occurring.

The δ^{18} O-NO₃⁻ values typically range between 52‰ (assuming 2/3 O₃ and 1/3 OH) to 102‰ (assuming 5/6 O₃ and 1/6 H₂O) (Li et al., 2020). These seasonal patterns related to solar radiation and subsequent oxidation pathways were observed in the present study with the winter season having the highest δ^{18} O-NO₃⁻ mean values, $69.9 \pm 1.7\%$, with summer having the lowest, $55.6 \pm 7.5\%$. Figure 5 shows the temporal pattern of δ^{18} O-NO₃⁻ values, reaching its lowest values in April 2019 (38.02‰) (early fall) and its highest value in August (71.15) (winter). δ^{18} O-NO₃⁻ values increase at the beginning of the dry season because of the decreased amount of solar radiation, favoring the N₂O₅ pathways, the deeper the season goes. The δ^{18} O-NO₃⁻ values began to decrease at the end of the dry season through the spring, as solar radiation begins to increase with the summer months, favoring the OH pathway and providing lower δ^{18} O-NO₃⁻ values.

While low δ^{18} O-NO₃⁻ values indicate large contributions from the OH reaction pathway about 29% of the rainwater samples had δ^{18} O-NO₃⁻ values lower than the value predicted from 100% OH pathway contribution (~52‰), which suggest that other reaction pathways are possibly present. One potential overlooked pathway which can contribute low δ^{18} O is the peroxy radical oxidation pathway represented as reaction R7 below. It can compete with R1 of the OH pathway to transfer the relatively low oxygen isotopic composition of O₂ rather than O₃ of R1 as seen below.

$$NO + RO_2 (or HO_2) \rightarrow + RO (or OH)$$
 R (7)

 O_2 has a $\delta^{18}O$ -NO₃⁻ value of about 23.5‰ and O_3 has a considerably higher $\delta^{18}O$ -NO₃⁻ value of 90-120‰. During this pathway, the lower $\delta^{18}O$ signature will be transferred to $\delta^{18}O$ -NO_x before reaction R2 takes place (Felix & Murgulet, 2020). This reaction pathway has been suggested to be more prevalent at low-latitudes similar to the study site location, however future work is needed in this area as a majority of $\delta^{18}O$ -NO₃⁻ investigations took place in mid-latitude locations.



a) b) **Figure 8**. Box plots summarizing seasonal distribution of δ^{18} O-NO₃ averages during a) wet and dry seasons and during b) fall, spring, summer, winter



Figure 9. Comparison of results of δ^{18} O-NO₃⁻ and NO₃⁻ concentrations for each wet deposition sample collected during the sampling period.

3.6 Ammonium concentration & N isotopic composition

The overall average NH₄⁺ concentration was $31.0 \pm 24.2 \,\mu$ M with a range of $3.0 \,\mu$ M to 106.9 μ M. The overall NH₄⁺ concentration corresponds to 70.4% of the dissolved inorganic

nitrogen concentration measured in Ribeirão Preto. This study reports higher NH_{4^+} mean concentrations than NO_3^- , and lower mean $\delta^{15}N-NH_{4^+}$ values than $\delta^{15}N-NO_3^-$.

The NH_{4^+} concentration in this study is higher compared to both rural and urban cities around the world in Thailand, Singapore, and the United States, listed values in Table 4. The NH_{4^+} concentration values in this study can be compared to values in urbanized cities throughout the state of São Paulo. The cities Cubatão and São Paulo city have lower NH₄+ concentrations than this study (23.5 μ M and 25.5 μ M respectively), however Limeira has higher average NH₄⁺ concentrations, 34.36 µM. NH₄⁺ concentrations of the comparison cities, Cubatão, São Paulo, and Limeira, increase as the city's location is further inland (i.e. Cubatão located on the coast and Limeira located furthest inland). The lower values near the coast are influenced by winds from the ocean, bringing clean air to the coastal cities, lowering the NH₄⁺ concentration in rain. The overall NH_{4^+} concentrations are higher in this study compared to NH_{4^+} concentrations from 2011 in Ribeirão Preto, $16.4 \pm 1.6 \,\mu$ M (Coelho et al., 2011) suggesting a potential increase, almost doubling, in NH₃ source emission in the region over the last decade. A previous study using the Meteorological Operational Satellite Program Infrared Atmospheric Sounding Interferometer NH₃ dataset reports substantial increase $(21.2 \pm 5.4\%)$ in NH₃ concentrations from 2008 to 2018 over Brazil and the authors suggest this is due to increasing pyrogenic emissions and increases in anthropogenic emissions in the southeastern region around São Paulo (Van Damme et al., 2021).

Table 6 distributes the NH₄⁺ concentration and isotopic composition in the four seasons and presents the concentration/ isotope weighted mean δ^{15} N-NH₄⁺ as (δ^{15} N-NH₄⁺ = $\sum [[NH_4^+] * \delta^{15}$ N-NH₄⁺/ $\sum [NH_4^+]]$). The weighted mean δ^{15} N-NH₄⁺ values ranged from -10.8‰ to 7.9‰. The overall average δ^{15} N-NH₄⁺ value was -4.0 ± 8.8‰ and ranged from -19.8‰ to 14.6‰. A

37

simple linear regression analysis comparing the δ^{15} N-NH₄⁺ and the NH₄⁺ concentration for each sample revealed no significant relationship (n = 42, R² = 0.0135, p-value = 0.4636), Figure 14.

The range of the δ^{15} N-NH₄⁺ values determined in this study were generally higher than studies performed elsewhere. The cities Guangzhou and Guiyang in China have δ^{15} N-NH₄⁺ values ranging from -12.4‰ to 0.4‰ and -28.7‰ to 6.6‰, respectively (Jia & Chen, 2010; Liu et al., 2017). Another earlier study in Guiyang, China reported δ^{15} N-NH₄+ values ranging from -19.8% to -10.4% (Xiao et al., 2012). These cities are rapidly developing cities within China, with Guangzhou having increase pollution from industrialized activity and Guiyang suffering from severe acid deposition. While in Bermuda, the values averaged $-5.5 \pm 2.9\%$ (Altieri et al., 2014) (Table 5). The values in Guangzhou and Bermuda are possibly lower than Ribeirão Preto because of them being in close proximity to bodies of water, which with a large marine influence, having δ^{15} N-NH₄⁺ value of -4.1 ± 2.6‰, will decrease the δ^{15} N value. Rural Beijing, China near Tai Lake region show δ^{15} N-NH₄⁺ values ranging from -16‰ to 22‰ (Xie et al., 2008). Another rural area, Mountain Yahiko, Niigatu Platin, Japan has δ^{15} N-NH₄⁺ average values ranging from -5.5‰ to -1.7‰ (Fukuzaki & Hayasaka, 2009). These values are averages of the top and foot of the mountain in warm and cold weather, with warm weather having δ^{15} N-NH₄⁺ values lower than this study and cold weather having values higher than this study.

Although rural locations have δ^{15} N-NH₄⁺ values lower than the present study, the same trends still follow. Lower δ^{15} N-NH₄⁺ values are present during the warm seasons, even lower in rural area, due to the increase in agricultural activities in the warm seasons. However, during the colder seasons, the rural area in Japan uses coal-fired power plants which will increase the δ^{15} N-NH₄⁺ values. Other studies have lower δ^{15} N-NH₄⁺ values from marine and agricultural influence however, the present study has more vehicular and biomass burning influence which will increase the δ^{15} N-NH₄⁺ values in the study area.

3.7 Temporal variation of NH_4^+ concentrations and $\delta^{15}N-NH_4^+$ values

The average NH₄⁺ concentration for the wet and dry seasons are $26.6 \pm 22.0 \,\mu\text{M}$ and $38.7 \pm 28.3 \,\mu\text{M}$, respectively. Figure 11 shows boxplots of the average NH₄⁺ concentrations during a) wet and dry seasons and during the b) four weather seasons of sampling. The NH₄⁺ concentration ranged from $3.0 \,\mu\text{M}$ to $106.9 \,\mu\text{M}$ in the wet season and $3.6 \,\mu\text{M}$ to $93.4 \,\mu\text{M}$ in the dry season. Average NH₄⁺ concentration in the wet vs dry seasons were not significantly different (ANOVA; p-value = 0.192) suggesting dilution effect by rainout is not as significant as it was for NO₃⁻.

Generally, NH_{4^+} concentrations increase in warm seasons and decrease in cold seasons following trends in agricultural activity (Kawashima & Kurahashi, 2011). A similar study in Guangzhou, South China followed this pattern with the wet and dry seasons. However, the NH_{4^+} concentrations in this study do not follow this pattern. The concentrations are generally higher during the colder, dry months, Figure 11. The increase in NH_{4^+} concentrations during the dry months are likely seen because of biomass burning such as sugarcane plantations burning from May to October that is not as prevalent in other areas of the world (Martinelli et al., 2002).

Table 6 presents the range and mean NH_{4^+} concentrations and isotopic composition by season. The highest mean NH_{4^+} concentrations occurred during the winter season (23.7 ± 13.9 μ M; n = 2) while the lowest mean NH_{4^+} concentrations occurred during the summer (n = 15) having 11.5 ± 1.6 μ M and were not significantly different (ANOVA; p-value = 0.074). The average NH_{4^+} concentrations by month are shown in Figure 10, with the highest concentration observed during the month of September (93.4 μ M) and the lowest in the month of April (8.04 μ M).

Analyte	n	Spring	n	Summer	n	Fall	n	Winter
$NH_{4^{+}}(\mu M)$	15	6.7 to 63.2	15	3.0 to 106.9	10	3.6 to 70.3	2	38.2 to 93.4
NH4 ⁺ Mean (µM)		30.5 ± 16.3		25.3 ± 27.0		33.3 ± 24.7		65.8 ± 39.1
δ^{15} N-NH ₄ ⁺		-15.6 to 14.6		-17.5 to 11.3		-19.8 to -0.1		4.5 to 9.2
δ^{15} N-NH ₄ ⁺ Mean (‰)		-1.1 ± 8.9		-4.1 ± 8.2		-10.5 ± 5.8		6.9 ± 3.3
Concentration / isotope weighted Mean		-1.4		-4.7		-10.8		7.9

Table 6. Seasonal mean $[NH_{4^+}]$ (μM), mean $\delta^{15}N$ -NH₄⁺ (‰), and weighted mean $\delta^{15}N$ -NH₄⁺ values (‰). (Note: 44 wet deposition samples were collected for analysis, 2 samples were unable to undergo proper analysis and were eliminated from the results interpretation therefore, n = 42.)



Figure 10. Wet Deposition mean concentration of NH_4^+ by month from October 2018 – February 2020 sampling period. Shaded area representing dry season.



a) b) Figure 11. Box plots of average NH_{4^+} concentrations during a) four weather seasons of sampling and during b) wet and dry seasons

During the wet and dry seasons, the δ^{15} N-NH₄⁺ values ranged from -17.5‰ to 14.6‰ and -19.8‰ to 9.2‰ respectively. The average δ^{15} N-NH₄⁺ values for the wet and dry season were - 2.6 ± 11.2‰ and -7.6 ± 14.0‰ respectively, Figure 13a. The weighted mean δ^{15} N-NH₄⁺ values ranged from -10.8‰ to 7.9‰. The average δ^{15} N-NH₄⁺ values were higher during the wet season than the dry season, (Figure 11a), however this difference was not significant (ANOVA; p-value = 0.0983). The lowest δ^{15} N-NH₄⁺ mean and concentration weighted mean for the four seasons occurred in the fall with -10.5 ± 5.8‰ and -10.8‰ respectively and the highest δ^{15} N-NH₄⁺ mean and concentration weighted mean 7.9‰).

Compared to a study in Bermuda, the δ^{15} N-NH₄⁺ values are lower in cooler seasons than warmer seasons (Altieri et al., 2014). In Bermuda, these values are seen due to a larger anthropogenic influence during the cooler season where there the air mass are derived mainly from continental than marine origin. A particulate study in Japan showed δ^{15} N-NH₄⁺ (p) values lower during the winter and higher during the summer (Kawashima & Kurahashi, 2011). The NH₃ volatilization from primary sources, livestock waste and fertilizer, increases as the temperature rises. However, this study did not follow the same trend, it had higher δ^{15} N-NH₄⁺ values in the winter and lower δ^{15} N-NH₄⁺ values in the fall. Studies in Guiyang, China and Niigata Platin, Japan and had δ^{15} N-NH₄⁺ values lower in warmer seasons than the cooler seasons regardless of urban or rural areas. In Guiyang, China, seasonal δ^{15} N-NH₄⁺ values are altered as a result of higher temperatures increasing microbial activities and increase the rate of volatilization of lighter isotopes such as NH₃ (Xiao et al., 2012). The seasonal temperatures also influence the isotopic fractionation factor (Xiao et al., 2012). In Niigata Platin, Japan, samples were collected at the top and bottom of a mountain. During the spring and summer, agricultural activities increase in the area, causing lower values near the bottom of the mountain where more people reside.

In the present study, during the winter, δ^{15} N-NH₄⁺ values are higher compared to the other seasons. The higher δ^{15} N-NH₄⁺ values are occurring due to the change in source contribution, primarily biomass burning. As mentioned in earlier sections, 2.9.1, biomass burning occurs throughout the state of São Paulo and Brazil. Biomass burning frequently occurs around the study site for agricultural purposes and clearcutting. As with the δ^{15} N-NO₃⁻ values, the δ^{15} N-NH₄⁺ values begin to increase in May 2019 and peak in September 2019, increasing from -3.1‰ to 9.3‰, due to detected fires increasing across the state throughout this time (INPE, 2021).

Agriculture emissions play a key role at the study site. Studies have determined that 57% of NH_3 deposition originate from agricultural and livestock activities, activities which are common throughout the state of São Paulo (de Almeida Souza et al., 2020). The increase of NH_4^+ concentration can be seen from October – March in Figure 10. During this time the northeastern part of the state applies large amounts of fertilizer to fields. As temperatures rise, an

42

increase in NH₃ volatilization occurs. This activity corresponds with negative δ^{15} N-NH₄⁺ values which can be seen during this time as well, Figure 12. Unlike the other NH₄⁺ sources in this study, vehicular emissions are likely to be consistent throughout the year, but the magnitude of the other sources are likely to change throughout thus altering the δ^{15} N-NH₄⁺ values.



Figure 12. δ^{15} N-NH₄⁺ values over time from October 2018 – February 2020. Shaded area representing dry season.



a) b) **Figure 13**. Box plots summarizing seasonal distribution of δ^{15} N-NH₄⁺ averages during a) wet and dry seasons and during b) fall, spring, summer, and winter



Figure 14. Linear regression of δ^{15} N-NH₄⁺ and NH₄⁺ concentrations for each wet deposition sample collected during the sampling period

3.8 Spatial variation of NH_4^+ concentrations and $\delta^{15}N-NH_4^+$ values

As mentioned previously, the dominant air mass back trajectory at the study area is northeast followed by the northwest. However, the NH₄⁺ concentrations are shown to have higher values from air masses originating in the southwest direction and lowest concentrations from the southeast direction. The average δ^{15} N-NH₄⁺ values are highest from air masses originating in the southeast direction and lowest from air masses originating from the southwest direction. The average NH₄⁺ concentrations for NE, SE, SW, and NW air mass directions are 27.61 ± 20.36 μ M, 26.77 ± 12.23 μ M, 56.21 ± 71.69 μ M and 33.24 ± 25.77 μ M, respectively. The average δ^{15} N-NH₄⁺ values for NE, SE, SW and NW air mass directions are -4.90 ± 8.45‰, -1.91 ± 12.83‰, -5.82 ± 7.83‰, and -2.90 ± 8.65‰. As previously mentioned, the SW region of the study area is largely influenced by the agroindustry (Allen et al., 2011). The higher NH₄⁺ concentration values are influenced by the large concentration of NH₄⁺ fertilizers used during agriculture production and NH₄⁺ from urea and animal waste. Lower δ^{15} N-NH₄⁺ values found in the SW air mass correspond to low agricultural δ^{15} N-NH₄⁺ values (volatized fertilizer, -30.6 ± 5‰; livestock emissions, -15 ± 7‰) (Silva, 2019; Martins et al., 2019). The SE air mass has the lowest NH₄⁺ concentrations interestingly as one of the largest cities in the state is located in this direction on the coast of the Atlantic Ocean, the metropolitan area of São Paulo city. Although the SE airmass have the lowest NH₄⁺ concentration, it also has the highest δ^{15} N-NH₄⁺ values. Higher δ^{15} N-NH₄⁺ values can be influenced by vehicle emissions (6.6 ± 2.1‰) and biomass burning emissions (12‰). Because large cities are located SE of the study area, the vehicular emissions in the urbanized and industrial areas are the likely explanation for relatively higher δ^{15} N-NH₄⁺ values.

$3.9 NO_x$ source apportionment

The monthly δ^{15} N-NO₃⁻ values fluctuate within the range of reported isotope signatures of different emission sources (-35 ± 10‰ to 1 ± 4‰) (Elliot et al., 2019). Due to the intensive agricultural practices and the urbanized location, it can be assumed that the dominant source of NO_x is biomass burning, vehicles, and biogenic in the Ribeirão Preto atmosphere. After fractionation effect correction (1.09‰) of δ^{15} N-NO₃⁻ values, the relative contributions of each source to the total NO₃⁻ deposition for each sampling event in the dry season was determined using a three-endmember mixing model. For the wet season, biomass burning was removed because the intensity of precipitation prevents large scale biomass burning and a two-endmember model was used (Allen et al., 2011). Figure 15 shows the average percent contributions of NO_x sources including biogenic, biomass burning, and vehicular emissions throughout the sampling period. Biogenic soil emissions are significant during vegetation growth in countries with welldefined seasons, such as Brazil's wet and dry seasons (Godoy-Silva et al., 2017). The biogenic emissions can be seen increasing from November 2018 (12%) to February 2019 (20%) and again starting September 2019 because of the increase in biogenic activity during the warmer seasons and the greater water availability during the wet summer months (Godoy-Silva, 2017). During the wet seasons, biomass burning is almost non-existent, resulting in the relative percent contribution of NO_x from vehicular emissions to increase greatly from 40.4 \pm 2.5% to 81.5 \pm 5.3% (Table 7). When biomass burning is eliminated during the wet season, the average NO₃⁻ concentrations decreased from 15.7 \pm 12.0 μ M in the dry season to 11.6 \pm 8.9 μ M. The actual percent decrease of NO₃⁻ concentration from the dry to wet season, 26.1%, was lower than the expected percent decrease of 51.6% or 8.1 μ M, the contribution of biomass burning during the dry season. Since the actual final NO₃⁻ concentration, 11.6 μ M, was higher than the expected final concentration, 7.6 μ M, it represents a potential increase in other emission sources from the dry to wet season, such as biogenic emissions.

A decrease in public transportation and an increase in personal vehicular use correlates with the major growth in local air pollution in larger cities across Brazil (De Melo et al., 2018). Between 2010 and 2014, fuel consumption increased in diesel oil, gasohol, and anhydrous ethanol by 22%, 46%, and 55%, respectively (De Melo et al., 2018). Brazil is listed to have a voluntary fuel economy vehicle standard, meaning that the country has little to no regulation prohibiting the manufacturing of vehicles that do not comply with specific limits of fuel economy. In comparison to other countries (i.e. China, EU, US, Japan, India, Canada, South Korea, and Mexico), Brazil is the only country having voluntary vehicle standards and a small portion of new vehicles are offered with energy efficiency technologies. Table 7 shows during the wet season NO_x emissions mainly originated from vehicular emissions at $81.5 \pm 5.3\%$. However, the majority of NO_x emissions during the dry season originated from biomass burning

46

at 49.8 ± 1.8%, Table 7. Biomass burning influences the NO_x emissions near the study site largely from reoccurring fires on sugar cane plantations burning from May to October, 1 km away from the study site (Giubbina, 2019, Martinelli et al., 2002). As previously mentioned, 3,362 fires were detected in the state of São Paulo during the sampling period (INPE, 2021). Other biomass burning influences include the active Amazon rainforest fires which cause worldwide concerns in regard to the rapid burning, the fate of the forest itself, and the life of biodiversity within the Amazon. Smaller fires that impact the δ^{15} N-NO₃⁻ values include agricultural fires, dried wood torched from clearcutting, bush fires, and other miscellaneous fires (Voiland, 2020).

The large deviations present for the source contributions occur from the overlapping of the biogenic, biomass burning, and vehicle source signatures. The isotopic source signatures for δ^{15} N-NO₃⁻ can be found in Table 1. The deviation of the source contribution demonstrates the complexities of using mixing models with overlapping source signatures. Therefore, additional research to better characterize these endmembers must be done to better constrain source apportionment.



Figure 15. δ^{15} N-NO_x source apportionments for Biogenic, Biomass burning, and Vehicles over time from October 2018 – February 2020. Shaded area representing dry season.

Table 7. Average NO_x and NH_3 source apportionments for dry and wet seasons. Samples from October 2018 – February 2020

Source	Average Emission (%)				
NO 1					
<u>NO_x dry season</u>					
Biogenic	9.8 ± 1.4				
Biomass burning	49.8 ± 1.8				
Vehicles	40.4 ± 2.5				
NOx wet season					
Biogenic	18.6 ± 5.3				
Vehicles	81.5 ± 5.3				
<u>NH₃ dry season</u> Volatized Fertilizer Livestock Vehicles Biomass Burning	$26.4 \pm 14.0 \\ 26.1 \pm 9.5 \\ 21.6 \pm 8.2 \\ 25.9 \pm 18.8$				
<u>NH₃ wet season</u> Volatized Fertilizer Livestock Vehicles	16.2 ± 11.2 26.6 ± 14.4 57.2 ± 23.3				



Figure 16. Average NO_x and NH_3 source apportionments for dry and wet seasons. Samples from October 2018 – February 2020

*3.10 NH*₃ source apportionment

The mixing model for NH₃ has a total of four-endmembers including volatized fertilizer, livestock waste, vehicles, and biomass burning. All four endmembers are used during the dry season and three are used during the wet season after eliminating the biomass burning endmember due to seasonal precipitation patterns. As with NO_x emission, the percent contribution of NH₃ emissions from vehicles increased from the dry to the wet season from 21.6 \pm 8.2% to 57.2 \pm 23.3%, respectively, and NH₄⁺ concentration decreases from 38.7 \pm 28.3 μ M in the dry season to 26.6 \pm 22.0 μ M in the wet season, due to no contribution of biomass burning during the wet season. A decrease in the percent contribution of livestock from October to March occurred (31.7 \pm 19.6% to 25.0 \pm 23.2%) however, percent contribution from volatized fertilizer remained constant (22.5% \pm 10.6 to 21.4 \pm 10.1) throughout this time period, Figure 17. A decrease in volatized fertilizer and livestock sources occurred from May to September (months during the dry season), 31.1 \pm 20.7% to 4.4 \pm 3.7% for livestock and 34.3 \pm 15.2% to 3.1 \pm 1.4% for fertilizer, then began to increase again afterwards for the rest of the sampling period to $23.4 \pm 11.3\%$ for fertilizer and $31.1 \pm 19.1\%$ for livestock.





The study shows the volatized fertilizer and livestock NH_4^+ contribution during the wet season averaged $16.2 \pm 11.2\%$ and $26.6 \pm 14.4\%$ with values in the dry season being higher for volatized fertilizer, $26.4\% \pm 14.0\%$, and remaining constant for livestock, $26.1 \pm 9.5\%$. Table 7 shows the average source apportionment percentage for each NH_3 source during the wet and dry seasons. During the dry season, volatized fertilizer is sourced with the highest percentage followed by livestock waste emissions, biomass burning, and vehicles. Whereas during the wet season vehicular emissions has the highest source apportionment value followed by livestock emissions, and volatized fertilizer. During the dry seasons, the combined livestock and volatized fertilizer emissions totaled 52.4% and while totaling 42.8% during the wet season. A potential cause for the decrease in these percent NH_3 emissions from the dry season to wet season could be due to influence by the amount of precipitation differing in the seasons, with reports showing rainfall suppresses NH_3 emissions (Kamp et al., 2021). The overall livestock and volatized fertilizer emissions in this study totaled 49.2%, comparable to values from previous studies stating that 57% of NH_3 deposition is estimated to be from agricultural and livestock activities (de Almeida Souza et al., 2020).

As with NO_x biomass burning emissions, the NH₃ emissions from biomass burning are attributed to both small and large fires surrounding the region and from the Amazon burning. Mentioned earlier were the Amazon wildfires occurring from August 2019 to January 2020. During this time, an increase in detected fires was seen starting at April 2019 (78 detected fires) to September 2019 (872 detected fires) (INPE, 2021). The increase in detected fires directly follows the increase in biomass burning source apportionment from April to September, increasing from 18.5% \pm 13.6% to 77.4% \pm 17.6%, Figure 18.



Figure 18. Fires detected in the state of São Paulo by satellite systems corresponding to the biomass contributions.

Vehicular traffic contributes to higher δ^{15} N-NH₄⁺ values. Vehicular regulation mentioned in section 2.9.2 describes three-way catalytic converters in vehicles. The large number of vehicles in use emit NH₃ from the catalytic convertors. The regulations and change in vehicular traffic in Brazil over time is briefly explained in section 2.9.2, highlighting the increase of vehicles on the road and relation to emissions. Table 7 shows during the wet season NH_3 emissions mainly originate from vehicular emissions at $57.2 \pm 23.3\%$. However, during the dry season, most NH_3 emissions originated from fertilizer emissions at $26.4 \pm 14.0\%$. Figure 16 can visually show that the NH_3 emissions during the dry season are almost equal in source apportionment, with a 4.8% difference of the lowest and highest.

CHAPTER IV: CONCLUSION / IMPLICATIONS

In this study, wet deposition rain samples were collected and stable isotopes were used to investigate the sources of NO_x and NH₃ emissions in Ribeirão Preto, São Paulo, Brazil. Concentrations of NO₃⁻ and NH₄⁺ and nitrogen isotopic composition of δ^{15} N-NO₃⁻, δ^{18} O-NO₃⁻ and δ^{15} N-NH₄⁺ in the precipitation samples were measured. The concentrations of NO₃⁻ and NH₄⁺ varied seasonally, with both having higher concentrations during the dry season vs the wet season. δ^{15} N-NO₃⁻ and δ^{15} N-NH₄⁺ also varied seasonally, with higher δ^{15} N-NO₃⁻ values in the dry season and higher δ^{15} N-NH₄⁺ in the wet season. The NO₃⁻ and NH₄⁺ concentrations and δ^{15} N-NO₃⁻ and δ^{15} N-NH₄⁺ values in this study are comparable to reported values from other studies. Rural areas tend to have lower values than values in the present study where industrialized and developed areas tend to have higher values. The overall NH₄⁺ concentrations are higher in this study compared to NH₄⁺ concentrations from 2011 in Ribeirão Preto, 16.4 ± 1.6 µM (Coelho et al., 2011) suggesting a potential increase, almost doubling, in NH₃ source emission in the region over the last decade.

Unlike δ^{15} N-NO₃⁻ and δ^{15} N-NH₄⁺ values, δ^{18} O-NO₃⁻ values are very similar when comparing the wet and dry season. Based on the range of the δ^{18} O-NO₃⁻ values in the present study, the oxidation pathways at the study area were favored to the OH pathway to form NO₃⁻. However, the peroxy radical pathway also contributed to the formation of NO₃⁻ due to the large O contribution present and the transfer of the O₂ rather than O₃ during reactions.

By using isotope mixing models, it was determined that the main source of NO_x emissions in the dry season was biomass burning and during the wet season was vehicle emissions. For NH_{4^+} emissions, the primary sources were determined to be volatized fertilizer during the dry season and vehicles during the wet season. Based on the isotope data, air masses

that originate over high agriculture activity occurred tend to show higher NH_{4^+} concentrations from an abundant of fertilizer use and lower $\delta^{15}N-NH_{4^+}$ values. Air masses that showed higher $\delta^{15}N-NO_{3^-}$ values tend to be influenced by biomass burning from wildfire or from controlled burning for agricultural purposes.

Overall, this study showed ag-related activities such as burning, fertilization and livestock production have a dominant influence on rainwater composition in Ribeirão Preto, mainly during the colder, dry seasons with biomass burning having a much more prevalent role than other regions of the world. This study provides stakeholders in the São Paulo region with a better understanding of N_r source dynamics and atmospheric chemistry affecting their air quality and ecosystems. This can aid future efforts to create informed mitigation techniques to reduce emission N_r rates.

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APPENDIX A

Overall data table including date	e, precipitation (mm)	, [NO ₃ ⁻] μΜ, [NH	$[4^{+}] \mu M, \delta^{15}N-NH_{4^{+}}$	$, \delta^{15}$ N-
NO_3^- , $\delta^{18}O-NO_3^-$, pH, back traje	ctory			

Date	Precipitation	[NO ₃]	[NH4 ⁺]	δ^{15} N-NH ₄ +	δ ¹⁵ N-NO ₃ ⁻	δ ¹⁸ O-NO ₃		Back
(d-m-yr)	(mm)	μM	μM	(‰)	(‰)	(‰)	pН	Trajectory
3-Oct-18 & 4-Oct-18	17 33	20.64	49.80	-156	-33	65.2	5 21	NE / E
7-Oct-18 &	6.56	11.19	22.62	-2.2	-3.2	58.8	<i>4</i> 99	NE/E
18-Oct-18&	10.12	18.08	28.89	5.2	1.2	61.1	4.95	N / SW
3-Nov-18 &	19.15	10.32	30.83	-5.2	-4.0	52.6	5.54	NF/N
4-Nov-18 & 5-Nov-18	22.24	5.90	10.50	-13.8	2.2	53.9	5.11	N/NE
9-Nov-18	11.42	2.86	6.67	-2.0	13.1	39.3	4.84	F
10 Nov-10	7.02	5 51	13.15	-2.0	2.4	40.0	4 70	
19-Nov-18 17-Dec-18 &	7.03	9.92	33.08	-11.3	2.4	49.0	4.70	IN W
12-Jan-19&	20.33			-5.0	2.1	49.0	4.04	INE / IN
15-Jan-19	23.695	18.02	31.19	-6.9	-0.6	56.7	5.13	E/N
2-Feb-19 3-Feb-19 &	7.00	16.78	37.22	-9.8	-1.5	58.8	6.16	NE
4-Feb-19	20.99	42.31	106.90	-0.3	-4.0	60.3	4.80	SW/SW
15-Feb-19	3.34	30.82	54.95	-6.6	-7.4	61.0		NW
16,17-Feb-19 & 26,27-Feb-								
19 12-Mar-19&		5.78	14.20	-5.9	-6.1	63.2		NW / N
13-Mar-19	17.56	2.13	3.03	11.3	4.3	45.4		NE/N
14-Mar-19	23.44	12.57	30.40	-17.5	-3.1	54.2		NW
8-Apr-19	35.85	2.05	5.52	-11.4	6.7	46.0	5.49	W
13-Apr-19 & 14-Apr-19	17.74	4.02	8.15	-11.6	1.7	49.1	5.46	NE / NE
14-Apr-19 & 15-Apr-19	17.26	1.68	3.55	-3.2	5.1	38.0	5.40	NE/N
16-Apr-19 & 17-Apr-19	6.27	5.98	14.95	-16.0	0.5	49.5	5.43	NE/SE
4-May-19& 5-May-19	4.59	36.79	60.55	-9.3	-1.5	57.7	5.59	NE / NE
9-May-19	3.86	25.13	70.30	-10.4	-2.2	57.4	5.63	NE
10-May-19	6.85	16.68	55.38	-14.4	-2.2	58.0	5.45	Ν
17-May-19	4.81	23.73	33.18	-19.8	-2.3	58.2	6.07	Е
24-May-19&	3 56	16.57	10.83	-8.6	0.2	537	5 73	NW / SW
$2.5^{-11}ay^{-17}$	2.50	7 00	31 71	-0.0	3.4	50.5	5 22	
3-Juli-19 4-Aug-19&	2.38	1.99	51./1	-0.1	3.4	59.5	5.55	IN W
5-Aug-19 &	2.47	13.91	38.15	4.5	-2.8	71.2	5.29	S / E
2-Sep-19	12.26	33.57	93.41	9.3	0.1	68.7	5.05	N/SW

6-Nov-19	11.31	14.03	24.66	14.6	-7.3	64.6	4.85	SE
7-Nov-19 &	51.00	12.25	22.96	2.5	5.0	52.0	5 10	
8-NOV-19 9-Nov-19&	51.60	13.35	33.80	2.5	-5.0	52.8	5.12	NE/NW
10-Nov-19	11.19	22.67	63.15	6.2	-7.8	64.6	5.00	NW / NW
13-Nov-19&								
14-Nov-19	24.4	15.59	49.91	6.8	-7.2	63.7		E/NE
23-Nov-19&	10.50	10.12	17 (0	10.0	<i>с</i> 7	50.4	C 41	N / C
24-Nov-19 27-Nov-19&	10.50	19.13	47.68	10.6	-5.7	52.4	6.41	N / S
28-Nov-19	55.40	7.38	15.28	6.4	-10.6	59.7	5.29	N/NW
29-Nov-19	5.42	11.36	27.04	-1.7	-6.6	51.7	5.40	NE
19-Jan-20&								
20-Jan-20	16.49	6.81	18.75	3.6	-4.2	48.2	5.25	NE/NE
23-Jan-20	6.98	10.76	18.11	6.5	-4.4	61.5	5.42	Ν
23-Jan-20&								
24-Jan-20	6.23	2.66	6.73	-0.3	-8.9	62.0		N/NW
29-Jan-20	8.14	4.79	8.73	-4.5	-6.7	63.7		NW
5-Feb-20	8.63	2.86	3.91	2.3	-4.5	61.9		Ν
5-Feb-20 &								
6-Feb-20	22.56	5.08	10.69	-16.1	-2.5	48.1		N / N
11-Feb-20	9.03	2.17	4.39	-13.4	-2.0	41.4		NW
16-Feb-20	23.6	8.59	29.99	-4.7	-0.4	47.3		Ν