Stable Isotopic Characterization of Nitrate Wet Deposition in the Tropical Urban Atmosphere of Costa Rica

Mario Villalobos-Forbes
Universidad Nacional de Costa Rica

Germain Esquivel-Hernandez (✉ germain.esquivel.hernandez@una.cr)
Universidad Nacional de Costa Rica   https://orcid.org/0000-0002-6890-6509

Ricardo Sánchez-Murillo
Universidad Nacional de Costa Rica

Rolando Sánchez-Gutiérrez
Universidad Nacional de Costa Rica

Ioannis Matiatos
International Energy Agency

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Mario Villalobos-Forbes[1,2,] Germain Esquivel-Hernández[1,2*], Ricardo Sánchez-Murillo[1,2], Rolando Sánchez-Gutiérrez[1,2], Ioannis Matiatos[3]

[1]Stable Isotopes Research Group, Chemistry Department, Universidad Nacional Costa Rica, Heredia 86-3000, Costa Rica

[2]Water Resources Management Laboratory, Chemistry Department, Universidad Nacional Costa Rica, Heredia 86-3000, Costa Rica

[3]International Atomic Energy Agency, Isotope Hydrology Section, Vienna International Centre, 1400 Vienna, Austria

* Correspondence: germain.esquivel.hernandez@una.cr; Tel.: +506 2277-3484; Fax: +506 2277-3349

Abstract

Increasing energy consumption and food production worldwide results in anthropogenic emissions of reactive nitrogen into the atmosphere. To date, however, little information is available on tropical urban environments where inorganic nitrogen is vastly transported and deposited through precipitation on terrestrial and aquatic ecosystems. To fill this gap, we present compositions of water stable isotopes in precipitation and atmospheric nitrate ($\delta^{18}O$-H_2O, δ^2H-H_2O, $\delta^{15}N$-NO_3^-, and $\delta^{18}O$-NO_3^-) collected daily between August 2018 and November 2019 in a tropical urban atmosphere of central Costa Rica. Rainfall generation processes (convective and stratiform) were identified using stable isotopes in precipitation combined with air mass back trajectory analysis. A Bayesian isotope mixing model forced with $\delta^{15}N$-NO_3^- values corrected for potential ^{15}N fractionation effects reveal the predominant contribution of biomass burning and lightning to nitrate wet deposition. $\delta^{18}O$-NO_3^- values in Caribbean convective rainfall reflect the oxidation chemistry of NO_x sources whereas $\delta^{15}N$-NO_3^- values in Pacific stratiform rainfall indicate the transport of nitrogen sources contributing to nitrate in atmospheric deposition. These findings provide necessary baseline information about the combination of water and nitrogen stable isotopes with atmospheric chemistry and hydrometeorological techniques to better understand wet deposition processes and to characterize the origin of inorganic nitrogen loadings in tropical regions.
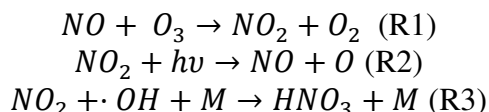
Keywords: stable isotopes; nitrate; wet deposition; rainfall generation processes; urban atmosphere; Costa Rica
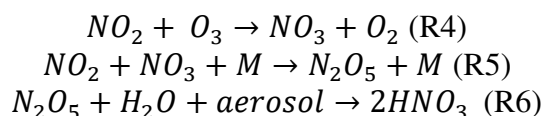
1. Introduction

Since the beginning of the industrialization era, human activities have dramatically increased the amounts of reactive nitrogen emitted to the atmosphere and deposited to the terrestrial and aquatic ecosystems, modifying the biogeochemical cycle of nitrogen (Harrison 2018; Kanakidou et al. 2016; Michalski et al. 2011). Anthropogenic emissions of reactive nitrogen come mainly from fossil fuels combustion (~30 Tg N/yr), accounting for

more than 50% of the total global emissions. Agriculture emissions (e.g., from fertilized soils) were estimated in 8 Tg N/yr. Other reactive nitrogen emissions include biomass burning (~5 Tg N/yr), biogenic soil processes (~18 Tg N/yr) and lighting (up to 5 Tg N/yr) (Fowler et al. 2013). Emissions of nitrogen oxides ($NO_x = NO + NO_2$) are of interest as they are important drivers of atmospheric chemistry since tropospheric ozone production is controlled by their availability (Fang et al. 2011; Wallington et al. 2019). Nitric acid (HNO_3) or nitrate (NO_3^-) are the major sink of NO_x and major contributors to the atmospheric acidity, placing second after sulfuric acid (H_2SO_4). Ammonia (NH_3) also plays an important role as it is the main neutralizing gas for these acidic compounds (Beyn et al. 2015; Felix et al. 2017; Kanakidou et al. 2016). Therefore, identifying the mechanisms controlling the transformation of NO_x into nitrate and its deposition (e.g., through precipitation) is important to underpin the potential impacts on the nitrogen cycles from local to regional and global scales.

The combination of environmental stable isotopes with atmospheric chemistry and hydrometeorological techniques is promising for gathering crucial information about the sources and cycling of nitrogen species beyond what concentration measurements alone can provide (Elliot et al. 2019; Hastings and Sigman 2003; Xiao et al. 2015). Overall, the oxidation mechanism of nitrogen in polluted atmospheres is controlled by O_3 and $\cdot OH$ during the day via:

$$NO + O_3 \rightarrow NO_2 + O_2 \text{ (R1)}$$
$$NO_2 + hv \rightarrow NO + O \text{ (R2)}$$
$$NO_2 + \cdot OH + M \rightarrow HNO_3 + M \text{ (R3)}$$

and at night via:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \text{ (R4)}$$
$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \text{ (R5)}$$
$$N_2O_5 + H_2O + aerosol \rightarrow 2HNO_3 \text{ (R6)}$$

In reaction 5, M is commonly N_2 or O_2 and stabilizes the product through collisions. Based on these reactions, it is possible to quantify the equilibrium fractionation of nitrogen isotopes associated with NO_x oxidation and HNO_3 formation pathways using mixing models that rely on the assumptions of two major NO_x oxidation and HNO_3 formation pathways (i.e., OH: daytime (R1-3) and N_2O_5: nighttime (R4-6)) (Song et al., 2019; Felix and Murgulet, 2020). Oxygen and nitrogen stable isotope ratios of nitrate can also be used to collect additional information about the sources and sinks of atmospheric nitrate. Nitrogen stable isotope ratios in atmospheric nitrate ($\delta^{15}N\text{-}NO_3^-$) can be used to trace NO_x sources. Source identification is possible due to the different $\delta^{15}N\text{-}NO_3^-$ signature of the potential endmembers, but the ^{15}N isotopic fractionation during the conversion of NO_x to nitrate needs to be considered (Liu et al. 2017; Michalski et al. 2011, Felix and Murgulet, 2020). On this matter, $\delta^{18}O\text{-}NO_3^-$ can provide information on the nature and the relative importance of NO_x oxidation pathways, ultimately leading to atmospheric nitrate (Fang et al. 2011; Savarino et al. 2013). However, the interpretation of this isotope information is more complicated and limited because $\delta^{18}O\text{-}NO_3^-$ is related to the mixing of different

92 oxygen sources (e.g., O_3, H_2O, $\cdot OH$) and isotopic fractionation during the photochemical
93 conversion of NO_x into NO_3^- (Michalski et al. 2011; Xiao et al. 2015).
94   In tropical regions like Central America, the formation of deep convective systems
95 is an important component of regional precipitation intensity and distribution (Durán-
96 Quesada et al. 2017). The deep convective activity is related to the influence of Mesoscale
97 Convective Systems (MCSs) and the formation of convective rainfall (i.e., small-scale
98 systems: 1-2 km and high intensity precipitation) and stratiform rainfall (i.e., large scale
99 ~100 km and low intensity precipitation) (Sánchez-Murillo et al. 2015, 2016). For the high-
100 intensity convective and lower-intensity stratiform systems, differences in vertical air
101 motions and microphysical processes govern the rain formation. Thus, these rainfall
102 generation processes impart characteristic water isotopic compositions (δ^2H and $\delta^{18}O$) to
103 convective and stratiform precipitation due to the condensation and riming associated with
104 boundary layer moisture (Aggarwal et al. 2016; Konecky et al., 2019). For instance,
105 stratiform rainfall related with MCSs has been shown to be mainly associated with large
106 negative excursions of $\delta^{18}O$ and δ^2H values in tropical rainfall (Kurita 2013; Sánchez-
107 Murillo et al. 2019). For two sites in Costa Rica, the average stratiform rainfall fraction
108 contributing to each precipitation event was modeled using a statistically significant
109 relationships of stratiform rainfall area fractions and the isotopic composition of
110 precipitation (i.e., $\delta^{18}O$; Munksgaard et al. 2019).

111   Regarding the ion composition of precipitation, rainfall from stratiform clouds
112 showed higher ion concentrations and lower pH than convective rainfall in tropical forests
113 of Congo and Amazonia (Andreae et al. 1990; Lacaux et al. 1992). This finding seems to be
114 linked to the higher liquid water content in convective clouds, which leads to a dilution of
115 the chemical content of the precipitation (Lacaux et al. 1992). However, little information is
116 available for regions like Central America where rainfall is defined by the intersection of
117 large-scale circulation patterns, the moisture inputs from the Caribbean Sea and the Pacific
118 Ocean, and local processes in which topography and vegetation cover play a relevant role
119 (Sánchez-Murillo et al., 2020). Recent observations in the mixing ratios of trace gases (e.g.,
120 carbon dioxide and methane) in the urban area of Costa Rica indicate that there is a strong
121 influence of the local atmospheric mixing conditions on the dispersion and chemical
122 transformations of atmospheric pollutants in the local atmosphere. Overall, these mixing
123 conditions are mostly controlled by the seasonal variation in the height of the local
124 boundary layer (Carballo-Chaves et al., 2020). Therefore, the analysis of stable isotopes in
125 precipitation and its chemistry can provide valuable insights of hydrometeorological
126 conditions and rainfall generation processes controlling the nitrogen wet deposition
127 mechanisms. We propose that $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values in atmospheric nitrate are
128 not only controlled by temporal nitrogen emission source changes and reaction chemistry
129 processes, but also by the proportions of convective versus stratiform rainfall.

130   Here, we present a unique dataset of the water and nitrate stable isotope
131 composition in precipitation in a tropical urban atmosphere of Costa Rica. Based on these
132 isotope datasets and other chemical information, this contribution addresses the following
133 research questions: i) What are the sources of atmospheric nitrogen in the main urban

134 atmosphere of Costa Rica, ii) What are the atmospheric processes influencing the temporal
135 variability of atmospheric nitrate), iii) How do the different rainfall generation processes
136 (i.e., convective vs. stratiform precipitation) affect the wet deposition of atmospheric
137 nitrate? This information is necessary for a better understanding of how nitrogen pollutants
138 from tropical urban environments are introduced in the terrestrial aquatic environments via
139 wet deposition.

140
141 **2. Materials and Methods**

142
143 **2.1. Study area**

144
145 The Central Valley of Costa Rica is characterized by an urban conglomerate, known as the
146 metropolitan area, which comprises the four major cities of Costa Rica (~60% population,
147 ~870 inhabitants per km^2) and includes significant industrial activity. The climate of Costa
148 Rica is influenced by four regional air circulation types: NE trade winds; the latitudinal
149 migration of the Intertropical Convergence Zone (ITCZ); cold continental outbreaks; and
150 the sporadic Caribbean cyclones (Waylen 1996; Hidalgo et al. 2013; Sáenz and Durán-
151 Quesada 2015). In the Central Valley, the dry season ranges from December to April and
152 the wet season ranges from May to November. Between 1982 and 2012, mean annual
153 rainfall was ~2,400 mm, with ~ 85% of the rainfall falling in the wet season (Sánchez
154 Murillo et al. 2016). Strong orographic effects are caused by a NW to SE mountain range
155 (or cordillera) with a maximum elevation of 3,820 m a.s.l., which divides the country into
156 the Caribbean and Pacific slopes, each slope having distinct precipitation and runoff
157 regimes.
158 Overall, the local anthropogenic emissions (e.g., fossil fuel combustion, transportation,
159 industrial activities) mainly control the accumulation of polluted air over this urban area.
160 Transportation is responsible for 66% of fuel consumption and 54% of these emissions.
161 This fuel consumption is dominated by gasoline, with 75% of the vehicles running on this
162 fuel (www.estadonacion.or.cr). However, industrial activities are based on the consumption
163 of other fuels like diesel which has a high sulfur content (3500–4000 ppm; Herrera et al.,
164 2009). Volcanic emissions from nearby volcanoes also contribute to the local SO_2
165 emissions. The volcano's plumes, due to the prevailing wind direction, are transported
166 directly to this region of Costa Rica (Campion et al., 2012).
167   The accumulation of air pollutants is enhanced during the wet season by a reduction
168 in the mixed layer height, which decreases the intensity of the gas mixing dynamics in the
169 local atmospheric boundary layer (Carballo-Chaves et al. 2020; Esquivel-Hernández et al.
170 2015). The chemical composition of precipitation collected in the capital city (San José) is
171 also affected by contributions from these anthropogenic emissions (e.g., NO_x and SO_2)
172 during the wet season (Herrera-Murillo and Rodríguez-Román 2009). However, other
173 remote sources of reactive nitrogen like fertilization-related soil emissions (Hergoualc'h et
174 al. 2008), biomass burning (Fibiger and Hastings, 2016) and lighting NO_x (Schumann and
175 Huntrieser, 2007) are also expected in the Central Valley. In Costa Rica, a land use
176 transition with a simultaneous increase in food production and forest cover was observed in
177 the past years (Lambin and Meyfroidt 2011). For instance, pineapple plantations have
178 proliferated in the lowlands of northern and southern Costa Rica, overtaken coffee to

179 become Costa Rica's second largest agriculture export after bananas (Ingwersen 2012). In
180 2010-2011, the consumption of fertilizers like ammonium nitrate and urea was estimated to
181 be 15 Gg-N/yr and 28 Gg-N/yr, respectively (MEIC 2011). It is also reported that the
182 production of sugarcane in the Pacific region of Costa Rica is based on biomass burning for
183 energy production (Ulloa et al. 2018). Therefore, these NO_x emissions can also be
184 transported to the Central Valley and contribute to the local budget of reactive nitrogen.
185 Regarding the production of NO_x from lighting, lightning is the primary contributor (up to
186 70%) to the total NO_x concentration in the subtropical and tropical free troposphere (Allen
187 et al., 2010; Felix and Murgulet, 2020). Findings in our region indicate that NO_x production
188 per flash is ∼100–250 mol/flash (Bucsela et al. 2010). Besides, under the influence of
189 strong convective activity (e.g., tropical cyclones) up to 1000 flashes/hour were recorded in
190 Costa Rica (Arce-Fernández and Amador, 2020). It is worth mentioning that NO_x
191 emissions from coal combustion can be ruled out for our study site because no coal
192 combustion is reported in Costa Rica.

194 **2.2. Sampling methodology**

196 The sampling site was located at the main campus of Universidad Nacional, Costa Rica
197 (Latitude: 10.005°, Longitude: -84.109°) which is a typical urban site of the Central Valley
198 of Costa Rica. Precipitation samples (N= 111) were collected after 24 hours (i.e., daily
199 basis) on 7:00-9:00 am of each day between August 2018 and November 2019 using a
200 passive collector (Palmex Ltd., Croatia) (Gröning et al. 2012). No samples were collected
201 between December 2018 and April 2019 (dry season). Samples were filtered using 0.45 μm
202 polytetrafluorethylene (PTFE) syringe membranes and divided in two portions: i) 30 mL
203 were stored at dark and frozen conditions (-10°C) until shipment for nitrogen isotopic
204 analysis at the International Atomic Energy Agency (IAEA), ii) 30 mL were stored at dark
205 and cool conditions (5°C) until ion and water isotope analyses at the Stable Isotopes
206 Research Group facilities (Universidad Nacional, Costa Rica). The pH and electrical
207 conductivity were measured after sample collection using a Benchtop Multiparameter
208 Meter Mi-180 (Milwaukee Instruments, USA). To account for the possible contamination
209 from dry deposition, the collector's funnel and the transfer line to the vessel was rinsed
210 with deionized water every day after the samples were collected. Hourly meteorological
211 conditions were registered at the sampling site with a Vantage Pro2 weather station (Davis
212 Instruments, Hayward, CA, USA).

214 **2.3. Laboratory analysis**

216 The concentration of major cations and anions in precipitation samples was analyzed using
217 a Dionex Ion Chromatograph ICS 5000+ (Dionex, CA). The following chemical parameters
218 were quantified: nitrate (NO_3^-), nitrite (NO_2^-), chloride (Cl^-), sulphate (SO_4^{2-}), ammonium
219 (NH_4^+), sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), and magnesium (Mg^{2+}). To assess
220 the quality of our data, the standard operating procedures described by the Global
221 Atmospheric Watch Precipitation Chemistry Programme were followed and the ion balance
222 of each sample was calculated (WMO 2004). For those samples with pH>5, bicarbonate
223 (HCO_3^-) concentration in μeq/L was calculated using the pH and the acid-base equilibrium
224 (WMO 2004):

$$HCO_3^- = \frac{5.10}{10^{(6-pH)}} \qquad (1)$$

Those samples with ion differences outside the range ±20% were flagged and checked for possible contamination issues (N=15). Of these samples, most were related to pH values greater than 6.3 (i.e., carbonated samples) and/or low electrical conductivities (<10 µS/cm). We also checked the nitrate concentration of our samples to see if the maximum nitrate concentration in rainfall reported for the Central Valley was exceeded (up to ~5 mg/L) as these high nitrate concentrations could indicate contamination issues (Herrera-Murillo and Rodríguez-Román 2009). Therefore, two samples were excluded from the data analysis. The detection limits were calculated as follows: NO_3^- (0.3 mg/L, expressed as NO_3^-), Cl^- (0.15 mg/L), SO_4^{2-} (0.2 mg/L), NH_4^+ (0.15 mg/L, expressed as NH_4^+), Na^+ (0.03 mg/L), Ca^{2+} (0.04 mg/L), K^+ (1.0 mg/L), and Mg^{2+} (0.03 mg/L). No nitrite data is reported because it was below the detection limit in all samples (<0.3 mg/L). Hereafter the ion concentrations are expressed in µeq/L.

Stable isotopes analysis of precipitation samples (N=110) was performed using a water isotope analyzer LWIA-45P (Los Gatos Research Inc., USA). The secondary standards were MTW ($\delta^2H = -131.4$ ‰, $\delta^{18}O = -17.0$ ‰), DOW ($\delta^2H = -1.7$ ‰, $\delta^{18}O = -0.2$ ‰), and CAS ($\delta^2H = -64.3$ ‰, $\delta^{18}O = -8.3$ ‰). MTW and DOW standards were used to normalize the results to the VSMOW-SLAP scale. The uncertainty of these international standards is 0.3 ‰ (^2H) and 0.02 ‰ (^{18}O) (IAEA 2017). The CAS standard was used as a quality control and drift control standard. The analytical long-term uncertainty was: ± 0.5 ‰ (1σ) for ^2H and ± 0.1 ‰ (1σ) for ^{18}O. Stable isotope compositions are presented in delta notation δ (‰, per mil), relating the ratios (R) of $^{18}O/^{16}O$ and $^2H/^1H$, relative to Vienna Standard Mean Ocean Water (V-SMOW).

Seventy-six precipitation samples, collected between August 2018 and July 2019, were shipped for nitrogen isotopic analysis ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-) to the Isotope Hydrology Laboratory (IAEA). This laboratory uses a Ti (III) reduction method, which involves a one-step chemical conversion employing $TiCl_3$ to reduce NO_3^- to N_2O gas in septum sample vials (Altabet et al. 2019). The N_2O headspace was measured for ^{15}N and ^{18}O by coupling with a continuous-flow Isotope-Ratio Mass Spectrometer-IRMS (Isoprime 100) and a Trace Gas N2O purification device. The analytical uncertainties were ±0.2‰ and ±0.4‰ for $\delta^{15}N/\delta^{18}O$-$NO_3^-$, respectively. The stable isotope ratios were expressed in delta (δ) and a permil (‰) notation relative to an international standard. Values of $\delta^{15}N$ were reported relative to N_2 in atmospheric air (AIR) and $\delta^{18}O$ values were reported relative to Vienna Standard Mean Ocean Water (VSMOW). The standards used for the analysis were USGS34 (-1.8 ± 0.1 for $\delta^{15}N_{AIR}$ and $+27.9 \pm 0.3$ ‰ for $\delta^{18}O_{VSMOW-SLAP}$), USGS35 ($+2.7 \pm 0.1$ ‰ for $\delta^{15}N_{AIR}$ and $+57.5 \pm 0.3$ ‰ for $\delta^{18}O_{VSMOW-SLAP}$) and IAEA-NO3 ($+4.7 \pm 0.2$ ‰ for $\delta^{15}N_{AIR}$ and $+25.6 \pm 0.4$ ‰ for $\delta^{18}O_{VSMOW-SLAP}$).

2.4 Air mass trajectory analysis

The HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model was used to calculate the preferential transport pathways followed by the air masses that arrived at

the Central Valley (Stein et al. 2015; Rolph et al. 2017). Air parcel back trajectories were estimated on 72 hours basis. The time frame was selected based on the lifetime of NO_x in the boundary layer which is generally less than two days and due to the proximity of the Caribbean Sea and the Pacific Ocean (Fang et al. 2011; Sánchez-Murillo et al. 2016). Each trajectory was calculated using NOAA's meteorological data files (GDAS, global data assimilation system: 2006-present; 0.5° (~50 km resolution) (Su et al. 2015). The ending altitude of air masses was set to the mean elevation of the Central Valley of Costa Rica (~1,100 m a.s.l.). Trajectory analyses ending times at the Central Valley were set to 12:00 UTC, which correspond to a local time of 06:00 a.m. in Costa Rica

2.5 Data analysis

Pearson's correlation analysis was performed to evaluate potential relationships between ion concentrations and isotopic values of precipitation and atmospheric nitrate. Statistical analyses were done using SigmaPlot software 11.0. An α level of 0.05 was inferred as indicating significance. Kruskal-Wallis test was performed for nitrate concentration and isotopic values in precipitation to identify the differences between Caribbean and Pacific air masses. Simple linear regression analysis was used to construct the local meteoric water line (LMWL) and the $\delta^{15}N\text{-}NO_3^-$ and the $\delta^{18}O\text{-}NO_3^-$ dual plot for atmospheric nitrate.

To calculate the average stratiform rainfall fraction contributing to each precipitation event, the following statistically significant relationship of stratiform rainfall area fractions, F_{st} (5°×5° box) and $\delta^{18}O$ values estimated for our study site was applied:

$$\delta^{18}O - H_2O = 18.4 x F_{st} - 49.7\text{‰} \ (E1)$$

Convective/stratiform classification data was based on Ku-band Precipitation Radar (KuPR) product of GPM (Global Precipitation Measurement) Core Observatory (Version 5, Level 2, https://pmm.nasa.gov/GPM), which is a successor of the TRMM Precipitation Radar. The above-mentioned relationship was estimated for the sampling period 2013–2017; (N=929; R^2=0.32, p<0.05) which comprises five-year precipitation data collected under varying climatic conditions (e.g., warm/cold ENSO episodes). Therefore, it can provide good approximations of stratiform rainfall fractions contributing to the precipitation collected during our sampling period (Munksgaard et al., 2019).

To quantify the equilibrium fractionation of nitrogen isotopes during NO_x oxidation and HNO_3 formation, we applied the mathematical formulations described by Felix and Murgulet (2020). In brief, the overall $\delta^{15}N$ fractionation (ϵ_N) can be predicted using the following isotope balance relationship:

$$\varepsilon_N = f_{OH} x \varepsilon_{OH} + f_{N2O5} x \varepsilon_{N2O5} \ (E2)$$

where f_{OH} is the fraction of ·OH pathway and f_{N2O5} is fraction of the N_2O_5 pathway. The ·OH and N_2O_5 fractions estimated by Alexander et al. (2009) for the tropics were applied in equation 2, namely 87% for the ·OH pathway and 13% for the N_2O_5 pathway. The ϵ_N requires the ambient temperature, NO_2 mixing ratio and the fraction of NO_2 to NO_x ($f_{NO2/NOx}$) for the study site. The average monthly temperature for the Central Valley during the study period was 21.4±0.5 °C (1σ). The average NO_2 mixing ratio of 38.6 ppbv

7

reported by Herrera et al. (2009) and Herrera-Murillo et al. (2011) was included in the calculations. However, no NO_x speciation is available for the Central Valley. Therefore, it is not possible to calculate the $f_{NO2/NOx}$ for our study site. It is reported that $f_{NO2/NOx}$ values may be in the range 0.20 to 0.75 in some urban areas (Rao and George, 2014; Richmond-Bryant et al., 2017). Nevertheless, it is expected that the $f_{NO2/NOx}$ ratios in our study site to be high because the ·OH pathway dominates in the tropical atmospheres (Alexander et al., 2009). Therefore, the calculations of ε_N were performed for $f_{NO2/NOx}$ ratios in the range 0.75 to 1.00 (N=6 corresponding to 0.05 ratio increments). Thus, we report the average ε_N value and the estimated error as the standard deviation of dataset. The temperature-dependent isotope effects on the fractionation factors, namely $^{15}\alpha_{NO2/NO}$ and $^{15}\alpha_{N2O5/NO}$, were estimated using the equations reported by Walters and Michalski (2015).

Overall, the $\delta^{18}O\text{-}NO_3^-$ values are determined by the reactions that produce NO_3^- (R1-R6) and not the original source of NO_x (Hastings and Sigman 2003; Shrestha et al. 2013). The $\delta^{18}O\text{-}NO_3^-$ values reflect the transfer from O_3 (R1 and R4) during cycling with NO_x ($\delta^{18}O$ in O_3 falls in the range ~+80 - +120‰ vs. VSMOW) and the reaction of NO_2 with ·OH (R3) that also contributes to the oxygen isotope of NO_3^- (Morin et al., 2008; Savarino et al., 2008; Michalski et al. 2011). However, the peroxy radical (RO_2) oxidation pathway has been suggested as a competing pathway leading to lower than usual $\delta^{18}O\text{-}NO_3^-$ values (Fang et al. 2011):

$$NO + RO_2 \rightarrow NO_2 + RO \ (R7)$$
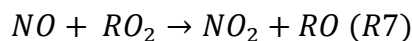
To account for this competing reaction, Felix and Murgulet (2020) also describe a mathematical approach to determine the % O_3 and RO_2 competing daytime oxidation reactions (R1) and (R7) that occur before subsequent ·OH oxidation reaction (R3). However, it is not possible to perform these calculations for our study area due to the complex atmospheric chemistry prevailing in our tropical environment. The Central American volcanoes are known to be important emitters of halogen emissions (e.g., BrO and ClO) in our region. There is evidence that these emissions can strongly interact with ozone and species like H_XO_Y and NO_X and impact the local atmospheric chemistry (de Moor et al. 2013; Rüdiger et al., 2020). Additionally, the local atmosphere of the Central Valley is under the strong influence of biogenic emissions like biogenic volatile organic hydrocarbons (BVOC; Esquivel-Hernández et al., 2011). Therefore, the air chemistry in our tropical atmosphere is highly sensitive because of the high solar radiation and concentrations of water vapor with plentiful BVOC emissions and the subsequent impact of the production of secondary organic aerosols (SOA) via the $RO_2 + HO_2$ pathway (Santos et al., 2018; Yañez-Serrano et al., 2020). Therefore, these additional chemical pathways associated to the halogen and organic reactive species should be accounted to perform a quantitative analysis of the $\delta^{18}O\text{-}NO_3^-$ variations for our study site (i.e., the % O_3 vs. RO_2 participating in the daytime oxidation). However, these calculations are outside the scope of our work and more investigation is needed on this matter.

2.6 Stable isotope mixing model

We applied the stable isotope mixing model from the R package Simmr to partition relative nitrogen sources for our study region using a Bayesian statistical framework based on a Gaussian likelihood (Parnell and Inger, 2016). Based on the identified NOx emissions

sources in our region, the following NO_x endmembers were included in the mixing model: lightning, fossil fuels (i.e., gasoline and diesel), soils emissions from biogenic activity, and biomass burning. The corresponding $\delta^{15}N\text{-}NO_3^-$ and deviations of these sources are: +0.5 ± 0.9‰, -3 ± 6‰, -13 ± 7‰, -35 ± 10‰, and +1 ± 4‰, respectively (Elliot et al., 2019; Felix and Elliot, 2014; Felix and Murgulet, 2020; Fibiger et al., 2014; Fibiger and Hastings, 2016; Heaton, 1987; Heaton, 1990; Li and Wang, 2008; Walters et al., 2015; Yu and Elliot, 2017).

3. Results

3.1 Precipitation chemical and isotopic characteristics

Data of ion concentrations and isotope compositions (water and nitrate) in precipitation are summarized in Table 1. Even though the study site is situated within an urban conglomerate, the average pH of 5.72 measured in the precipitation was not lower than the global average of 5.7 for pollution-free areas (Balestrini et al. 2016). The major anion was sulphate, contributing with ~18% to the total ion concentration, whereas calcium was the major cation, with a contribution of ~11% to the total. As for nitrate, the $25^{th}\text{-}75^{th}$ percentil range was between 14.5 and 26.6 µeq/L for the entire dataset. Some values (N=9) fell outside this range with values up to 85.5 µeq/L. The average contribution of nitrate to the total ion concentration was ~ 8%. The average depositon flux of nitrate for the study site, based on the daily precipitation amounts and the daily nitrate concentrations, was calculated as 4.5 mg $N\text{-}NO_3^-/m^2$ day (range: 0.2 – 16.7 mg $N\text{-}NO_3^-/m^2$ day).

The average oxygen isotope composition ($\delta^{18}O\text{-}H_2O$) in precipitation was -8.61 ± 3.45‰ (range: -20.38‰ – -0.52‰, Table 1), whereas the average $\delta^2H\text{-}H_2O$ was -59.37 ± 28.21‰ (range: -1.86‰ – -153.35‰, Table 1). Based on these isotope data, the LMWL was constructed (Figure 1A and 1B). The following meteoric water line (LMWL) was calculated for the study site: $\delta^2H\text{-}H_2O=8.05\cdot\delta^{18}O\text{-}H_2O+9.68‰$ (p<0.001; R^2=0.97, Figure 1A). The slope and intercept parameters of the LMWL are consistent with those of the GMWL and with the historical data reported for the Central Valley of Costa Rica (Munksgaard et al. 2019; Craig 1961; Sánchez-Murillo et al. 2013). The relationships between selected chemical and isotopic parameters in precipitation are shown in Figure 2.

3.2 Temporal variations of nitrate, $\delta^{18}O\text{-}H_2O$, $\delta^{15}N\text{-}NO_3^-$, and $\delta^{18}O\text{-}NO_3^-$

The wet/dry-season precipitation pattern of the Central Valley, with two rain maxima in May-June and in September-October, is shown in Figure 3A. Average daily precipitation during the wet season was 18 mm/day, with values up to 86 mm/day. The overall trend in the nitrate concentrations (µeq/L) shown in Figure 3B indicate that during those rain maxima? periods, higher nitrate values were recorded (up to 85.5 µeq/L), particularly after a long dry period. This characteristic was more visible during the transition periods (Apr-May and Nov-Dec).

As for $\delta^{18}O\text{-}H_2O$, the strongest depletion in ^{18}O registered during the rainiest periods, for instance in October 2018 (up to -20.38‰, Figure 3C), are likely the result of the passage of the ITCZ over Costa Rica and higher stratiform fractions, whereas higher $\delta^{18}O\text{-}H_2O$ values were registered when convective rain exceeded stratiform precipitation during the transition

seasons and the Mid-Summer Drought (MSD) (Munksgaard et al. 2019; Sánchez-Murillo et al. 2019). The variation in $\delta^{15}N$-NO_3^- shown in Figure 3D was systematic along the first study period (August 2018-November 2018). A decrease in $\delta^{15}N$-NO_3^- was observed toward the end of the rainy period in August 2018-October 2018 (up to -3.81‰), whereas an increasing trend was registered at the beginning of rainy period in April-July 2019 (up to +4.09‰). For the period August-November 2019, random variations in the range -1.6‰ – +5.2‰ were observed. As for $\delta^{18}O$-NO_3^- (Figure 3E), these values did not follow the trend observed in $\delta^{15}N$-NO_3. For instance, the strongest enrichment in ^{18}O-NO_3 were recorded during the rainiest periods (October and May), with values up to +65.3‰. The lower isotopic values were registered during the transition seasons and the MSD (up to +33.7‰). Between August 2019 and November 2019, the $\delta^{18}O$-NO_3^- showed relatively smaller variations (+54.9 ± 3.4‰).

3.3 Nitrate wet deposition

Based on the HYSPLIT trajectory analyses, air masses that arrived at the Central Valley of Costa Rica mostly came from the Caribbean Sea (N=80, 73%), whereas the moisture contribution from the Pacific Ocean was less common (N=30, 27%, Figure 4A). At $p<0.001$, the average stratiform fraction calculated for the Caribbean samples (0.403±0.158, 1σ) was lower than the average stratiform fraction of the Pacific samples (0.522±0.147, 1σ).
As shown in Figure 2, a poor correlation between $\delta^{18}O$-H_2O and NO_3^- was preliminary found for the whole dataset (r=0.248, p>0.05). However, if the air mass pathways of the precipitation events are considered and the data are further split into the two groups, namely Caribbean and Pacific, differences were found between the $\delta^{18}O$-H_2O values and NO_3^- concentrations (Figure 5A and 5B). The average $\delta^{18}O$-H_2O value of the Caribbean samples was significant higher than the corresponding value of the Pacific samples (-8.02‰ and -10.51‰, p<0.001). As for the NO_3^- concentrations, the average concentration of NO_3^- in the Caribbean samples was higher than the corresponding value in the Pacific samples (22.5 µeq/L and 17.8 µeq/L, p=0.068). The average $\delta^{15}N$-NO_3^- value in the Pacific samples (+1.6‰) was higher than the corresponding value (+0.5 ‰) in the Caribbean samples (p=0.064 Figure 5C). No correlation (r=-0.052, p=0.654, N = 76) was found between $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- (Figure 6A). $\delta^{15}N$-NO_3^- values in nitrate, resulted in a normal distribution (Figure 6B, p>0.05), whereas $\delta^{18}O$-NO_3^- in nitrate showed a depleted and slightly left-skewed distribution (Figure 6C, p<0.05). For the Caribbean samples, we found a direct proportional relationship between the $\delta^{18}O$-NO_3^- and the nitrate concentration (r=0.288, p<0.05; N=59; Figure 6A). However, no relationship was found between $\delta^{15}N$-NO_3^- and nitrate concentration (p>0.05). For the Pacific samples, in turn, no proportional relationship between $\delta^{18}O$-NO_3^- and the nitrate concentration was found (p>0.05) but a direct proportional relationship between $\delta^{15}N$-NO_3^- and the nitrate concentration (r=0.481, p=0.05, N=17, Figure 6A).

3.3 NO_x emission sources and fractionation processes

To account for the ^{15}N fractionation during the oxidation of the NO_x emissions, we calculated a NO_x to HNO_3 ε value of 8.89 ± 4.04‰ and corrected our $\delta^{15}N$-NO_3^- values for

potential fractionation effects before applying the Bayesian model to partition the relative nitrogen sources for our study region. The ε values varied from 14.31 ($f_{NO2/NOx}$ = 0.75) and 3.51 ($f_{NO2/NOx}$ = 1.00). Overall, this ε value is somewhat higher compared to the corresponding value of ~5.6‰ reported by Felix and Murgulet (2020). For the Caribbean samples, the contributions of nitrogen sources were 42.7 ± 6.2% (biomass burning), 0.8 ± 0.4% (soils biogenic emissions), 15.8 ± 6.3% (gasoline), 2.1 ± 1.2% (diesel), and 38.6 ± 6.3% (lightning). The corresponding contributions for the Pacific samples were 46.0 ± 13.9%, 1.6 ± 1.0%, 12.3 ± 9.1%, 3.6 ± 2.7%, and 36.5 ± 13.8%, respectively (Figure 7).

4. Discussion

The available data on precipitation chemistry for the Central Valley of Costa Rica are scarce. Two previous research efforts reported that most samples showed pH values between 4.0 and 5.6, and only 26% of them were basic (pH>7) (Herrera-Murillo and Rodríguez-Román 2009; Herrera et al. 2009). As for our study, the pH range was relatively higher with most samples falling between 4.9 and 6.3 and only ~13% of these samples had pH values greater than 7. Overall, most low pH values were found in September and October when the influence of the ITCZ intensifies precipitation but also reduces wind speed across the Central Valley, which in turns enhances the wet deposition of NO_3^- and SO_4^{-2} and acidifies the precipitation (Esquivel-Hernández et al. 2015). As for the ion composition, our data agree well with the available information that reported SO_4^{2-} among the most abundant ions, but also a high correlation with NO_3^- and NH_4^+ indicating a common anthropogenic origin (Herrera et al. 2009). At other tropical locations, like São Pablo, Brazil and the Indo-Gangetic Plains in India, authors also reported similar ion species in the local precipitation (Martins et al. 2019; Tiwari et al. 2019). Due to its location in the narrow land bridge of Central America and proximity to the Caribbean Sea and the Pacific Ocean (Figure 4), some contributions from sea salt could be expected in the precipitation of the Central Valley (Kajino and Aikawa 2015; Vet et al. 2014). However, a predominant contribution from Non-Sea-Salt sulphate (NSS-SO_4^{2-}) was found in the precipitation of our study site with an average percentage of 93±5% (range: 76 – 100%). Therefore, it seems that the average contribution is mainly produced from natural and anthropogenic sources (e.g., SO_2 from volcanoes, industrial and traffic emissions). The correlation between NO_3^- and SO_4^{2-} (r=0.270; p<0.05) also suggests the influence of a common anthropogenic source like fossil fuels (SO_2, NO_x, Figure 2). Besides, the photochemical oxidation in the atmosphere may also control and enhance the nitrogen wet deposition in the urban conglomerate (Shresta et al. 2013; Xiao 2016; Decina et al. 2019; Martins et al. 2019). As ammonia (NH_3) plays an important role as it is the main neutralizing gas for acidic compounds like HNO_3 and H_2SO_4 in the atmosphere, the correlation between NH_4^+ and SO_4^{2-} (r=0.525, p<0.001) is also an indication of common anthropogenic sources of NH_3 and SO_2.

It was possible to separate the convective rain events, typically more enriched in ^{18}O, from the stratiform ones using the relationship between $\delta^{18}O$-H_2O and stratiform fraction (Equation 1). Overall, the relationship between precipitation amount and $\delta^{18}O$-H_2O showed that the "amount effect" is in convective precipitation than in the stratiform rainfall (Dansgaard 1964; Tharammal et al. 2017). For the Caribbean samples, a correlation was indeed found between P (precipitation amount) and $\delta^{18}O$-H_2O and a correlation between P

501 and NO_3^- was also verified. On the other hand, no "amount effect" was found between P,
502 $\delta^{18}O$-H_2O, and NO_3^- in the Pacific samples. Therefore, the wet deposition of nitrate seems
503 to be affected by the rainfall generation processes, namely by the formation spatial-limited
504 and high-intensity convective precipitation or widespread and lower-intensity stratiform
505 rainfall (Aggarwal et al. 2016; Galewsky et al. 2016). When the formation of precipitation
506 is mostly controlled by deep convection and air masses arriving from the Caribbean Sea
507 (i.e., high $\delta^{18}O$-H_2O values), relatively higher concentrations of nitrate were found in the
508 precipitation samples due to increased dilution effect (Lacaux et al., 1992) (Figure 5B).
509 This characteristic was more evident at the beginning of the rainiest periods, namely
510 August 2018, May 2019, July 2019, and August 2019 (Figure 3C), when high-intensity
511 precipitation events of short duration were recorded. With regard the Pacific samples, as the
512 wet season advances (September-November), the contribution of frontal and continuous
513 precipitation events from Pacific air masses increased (Sánchez-Murillo et al. 2016;
514 Munksgaard et al. 2019). These higher stratiform factions in rainfall (i.e., low $\delta^{18}O$-H_2O
515 values) was related to the scavenging of smaller amounts of NO_3^- due to the "wash-out"
516 effect, namely the decrease in the concentration of solutes in precipitation after succeeding
517 precipitation events (Kajino and Aikawa 2015; Guo et al. 2016).
518 $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios are impacted by source changes and variations in
519 reaction chemistry prior to NO_3^- deposition (Michalski et al. 2011; Hastings and Sigman,
520 2003). Our findings show that these source changes and chemistry variations can be
521 inferred from the rainfall generation processes, namely the convective vs. stratiform
522 fractions. The higher relative contribution of gasoline NOx emissions found in the
523 Caribbean samples seems to reflect the oxidation of these emissions and the removal via
524 high-intensity convective precipitation in the Central Valley. There is also a higher relative
525 contribution of NO_x lightning in these samples, probably due to the convective activity
526 formed over the Caribbean Sea (Altieri et al., 2013). In turn, $\delta^{15}N$-NO_3^- variations in Pacific
527 samples are related to the frontal, continuous and wide-spread character of stratiform
528 clouds and higher contributions of diesel, biomass burning, and soils biogenic emissions.
529 The latter emissions are mostly transported from the Pacific and Caribbean lowlands to the
530 Central Valley, where cultivated areas are spatially distributed (Figure 4B). The relatively
531 high concentration of K^+ in our samples (with an average concentration of 24.6 µeq/L,
532 Table 1) also seems to point out the contribution of biomass burning to nitrate wet
533 deposition (Vieira-Filho et al. 2013). Due to the predominant influence of air masses
534 travelling over the Caribbean Sea on our study site, the regional transport of NO_x
535 emissions, for example from ships sailing to or from the Panama Canal and marine
536 aerosols, cannot be excluded (Wankel et al., 2010; Gobel et al., 2013; Beyn et al. 2015).
537 We found some nitrate samples enriched ^{15}N that may be related to the input of emissions
538 from ships (Figure 3).
539 Regarding our $\delta^{18}O$-NO_3^- data, the correlation found between $\delta^{18}O$-NO_3^- and NO_3^-
540 (r=0.265; p<0.05) could reflect the atmospheric processing of NO_x prior to deposition of
541 NO_3^-. Overall, these isotope values provide information about the oxygen transfer to NO_x
542 due to ·OH formation pathway when the convective fractions I rainfall increase.
543 Nevertheless, there are also relatively low $\delta^{18}O$-NO_3^- values (up to +33.7‰) in our samples
544 that may be related to the RO_2 oxidation pathway (R7). Generally, in convective clouds like
545 cumulus or cumulonimbus, the condensation particles are formed near the cloud base and
546 grow as they are lifted in strong updrafts (Aggarwal et al. 2016; Galewsky et al. 2016;

547 Schumacher and Houze, 2003). As recognized by Felix and Murgulet (2020), these strong
548 vertical motions can effectively transport $\cdot OH$ and RO_2 to the upper troposphere and then
549 react with lightning NO_x, increasing the probability of NO_x oxidation via the RO_2 pathway.
550 Nevertheless, unlike convective clouds, in stratiform clouds the vertical air motions are
551 weak and the upward air velocity is low (Aggarwal et al. 2016) and the NO_x oxidation via
552 RO_2 may be less important. The less variation observed in $\delta^{18}O\text{-}NO_3^-$ values during the
553 rainiest period (August-November) may indicate a decrease in the convective activity in the
554 Central Valley.

5. Conclusions

558 The stable isotope data in precipitation and atmospheric nitrate described here provide a
559 novel contribution to the study of wet deposition processes and the origin of inorganic
560 nitrogen loadings in tropical regions like Costa Rica. Our results reveal that the ^{15}N and ^{18}O
561 fractionation via photochemical oxidation and the rainfall generation processes (i.e.,
562 convective and stratiform rainfall) inform about the atmospheric oxidation pathways and
563 the nitrate wet deposition processes in the local urban atmosphere. Overall, $\delta^{18}O\text{-}NO_3^-$
564 values reflect the $\cdot OH$ and RO_2 oxidation pathways when convective rainfall fractions from
565 the Caribbean Sea predominated (i.e., small-scale systems ~1-2 km and high intensity
566 precipitation). In turn, $\delta^{15}N\text{-}NO_3^-$ values, corrected for potential ^{15}N fractionation effects,
567 indicate higher contributions from diesel, biomass burning, and soils biogenic emissions
568 when stratiform rainfall fractions from the Pacific Ocean dominated (i.e., large scale ~100
569 km and low intensity precipitation). Air mass trajectory analysis also supports the possible
570 transport of NO_x emissions from cultivated areas from the Caribbean and Pacific lowlands
571 to the Central Valley.
572   These results highlight the advantage of combining water and nitrogen stable
573 isotopes with atmospheric chemistry and hydrometeorology to study the wet deposition of
574 secondary atmospheric pollutants like nitrate. Given the recent advances in the modeling
575 approaches to simulate atmospheric deposition, the consolidation of a wet deposition
576 network in the Caribbean and Pacific regions of Costa Rica could allow the simulation of
577 distribution maps of nitrogen isotopes in precipitation as a potential source of nitrogen
578 pollution in water systems. Besides, the incorporation of other tracers like $\delta^{34}S$ in
579 atmospheric sulphate and $\Delta^{17}O$ in atmospheric nitrate could also improve the understanding
580 of the fundamental chemical processes that control the wet deposition of nitrogen and its
581 isotopic variability. In this same regard, these new studies could also examine how daytime
582 nitrate wet deposition differ from that occurring at night which in turn is related to how the
583 different photochemical reactions control the NO_x atmospheric oxidation. However, these
584 studies need to account for other oxidations pathways (e.g., BrO and SOA) to determinate,
585 for instance, the % O_3 and RO_2 competing daytime oxidation reactions.

Declarations

589   - *Ethics approval and consent to participate*
590 Not applicable

592   - *Consent for publication*

Not applicable

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Table 1. Overview of main chemical and isotopic parameters of precipitation samples collected between August 2018 and
November 2019 (N: number of samples, SD: standard deviation).

Variable	$\delta^{18}O$-H_2O (‰)	$\delta^{2}H$-H_2O (‰)	$\delta^{15}N$-NO_3^- (‰)	$\delta^{18}O$-NO_3^- (‰)	pH	NO_3^- (μeq/L)	Cl^- (μeq/L)	SO_4^{2-} (μeq/L)	NH_4^+ (μeq/L)	Na^+ (μeq/L)	Ca^{2+} (μeq/L)	Mg^{2+} (μeq/L)	K^+ (μeq/L)
N	110	110	76	76	109	109	109	109	109	109	109	109	109
Average	-8.61	-59.37	+0.7	+51.7	5.72	22.2	48.5	52.7	31.0	26.0	30.4	13.8	24.6
Median	-8.42	-56.00	+0.7	+52.5	5.55	19.0	28.5	44.1	24.8	27.8	19.5	15.7	17.4
SD	3.45	28.21	2.2	6.5	0.97	13.5	50.6	33.0	27.6	20.7	31.1	8.8	36.7
Minimum	-20.38	-153.35	-3.8	+33.7	4.02	3.0	7.3	14.8	6.7	1.3	3.5	2.5	5.2
Maximum	-0.52	-1.86	+7.1	+65.3	8.18	85.5	372.6	225.3	224.4	120.7	232.4	57.8	299.6

Figures captions

Figure 1. A) Dual isotope diagram for $\delta^{18}O-H_2O$ and δ^2H-H_2O in precipitation (blue circles) used to calculate the local meteoric water line (LMWL, dashed blue line). The global meteoric water line (GMWL) is included as reference. B) and C) Histograms showing δ^2H-H_2O and $\delta^{18}O-H_2O$ values, respectively.

Figure 2: Network correlation diagram based on Pearson´s correlation coefficient for precipitation isotopes, nitrogen isotopes in nitrate, and selected ion composition data (including the precipitation amount, P). Significance (based on p-values) increases as the line thickness increases. Blue and red colors represent positive and negative correlations, respectively. Grouping indicates stronger variable relationships.

Figure 3. Time series plots showing: A) Rainfall (in mm/day, blue bars), B) NO_3^- (in µeq/L, green circles), C) $\delta^{18}O-H_2O$ (in ‰, blue circles), D) $\delta^{15}N-NO_3^-$ (in ‰, red circles), and E) $\delta^{18}O-NO_3^-$ (in ‰, cyan circles). The dry season period when no sampling was carried out is also shown.
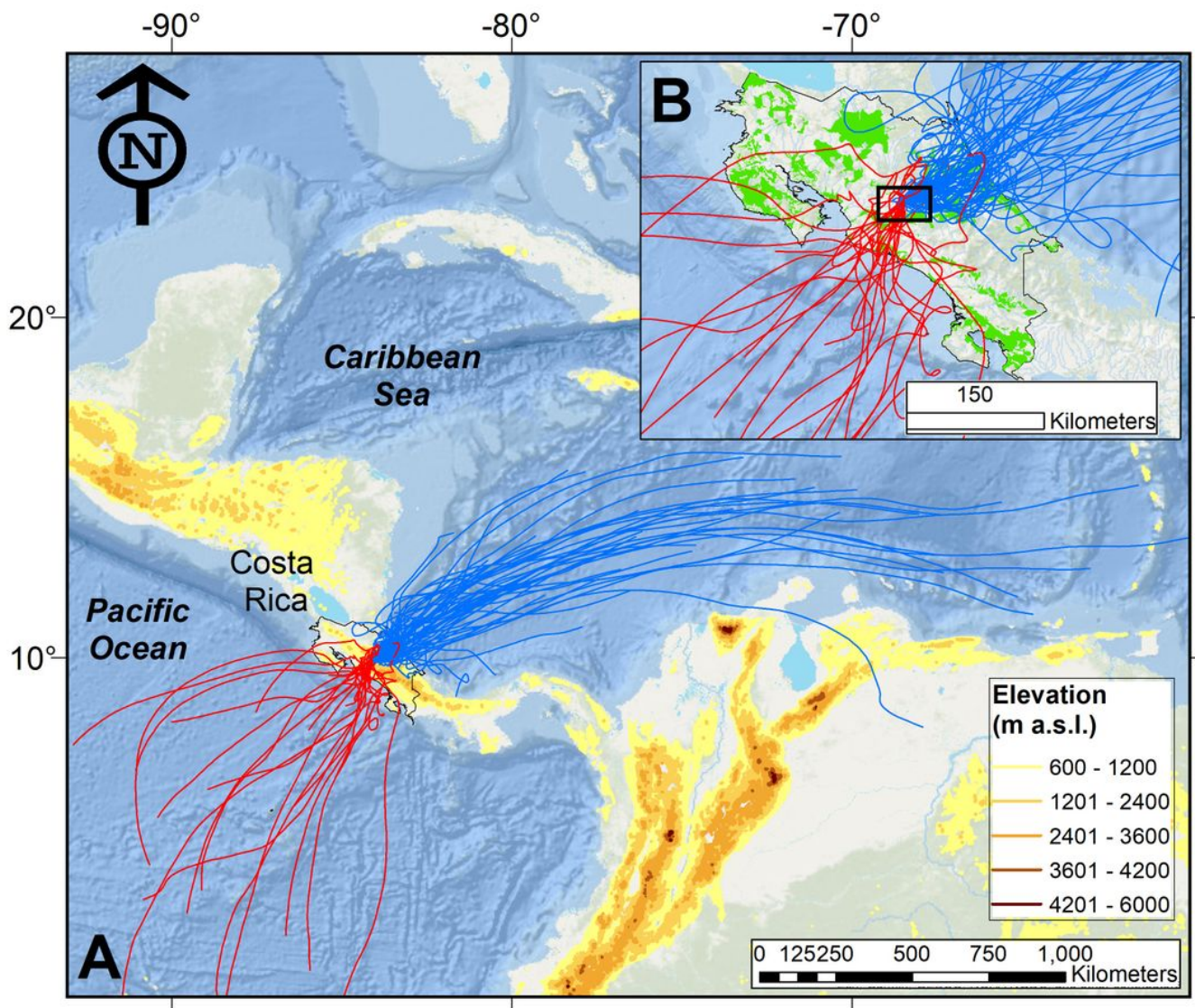
Figure 4. (A) 72-hour air mass back trajectories calculated using the HYSPLIT model for the sampling period August 2018-November 2019 (N=109). Trajectories were separated according to their preferential pathway (i.e., Pacific Ocean: red lines; Caribbean Sea: blue lines). (B) Inset map showing the distribution of the air mass trajectories in relation to the permanent cultivated areas (green-colored areas) located in the Caribbean and Pacific domain of Costa Rica. The black rectangle shows the approximate extension of the Central Valley where most NO_x emissions come from fossil fuels.

Figure 5. Box plots of: A. $\delta^{18}O-H_2O$ (‰), B. NO_3^- (µeq/L), and C. $\delta^{15}N-NO_3^-$ considering air mass trajectory (Caribbean or Pacific). The grey box indicates the 25th and 75th percentiles with the median in middle. The error bars indicate the minimum and maximum values. The black circles indicate outliers (1.5 times the central box).

Figure 6. A) Dual isotope diagram for $\delta^{15}N-NO_3^-$ versus $\delta^{18}O-NO_3^-$ in precipitation. Samples were segregated into Caribbean samples (blue circles, N=59) and Pacific samples (red circles, N=17). Circles were classified into three categories based on the nitrate concentration of this dataset: <16.6 µeq/L (<25th percentile), 16.6-30.8 µeq/L (25th-75th percentile), and > 30.8 µeq/L (>75th percentile). The average ± standard deviation values of $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ are shown as reference. B) and C) Histograms showing the $\delta^{15}N-NO_3^-$ and $\delta^{18}O-NO_3^-$ values, respectively.

Figure 7. Bar plot showing the Bayesian model results of proportion and error estimations of NO_x emission sources contributing to the wet deposition in the Central Valley of Costa Rica. Precipitation samples were classified according to the preferential air mass pathway (Caribbean Sea: black bars, Pacific Ocean: gray bars). The average ε value of 8.89‰ calculated with reference to percent formation pathways is applied to correct for N fractionation.
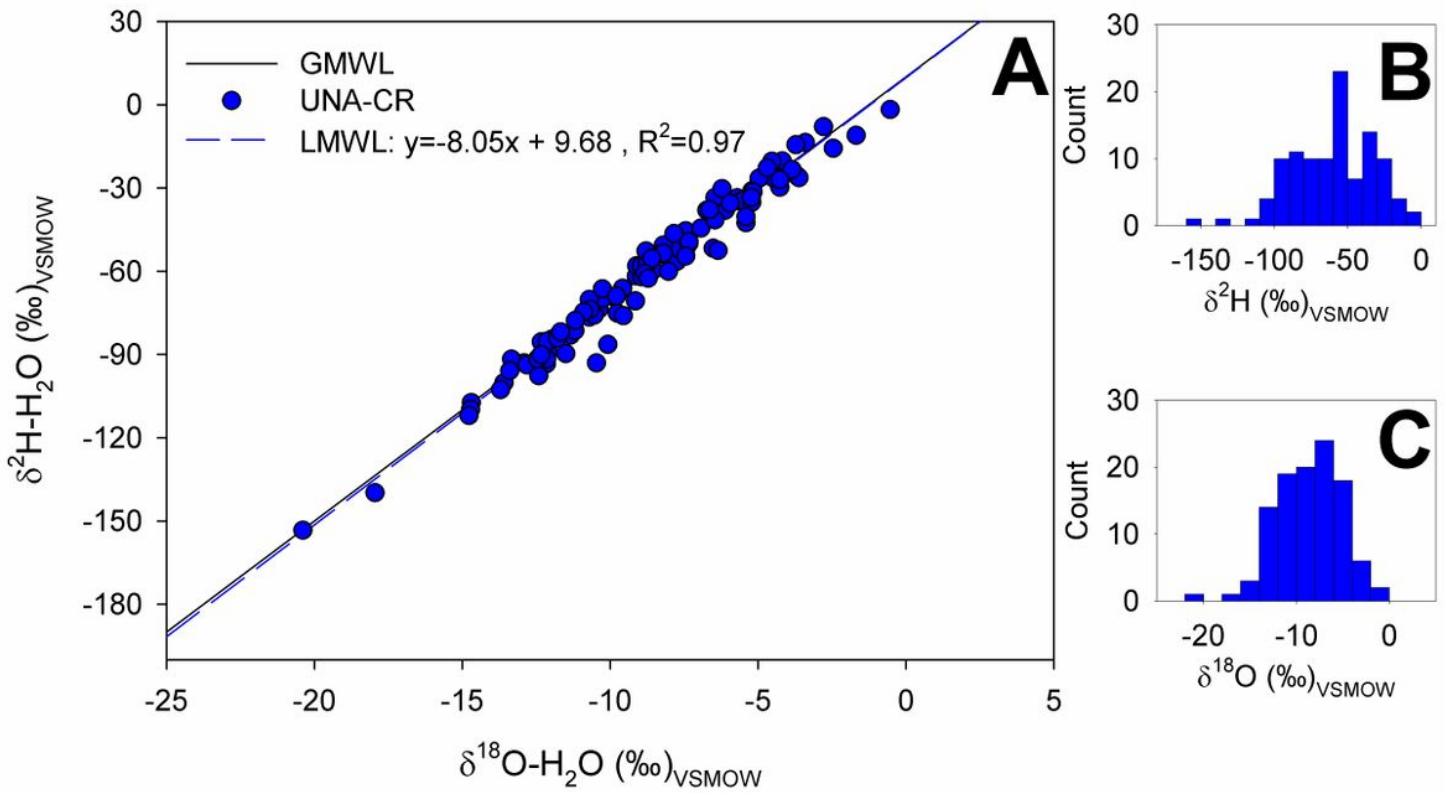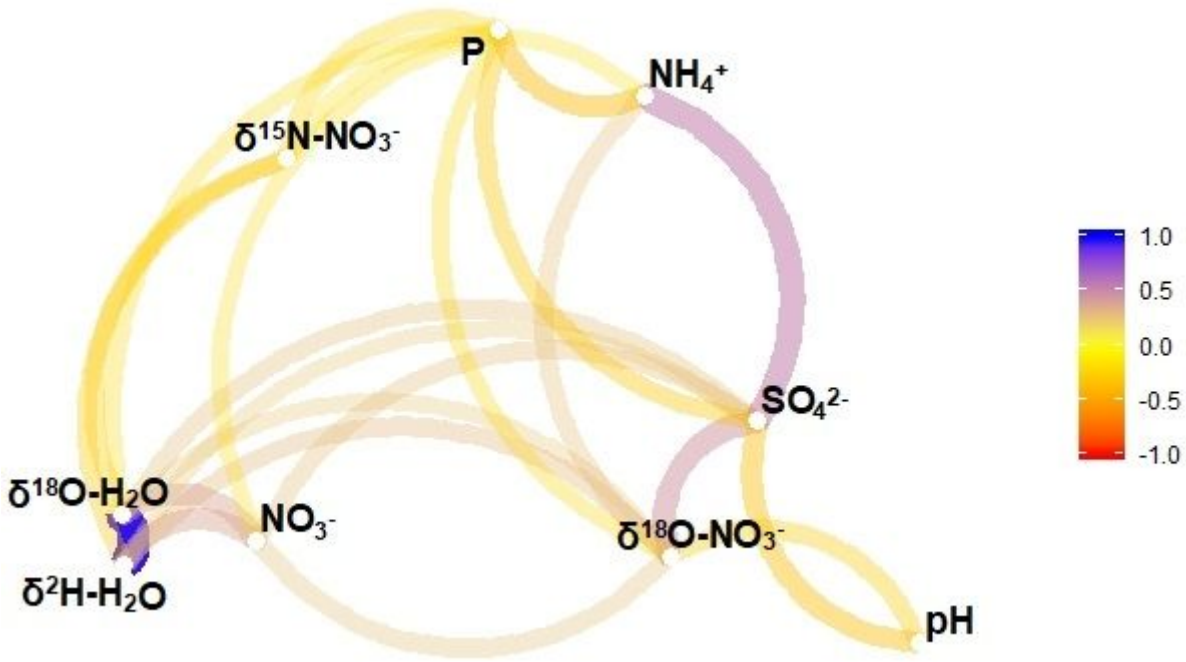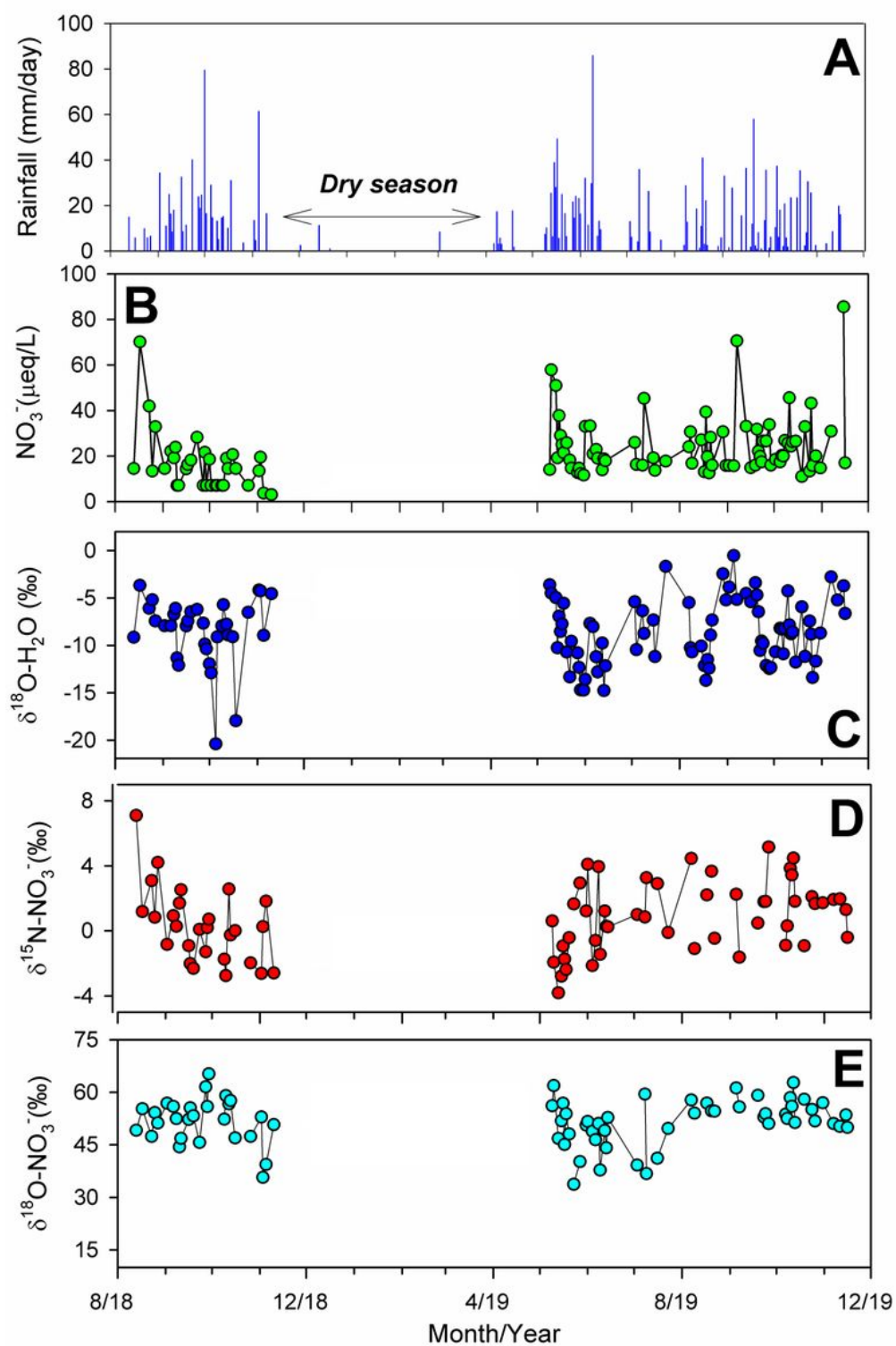
Figures

Figure 1

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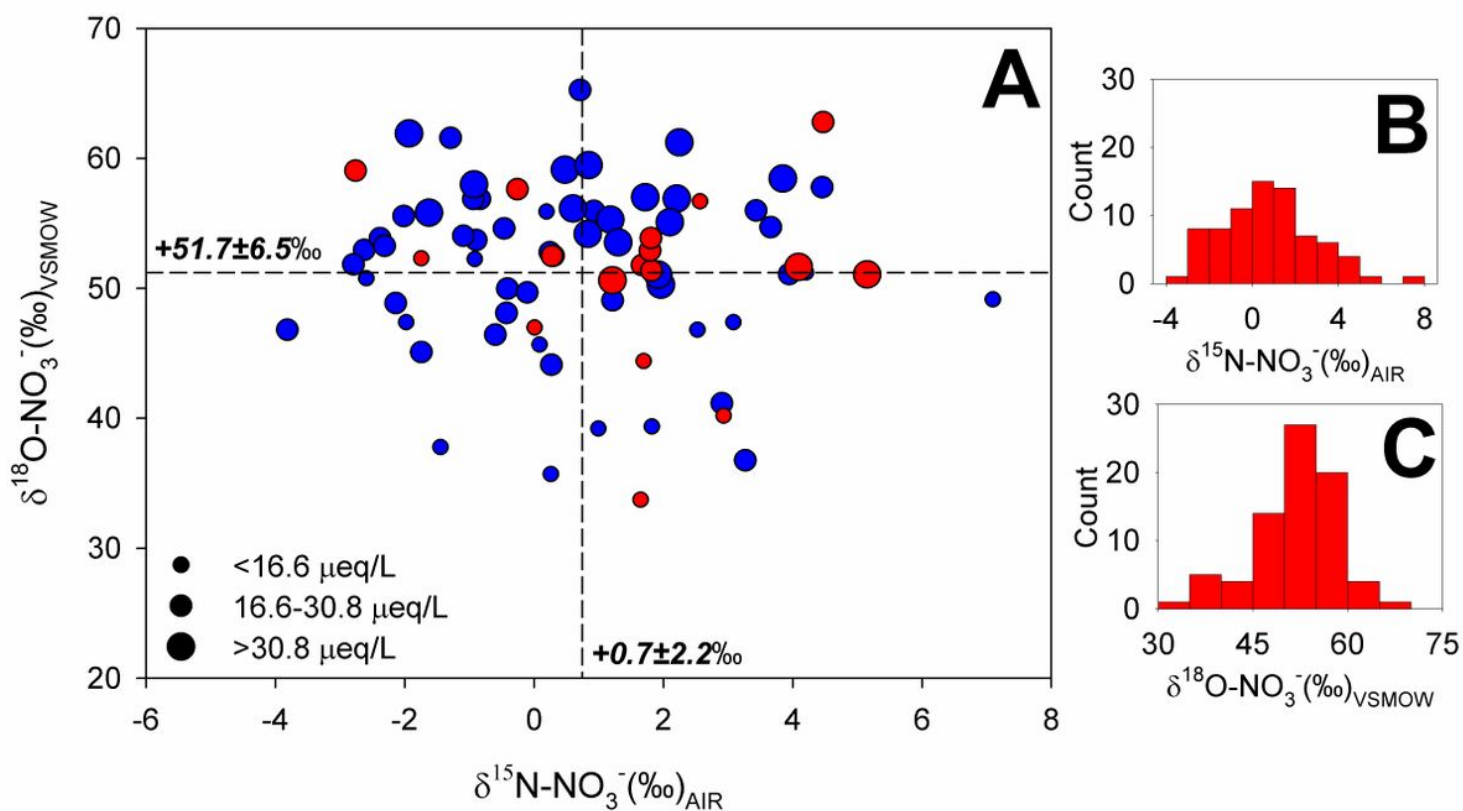
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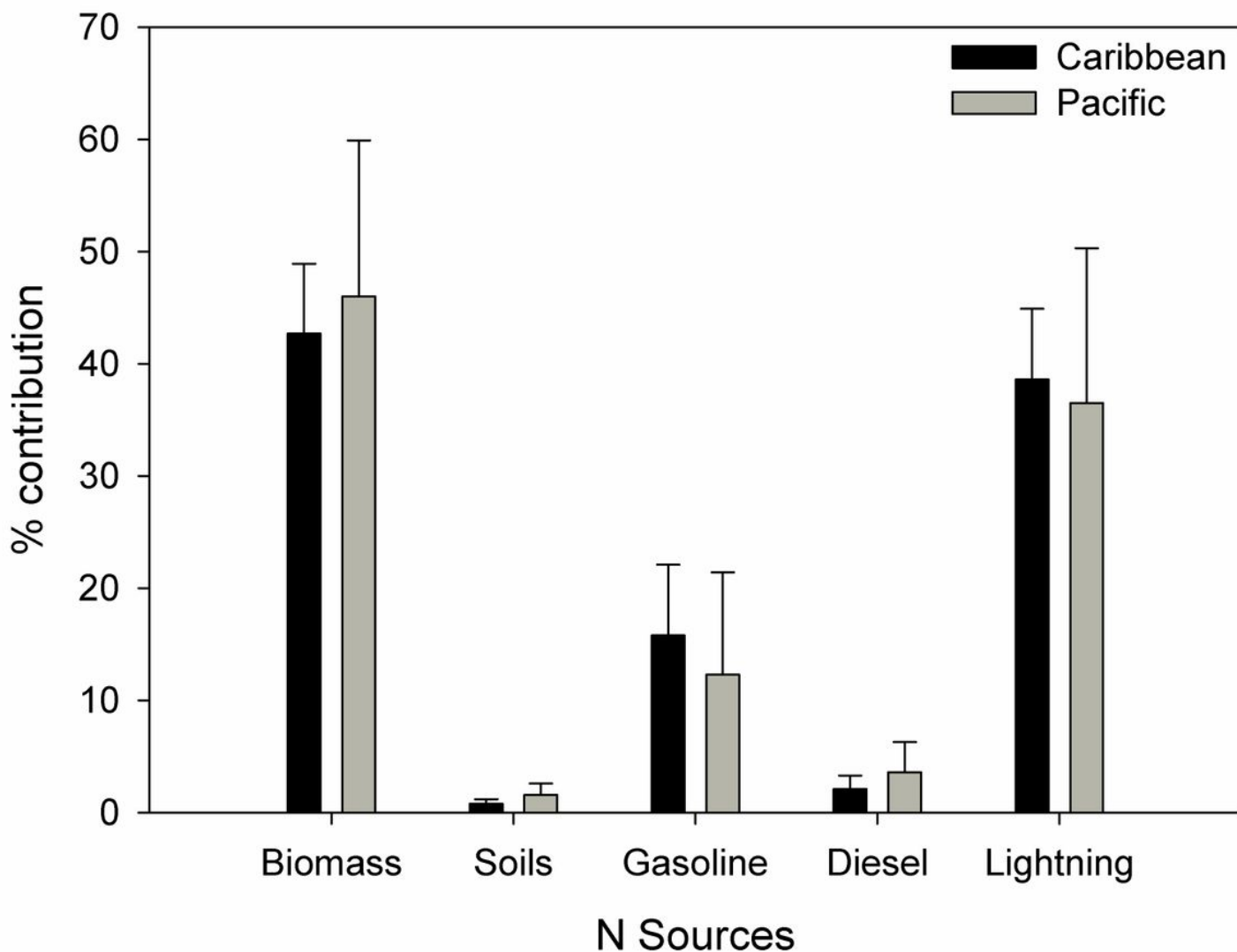
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