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Atmospheric nitrogen species distribution under influence of agricultural sources in a Brazilian region†

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Abstract: Atmospheric deposition is a key process to improve the understanding of human impacts on the nitrogen biogeochemical cycle. We quantified the dissolved inorganic (DIN = NO_3^- + NH_4^+) and organic nitrogen (DON) fluxes, and our results showed that DON was dominant in relation to DIN. The predominance of lower values of NO_3^-/NH_4^+ ratios were associated an alkaline behavior, suggesting dominance of NH_3 in the atmosphere neutralization processes. The nitrogen total fluxes were concentrated in the wet period (76%). This pattern was associated with seasonal rainfall distribution, and with the volatilization of NH_3 and NO_x species due to fertilizers applications.

Keywords: Nitrogen deposition; NO_3^-/NH_4^+ ratio; Dissolved organic nitrogen; Dissolved inorganic nitrogen.

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1. Introduction

The nitrogen cycle is essential to living organisms and triggers several natural reservoirs processes, and in the last centuries such processes have been changed ascribed to anthropogenic sources inputs [1]. From the local to global scale, several activities, such as fossil fuel combustion, mobile exhaust engines and agricultural activities including fertilizer use and livestock husbandry account to specific variations and the increase of atmospheric reactive nitrogen (Nr) emissions [2,3]. Galloway et al. [4] estimated that global atmospheric Nr emissions (NO_x and NH_3) will increase from 23 Tg N yr^{-1} in 1860 to 189 Tg N yr^{-1} in 2050. The main forms of Nr in the atmosphere are divided among: (i) the inorganic reduced forms of nitrogen (e.g., NH_3, NH_4^+); (ii) inorganic oxidized forms (e.g., NOx, HNO_3, N_2O, NO_3^-), and; (iii) organic compounds (e.g., urea, amines, proteins, nucleic acids) [2,4,5]. These species

may be considerably modified by (photo)chemical reactions and enter into biogeochemical cycles of terrestrial and aquatic ecosystems [6].

The nitrogen species analysis through wet , dry or bulk deposition are a key process in better understanding the human impacts on the nitrogen biogeochemical cycle [7–9]. Since net primary production of most terrestrial ecosystems is limited by nitrogen availability, deposition of reactive nitrogen becomes a source of nutrients in these sites and could improve productivity [10–12]. In contrast, the excessive nitrogen input may cause acidification of forest soils, eutrophication, unbalance and decreases in biodiversity, and enhanced greenhouse gas emissions [13–15].

During the wet atmospheric deposition, nitrogen is supplied in soluble form (total dissolved nitrogen – TDN), which encompasses dissolved inorganic (DIN: NH_4^+ + NO_3^-) and organic nitrogen (DON) [16–18]. TDN atmospheric deposition have been extensively investigated worldwide [18–22]. Cui et al. [23] and Tu et al. [24] reported that wet deposition fluxes of TDN in agricultural and forest ecosystems in China ranged from 37.37 $kgNha^{-1}yr^{-1}$ to 113.8 $kgNha^{-1}yr^{-1}$, respectively, with DON accounting for about 26% of TDN. In Brazil, some studies have shown that both urban and forest regions receive a considerable TDN deposition (5 – 18 $kgNha^{-1}yr^{-1}$) by way of bulk deposition [25–27]. According to these sites, DON deposition ranged between 30 and 58 % of TDN, highlighting its potential importance to N cycling in different ecosystems. DON contribution to TDN varies due to local sources, seasonal patterns and mixed sources, therein it is challenging to evaluate the partition from natural to anthropogenic sources and their environmental impacts. Moreover, studies from 2010's highlights some of these mechanisms, and also point out the ubiquitous role of DON in atmospheric deposition [16,28–30].

Despite nitrogen atmospheric deposition have been adequately estimated in Asia, Europe and North America through monitoring networks [14], available data for many Southern hemisphere developing countries are either scarce or non-existent [11]. As it pertains to Brazil, nitrogen atmospheric deposition data comes from private and isolated initiatives or from research groups limited to specific regions for restricted periods, which impoverishes the global analysis of the nitrogen input impacts in ecosystems of said country. In this perspective, we evaluated and quantified the atmospheric deposition fluxes of TDN, DIN and DON in a region with agricultural influences in the Southern Minas Gerais region, Brazil.

2. Material and Methods

2.1. Sampling site

The state of Minas Gerais is located in the Southeastern region of Brazil, where the largest cities are located, e.g., São Paulo, Rio de Janeiro and Belo Horizonte (Fig. 1). The major atmospheric pollutant emissions in this region are related to transport, farming, biomass burning and industrial activities such as mining, metallurgical, agro-industrial and chemical plants [31,32]. This study was conducted in the Southern Minas Gerais region, which comprises an important economic region responsible for 21.8% of agricultural commodities (mainly from coffee producing regions), and accounts for about 12% of the state's Gross Domestic Product [31].

The sampling collection was conducted specifically in Lavras city (21° 13' 45.3"S and 44° 58' 32.4"W), 241 km from the Atlantic Ocean (Fig.1). Lavras has an area of 564.744 km², 919 m of altitude and a population of 102,728 inhabitants, occupying the fifth place among the most populous cities in Minas Gerais' Southern region [33]. Approximately 19% (107 km²) of its total area is associated with agricultural activities, mainly coffee production [34], also IBGE [35] estimated an average synthetic nitrogen fertilizers application rate in Minas Gerais region around 110.4 $kgha^{-1}yr^{-1}$. Its vehicular fleet has about 50 thousand light-duty vehicles, comprising 54% automobiles and 26% motorcycles. Moreover, its vehicle fleet is about 15 years old on average, with 62% of its passenger cars produced before 2010 and 14% before 1990 [36].

The Köppen-type climate of the region is subtropical Cwa with well-defined seasons, and rainfall concentrated in Summer (Junqueira Junior et al. 2019). Long-term average annual precipitation (1981-2010) is 1462 mm, and 85% of the rainfall occurs in the wet period (October to March) [37]. The mean annual temperature is 20.3°C ranging from 16.9°C in June and July to 22.5 °C in February [37].

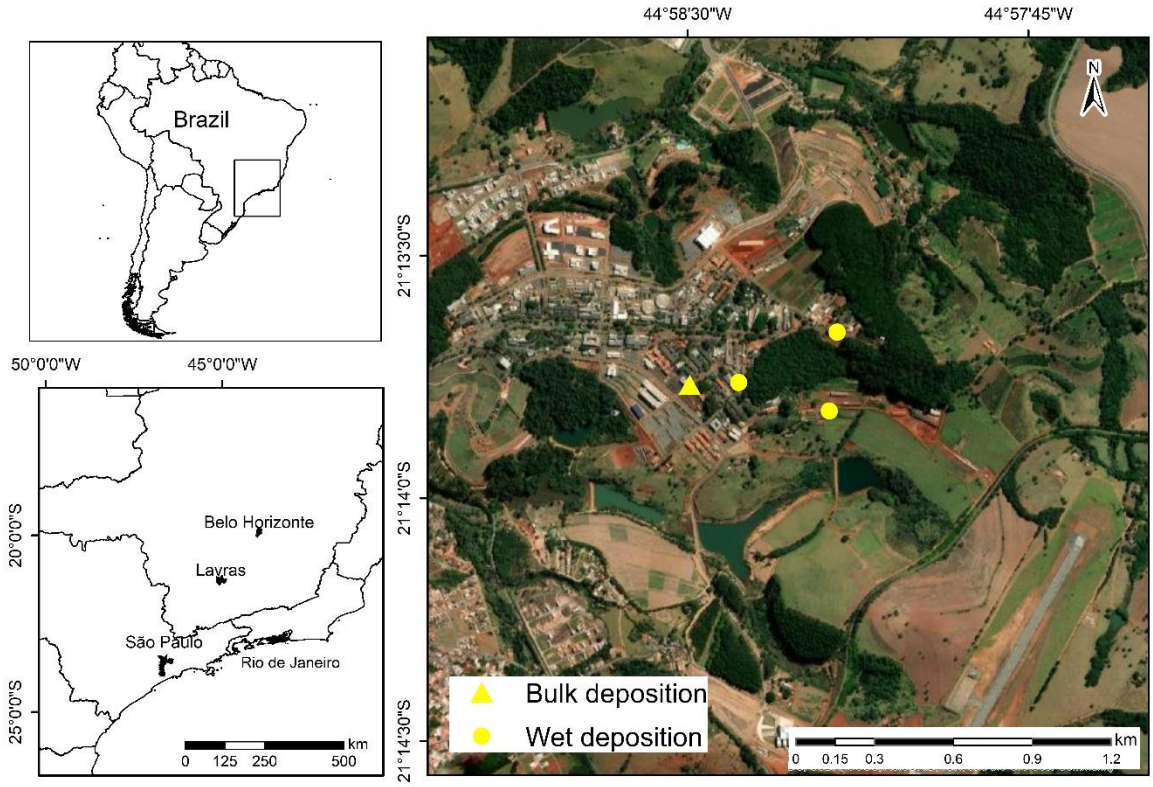

Figure 1. Location of sampling points in Lavras city, Southern Minas Gerais region, Brazil. Bulk and wet deposition samples are depicted in yellow.

2.2. Sampling campaign

From May 2018 until April 2019 wet deposition samples were collected after each precipitation event (daily at 9:00 AM local time) using 3 Ville de Paris-type rain gauges. Moreover, 61 different precipitation events were collected with at least 5 mm (critical volume necessary for laboratory analysis). In addition, monthly samples were analyzed, adding an aliquot of each rain-gauge in the same flask. Regarding preservation procedures and analytical methodologies, we followed the criteria adopted by Standard Methods for Examination of Water and Waste Water [38].

In the same period (May 2018 – April 2019), we also collected 36 bulk deposition samples through a high-density polyethylene bucket (NALGON) of 10L with a collecting area of 439 cm^2. To prevent sunlight effects and reduce litter fall in samples, the collector was placed inside a sun-protective PVC structure and covered with a nylon mesh. In this case, the sampling period was around 7 days, but specific sampling times were collected in some rainfall events. In the absence of precipitation, 50 mL of deionized water was added in order to analyze soluble species. It is noteworthy that the sampling collector were installed 1.5 m above ground level and rinsed several times with ultrapure water Milli-Q (Millipore, electrical resistivity 18 MΩ) in order to follow GAW´s sampling procedures [39]. In addition, blank samples analysis were carried out throughout the experimental campaign.

2.3. Analytical Procedures

Total Kjeldahl nitrogen (TKN) was determined according to macro-Kjeldahl method [40] for quantification ammonium and organic nitrogen in the monthly wet deposition samples. The process for TKN analysis consists in converting organic nitrogen to ammoniacal nitrogen by acid digestion, therefore the sample pH is raised due to ammoniacal nitrogen and after distillation, the nitrogen was quantified by titrimetric method. For TKN analysis the detection limit was calculated as 0.36 mgL^{-1}.

We measured pH and DIN concentrations from bulk deposition samples. The pH measurements were obtained by using pHmeter (AKSO AK model 151), calibrated with buffer solutions (pH 4.0 and 7.0). In order to quantify nitrogen inorganic species (NH_4^+ and NO_3^-), one sample aliquot was filtered with a 0.22µm diameter membrane (Millex), stored in conditioned polyethylene bottles kept at -18°C prior to ion chromatography (IC) analysis (Metrohm model 851) with anionic column (Metrosep ASupp5 - 250 mm x 4 mm) and cationic column (Metrosep C2 150 - 150 x 4 mm). Analytical quantification was performed using an external calibration curve from the standards concentrations for each ion [39]. We calculated detection limits (DL) values from the parameters obtained from the analysis, by the method of the least squares, from the calibration curve (y = a + bx) and corresponded to the white sign (or linear coefficient) plus 3 times the standard deviation (sd) of the angular coefficient (sdy/x), that is, DL = a + 3 sdy/x. Both NH_4^+ and NO_3^- species presented DL less than 0.01 mgL^{-1}. Blank samples concentrations were quantified and subtracted by 0.36, 0.05 and 0.15 mgL−1 for TKN, NH_4^+ and NO_3^-, respectively.

2.3. Data Analysis

We estimated nitrogen inputs as the product between concentrations of TKN, NH_4^+ and NO_3^- species and collected precipitation amount. The monthly and annual nitrogen deposition flux was expressed using equation 1[30,41].

$$I = 0.01 \sum_{i=1}^{n} C_i \left(\frac{V_i}{A}\right), \quad (1)$$

Where I represents the input ($kg.ha^{-1}.month^{-1}$ or $kg.ha^{-1}.yr^{-1}$), C represents the nitrogen specie concentration ($mg.L^{-1}$), V represents the volume sample (L), A represents the collector area (m^2), i refers to the number of sample and n is the amount of samples at the corresponding monthly or annual scale. For bulk deposition samples in which we added 50 mL of deionized water due to precipitation absence, we considered that volume for calculations.

From wet deposition inputs, we calculated DON by determining the difference between TKN and NH_4^+ and calculated TDN by adding the deposition fluxes of DON, NH_4^+ and NO_3^-. It is valuable to report that, for bulk deposition samples, we estimated wet deposition inputs according to Filoso et al. [42], in which N inputs from wet deposition was

considered 50% of bulk deposition. This study was conducted in the countryside of Brazil's Southeastern region, where ~31% of the area is associated to agricultural activities. In a later study, also developed in the same location, Allen et al. [43] showed that on average, dissolved nitrogen species contributed about 49% to total nitrogen deposition.

All statistical analysis, correlation and analysis of variance (ANOVA) and data processing was performed in R environment, through which we applied the functions contained in the *stats* and *ggplot2* packages [44,45].

3. Results and Discussion

3.1. Rainfall patterns

From May 2018 until April 2019, the total rainfall collected by wet deposition (Fig.1) was 1524.6 mm, which represents 99% of the total rainfall reported by Lavras' weather station for the same period [46]. Regarding climatological values, the sampling period showed a surplus of 63 mm (rainfall positive anomaly) in comparison with climatological values, such differences represent almost 5% above long-term annual average rainfall (1981-2010) (Fig. 2a).

Regarding bulk deposition, the total rainfall collected in the sampling period was 1050.4mm, which in comparison with Lavras' weather station represents 68%. In addition, such differences were associated with sample loss by evaporation and sampling period variation, which went from 7 to 14 days. The same pattern could be identified in relation to climatological standard normal (1981 to 2010), since total rainfall collected represents a deficit of 412mm, accounting for 72%.

Approximately 86% of the rainfall occurred in the wet season (October to March), which is in accordance with the expected pattern of the region. Thus, we can assume that most of the atmospheric processes were represented by the atmospheric deposition samples collected.

3.2. Nitrogen Deposition Fluxes

Deposition flux of TDN ranged from 0.328 to 2.869 $kg.ha^{-1}.month^{-1}$ in June and December, respectively (Fig 2b). TDN fluxes showed significant correlation (p-value<0.05) with rainfall collected by wet and bulk deposition ($r = 0.94$ and $r = 0.68$, respectively). Thus, this pattern suggests that monthly variability of TDN deposition was influenced by the rainfall distribution pattern.

We calculated an annual TDN atmospheric deposition of 16.73 $kg.ha^{-1}.year^{-1}$, which was comparable with the global estimates at sites like eastern North America, Southern Brazil, Europe and Asia (wet atmospheric deposition of nitrogen > 8 $kg.ha^{-1}.year^{-1}$) [11]. In this perspective, Souza et al. [27] ($n = 40$) reported a similar TDN bulk atmospheric deposition of 15.1 $kg.ha^{-1}.year^{-1}$ in an Atlantic Forest area, Southeast Brazil region, where annual average precipitation

is 2800 mm, almost 2 times higher than the studied region. In contrast, Tu et al. [24] monitored a Subtropical Bamboo Forest, China region, with the same annual average precipitation (1490 mm) that our study region and reported that bulk TDN deposition of 113.8 $kg.ha^{-1}.year^{-1}$. These behaviors suggest that others factors controlled TDN fluxes besides rainfall, like anthropogenic sources.

In the period of data analyses, DON deposition ranged from 0.203 to 2.103 $kg.ha^{-1}.month^{-1}$ in June and December, respectively (Fig. 2b). Concerning inorganic species, NO_3^- fluxes ranged from 0.011 (August) to 0.831 $kg.ha^{-1}.month^{-1}$ (January), while NH_4^+ deposition varied from 0.003 $kg.ha^{-1}.month^{-1}$ at May to 0.343 $kg.ha^{-1}.month^{-1}$ in March (Fig. 2b). In this sense, DON was the predominant specie throughout the sampling campaign, with a monthly relative TDN contribution ranging from 50% to 98%. Considering all the sampling period, the contribution of DON, NH_4^+ and NO_3^- to TDN were 67.4%, 8.4% and 24.1% respectively. Such high relative contributions were reported in Chinese inland regions [47,48] and are reasonable due to fertilizer application in croplands.

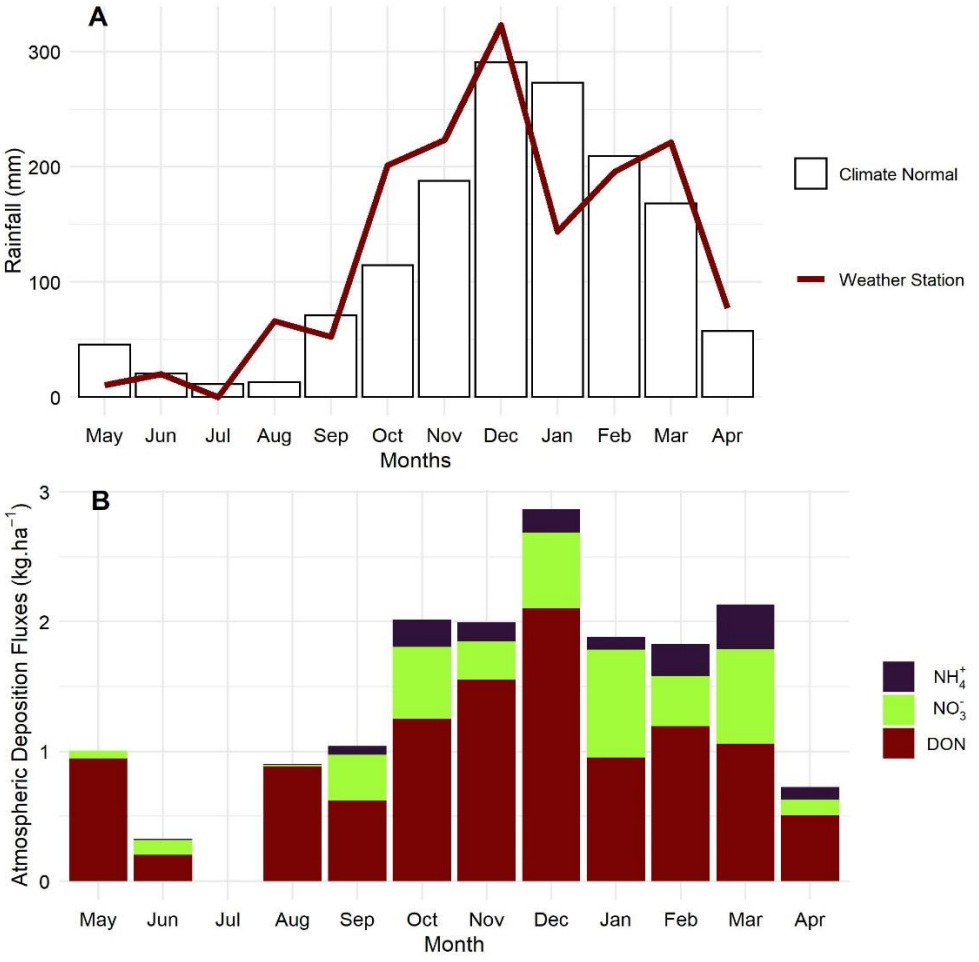

Figure 2 (A) Comparison between long-term annual rainfall (1981-2010) and rainfall reported by Lavras' weather station from March 2018 until April 2019 (in units of mm), **(B)** Wet deposition fluxes of nitrogen species (NH_4^+, NO_3^- and DON) in kg.ha^{-1} from samples collect in Lavras, Brazil from May 2018 until April 2019.

In order to characterize the seasonal variability, monthly deposition fluxes of DON, NO_3^- and NH_4^+ were combined according to seasons: the wet season (October – March) and the dry season (April – September). Nitrogen deposition fluxes in the wet season reached values of 1.23, 3.38 and 8.11 kg.ha^{-1} for NH_4^+, NO_3^- and DON respectively, shown a distinct seasonal pattern significant in comparison with the dry season (ANOVA test; p-value < 0.05). Moreover, NH_4^+, NO_3^- and DON fluxes increased by 6.74, 5.15 and 2.56 times, respectively, during the October to March period.

3.3. pH and NO_3^-/NH_4^+ ratio

Several studies have been using the NO_3^-/NH_4^+ ratio as a reliable proxy for assessing the relative contributions of oxidized and reduced nitrogen species in the atmospheric deposition [29,49,50]. In our study, the monthly mean values of NO_3^-/NH_4^+ ratios varied between 1.36 in April and 33.7 in May, with annual average of 8.25 (Fig.3). Broadly, the presence of NH_4^+ can be directly attributed to NH_3 emissions, mainly due to agricultural activities, such as fertilizer production and application and livestock production [5,26]. Regarding NO_3^-, although it is linked to high NOx emissions mainly from the combustion of fossil fuels [48], recent findings have suggested that agriculture is one of the dominant sources of NO_x [51]. Our results showed NO_3^-/NH_4^+ ratios above 1 throughout the study period, suggesting predominance of oxidized nitrogen species. When associated with data on existing mobile and stationary fossil fuel sources, our results point to NO_x emissions from agricultural soils. In addition, although it did not show statistically significant differences between seasons, the mean value of NO_3^-/NH_4^+ ratio was 12.8 in dry season, which is 2.8 times higher than in wet season (NO_3^-/NH_4^+ = 4.48).

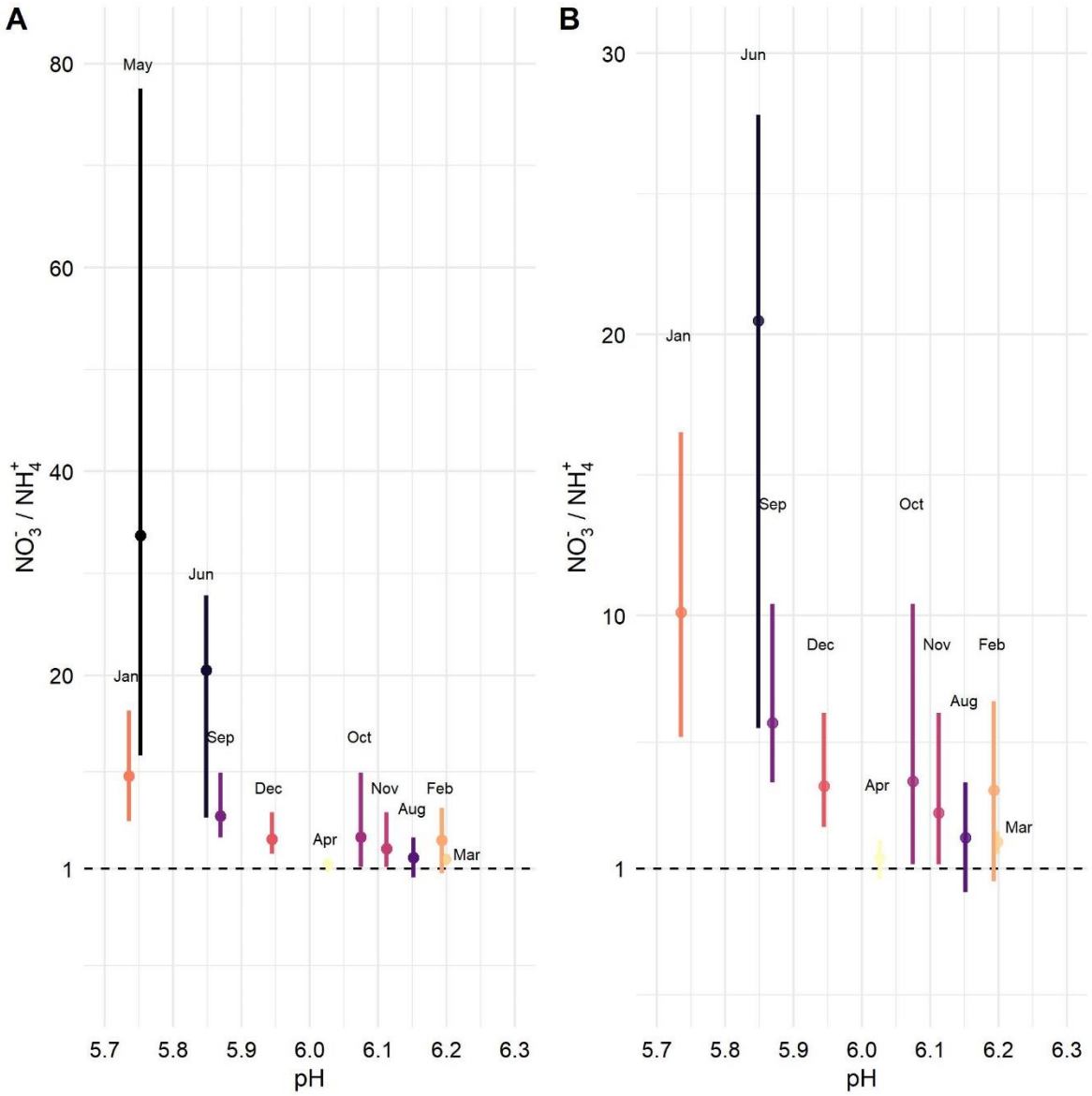

Figure 3 Monthly variability of NO_3^-/NH_4^+ ratio and pH values in wet atmospheric deposition for samples collect in Lavras, Brazil from May 2018 until April 2019. The vertical lines represent the interval between the minimum and maximum values of the NO_3^-/NH_4^+ ratios.**(A)** Depicts all the sampling period; and **(B)** magnifies the months with ratios between 1 and 30.

4. Conclusions

We analyzed the seasonal patterns of wet deposition of dissolved inorganic and organic nitrogen species for a region with agricultural influences in the Southern Minas Gerais region, Brazil, from March 2018 to April 2019. TDN ranged from 0.328 to 2.869 $kg.ha^{-1}.month^{-1}$ with annual flux of 16.73 $kg.ha^{-1}.year^{-1}$, in which DON, NH_4^+ and NO_3^- accounted for 67.4%, 8.4% and 24.1% respectively. Thus, further study on the compositions and specific sources of DON should be clarified in the future due to its important role. In addition, wet deposition fluxes for all nitrogen species increased significantly (ANOVA test; p-value < 0.05) at an average rate of 3 $kg.ha^{-1}$ during the wet season in comparison with dry season, suggesting influences by the rainfall distribution pattern and agricultural sources inside the county air

basin. We also found high NO_3^-/NH_4^+ ratios values (average = 8.25), indicating NO_x emissions from agricultural soils. Our findings are similar to other places in the world, though some local studies display the opposite, which might have important implications for improve the knowledge of the of nitrogen biogeochemical cycling in the study region in the future.

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