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Chemical characterization and source apportionment of rainwater in Cuieiras Biological Reserve, central Amazon, Brazil

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ABSTRACT

The Amazon rainforest plays a crucial role in the global climate system, acting as a major carbon sink and influencing regional and global weather patterns. Understanding the chemical composition of rainwater is essential for assessing the impact of anthropogenic activities, such as deforestation and industrial emissions, on atmospheric chemistry and hydrology. This work aimed to characterize the chemical composition of rainwater in a biological reserve of primary forest in the central Brazilian Amazon at 60 km of a large urban center. Rainwater samples were collected from March 2008 to March 2010 and were analyzed by ion chromatography, ICP-MS, and TOC-V. This is the only and longest rainfall monitoring carried out in this reserve. The results showed that the rainwater is rich in organic carbon (TOC), representing 77% of total carbon. The most abundant ions were NH_4^+ and Cl^-. Few elements were detected, with emphasis on Al and Fe. In the dry season, most species were enriched. The lower amount of precipitation, biomass burning and the lower capacity to remove pollutants from the atmosphere are the main reasons for this seasonal difference. Only 7% had characteristics of acid rain (pH < 4.5), with acidity dominated by NO_3^-. A positive matrix factorization indicated contribution of sources: crustal (48%), secondary aerosol (26%), biogenic (22%), and industrial emissions (4%). Although the forest has primary characteristics, the proximity to the urban center indicates some anthropogenic influence on the chemical composition of rainwater.

KEYWORDS: ions, metals, soluble carbon, wet deposition, positive matrix factorization

Caracterização química e rateio de fontes de águas pluviais na Reserva Biológica de Cuieiras, Amazônia central, Brasil

RESUMO

A floresta amazônica desempenha um papel crucial no sistema climático global, atuando como um importante sumidouro de carbono e influenciando os padrões climáticos regionais e globais. Compreender a composição química da água da chuva é essencial para avaliar o impacto das atividades antrópicas, como o desmatamento e emissões industriais, na química atmosférica e hidrologia. Este trabalho objetivou caracterizar a composição química da água da chuva em uma reserva biológica composta por floresta primária na Amazônia central brasileira, distante 60 km de um grande centro urbano. Amostras de água de chuva foram coletadas de março 2008 a março 2010 e analisadas por cromatografia iônica, ICP-MS e TOC-V. Este é o único e mais longo monitoramento pluviométrico realizado nessa reserva. Os resultados mostraram que a água da chuva é rica em carbono orgânico (COT), representando 77% do carbono total. Os íons mais abundantes foram NH_4^+ e Cl^-. Poucos elementos foram detectados, com destaque para Al e Fe. Na estação seca, a maioria das espécies foi enriquecida. A menor quantidade de precipitação, a queima de biomassa e a menor capacidade de remoção de poluentes da atmosfera são os principais motivos desta diferença sazonal. Apenas 7% apresentaram características de chuva ácida (pH < 4,5), com acidez dominada pelo NO_3^-. Uma fatoração de matriz positiva indicou contribuição de fontes: crustal (48%), aerossol secundário (26%), biogênico (22%) e emissões industriais (4%). Embora a floresta possua características primárias, a proximidade com o centro urbano indica alguma influência antrópica na composição química das águas de chuva.

PALAVRAS-CHAVE: íons, metais, carbono solúvel, deposição úmida, fatoração de matriz positiva

INTRODUCTION

Climate change has affected several ecosystems around the world, including the Amazon region (Flores et al. 2024). The region has been experiencing an intensified variation of atmospheric composition in the last decades, mainly due to the presence of particulate matter (PM) (Artaxo et al. 2006). PM influences the world's energy balance, atmospheric circulation, and the hydrological cycle, and plays an important role in the rain cycle, affecting the mechanism of cloud formation during the rainy and dry season (Tavares 2012).

The Amazon rainforest is an important source of natural trace gases, PM, and water vapor (Ramsay et al. 2020). However, there is also a large contribution from biomass burning during the dry season, resulting in unusual PM concentrations in remote sites (Herbert et al. 2021). In addition, there is an annual contribution of 28 million tons of African dust to the Amazon basin (Rizzolo et al. 2016).

The emissions of PM strongly impact the atmospheric dynamics since it can disperse and absorb solar radiation, interfere with the process of cloud formation, and, consequently, with rainfall (Fiore et al. 2015). In general, PM has a predominant chemical composition of sulfate, nitrate, ammonium, sea salt, mineral dust, organic compounds, and black or elemental carbon (Moran-Zuloaga et al. 2018). Hydrophilic species present in PM contribute to cloud formation (Wang et al. 2023).

There are many studies about gases and aerosol in the Amazon region, but few about chemical composition of rainwater (Williams et al. 1997; Artaxo et al. 2006; Honório et al. 2010; Pauliquevis et al. 2012). Here we analyze the data of monitoring of the chemical composition of rainwater in the central Amazon over two years of weekly measurements (from 2008 to 2010) in an area of primary forest relatively close to a large urban center. This monitoring was part of the EUCAARI project (European Integrated Project on Aerosol Cloud Climate Interactions) (Kulmala *et al.* 2009). Although the data are over a decade old, they still represent the longest monitoring of rainwater composition carried out to date in the central Amazon, allowing to establish a baseline to which compare changes over time. This is essential to assess the impacts of human activities, such as deforestation and biomass burning, on the characteristics of rainfall in the Amazon region.

Our aim was to assess the magnitude of anthropic influence on rainfall in the forest at this spatial scale and provide a basis for comparison with later data on rainfall composition in the region. We quantified ions, elemental composition, and total carbon from rainwater samples in the rainy and dry season of the year, and discuss the likely sources of the rainfall components. Positive matrix factorization (PMF) was used for the first time in the Amazon region with rainfall samples to identify sources.

MATERIAL AND METHODS

Study area and sampling procedures

The study was carried out in the Cuieiras Biological Reserve (CBR) (02°35′21.08"S, 60°06′53.63"W, 130 m.a.s.l), located about 60 km north-northwest of the city of Manaus, stae of Amazonas (Brazil), and 2000 km from the Atlantic Ocean (Figure 1). It has an area of 22,735 ha covered by relatively undisturbed primary forest. The prevailing winds blow from the northeast over vast expanses of intact tropical forest, bringing Atlantic Ocean air masses, long-range transported Saharan dust and regionally originated pollutants from biomass burning (Moran-Zuloaga et al. 2018).

Rainwater samples were collected from March 2008 to March 2010. Samples were collected at intervals of two to four days, totaling 114 samples (100 to 1000 mL), with 47 in the dry (June to October) and 67 in the rainy (November to May) season. Samples were collected with a ""wet-onl"" collector (AeroChem Metrics, Model 301 automatic sensing wet/dry) that was installed about 1 m above the ground. This collector uncovers the sample container after detecting (through an infrared optical rainfall sensor) five drops of rainfall. The cover returns to its place within 2 min after rainfall stops, to minimize dry deposition and evaporation.

Data quality of individual rainwater samples was checked by ionic balance, according to US NADP criteria, i.e., the samples were discarded when the ion difference in the samples was 15%–30% for samples having total ion concentrations > 100 μeq L^{-1}, and 30 %–60 % for samples having total ion concentrations of 50–100 μeq L^{-1}.
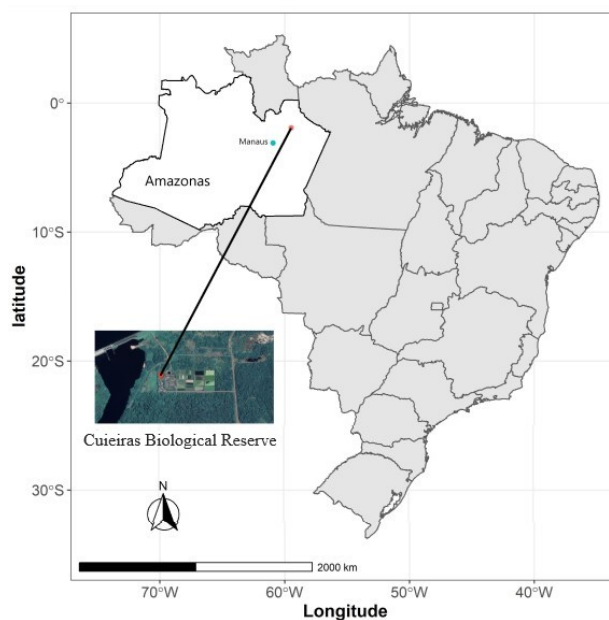
Figure 1. Location of the sampling site (Cuieiras Biological Reserve) in Amazonas state, Brazil.

Chemical analyses

The ionic conductivity and pH were measured at the end of each sampling. Immediately after sampling, the samples were subdivided and properly preserved: a) one aliquot was preserved with Thymol in order to minimize biological activity and to determine ion concentrations by ion chromatography; b) other aliquot was preserved with mercury chloride in order to determine TOC; and c) the third aliquot was preserved with HNO_3 to determine metals and other elements by ICP-MS. All samples were filtered (Whatman – 41 filters) and stored in a refrigerator at 4 °C before analyses.

Elements such as Al, Ca, Fe, Mg, K, Na, Li, Ti, V, Cr, Mn, Co, Ni, Cu, As, Zn, Se, Rb, Sr, Y, Cd, Sb, Cs, Ba, La, Ce, Nd, W, Pb, Bi were determined by the ICP-MS technique (Perkin–Elmer ELAN 6000). The concentrations of the elements were determined using In and Tl as internal standards. More details can be found in Godoy et al. (2009). The ion concentrations (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, CH_3COO^-, $HCOO^-$, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}) were determined by ion chromatograph (Dionex model ICS-2000, USA) in the same way as described by Gioda et al. 2023. Total organic carbon (TOC), total carbon (TC) and inorganic carbon (IC) were determined by TOC-V CPHCPN (SHIMADZU, TOC-4200, Japan). TC – IC result in TOC concentration and calculated by subtracting inorganic carbon (IC) (Gioda et al. 2011; Duarte et al. 2013). The instrument´s detection limit was calculated as three times the standard deviation of ten replicated blank values for all techniques.

Volume-weighted mean and wet deposition

The volume-weighted mean (VWM) of ionic constituents and seasonal wet deposition (WD) fluxes in the rainwater samples were calculated according to equations [1] and [2], respectively.

$$C_{VWM} = \frac{\sum_{i=1}^{n}(C_i \cdot P_i)}{\sum_{i=1}^{n} P_i} \qquad [1]$$

$$WD = C_{VWM} \cdot \frac{P_t}{1000} \qquad [2]$$

where C_{VWM} = VWM concentration; C_i = ionic concentration of individual element (µmol L^{-1}); P_i = individual rainfall (mm) for each rainy event; P_t = total rainfall (mm); n = total number of rainfall events; WD = seasonal/total wet deposition flux expressed (mg m^{-2} yr^{-1}) (Xing et al. 2017).

The weighted standard deviation (sd$_w$) of the results was calculated based on equation [3].

$$sd_w = \sqrt{\frac{\sum_{i=1}^{N} w_i(x_i - \bar{x}_w)^2}{\frac{(N'-1)}{N'} \sum_{i=1}^{N} w_i}} \qquad [3]$$

where N = number of samples; w_i = sample weight; x_i = sample values; x_w = weighted average; N' = number of non-zero weights.

Enrichment factor

The enrichment factor (EF) was applied to identify the potential sources of elements and was calculated through the ratio of the concentration measurement of the elements in the rainwater samples to ratios for elements measured present in the seawater and Earth´s crust. For this, Ca^{2+} and Na^+ were used as the reference for soil and marine sources, respectively, according to equations [4] and [5] (Zhang et al. 2007). An EF < 10 was diluted, while an EF > 10 indicates enrichment relative to the reference source.

$$EF_{(soil)} = [X/Ca^{2+}]_{sample}/[X/Ca^{2+}]_{crust} \qquad [4]$$

$$EF_{(marine)} = [X/Na^+]_{sample}/[X/Na^+]_{seawater} \qquad [5]$$

where, X is the concentration of the element of interest; X/Na^+ of seawater is the ratio of seawater composition; X/Ca^{2+} of the crust is the ratio of crustal composition (Taylor and McLennan 1995).

Positive matrix factorization

For the positive matrix factorization (PMF), the PMF 5.0 model was used for source apportionment and characterization of the collected rainwater over the study period. Principles and modes of use are detailed in the user manual (Hristova et al. 2020). This model uses two input files: i) measured concentrations of the species, and ii) estimated uncertainty of the concentration. Here, the PMF 5.0 was applied to datasets composed of 22 species (TC, Ca^{2+}, NH_4^+, $HCOO^-$, Cl^-, NO_3^-, SO_4^{2-}, Na^+, Mg^{2+}, Al, K^+, V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Cd, Ba, Pb). Uncertainties of the sample concentration were calculated using the method detection limit (MDL) in Equation [6] (EPA 2014).

For concentrations < MDL: Uncertainty = 5 x MDL/6

For concentrations ≥ MDL: Uncertainty = (MDL^2 + Precision^2)$^{0.5}$ [6]

The PMF was applied to the entire database, without separating rainy and dry seasons, since this type of analysis separately would cause a reduction in the number of degrees of freedom.

Statistical analysis

Differences between average concentrations of chemical measurements in the dry and wet season were determined using Student´s t-test. A value of $p < 0.05$ was considered significant. All analyses were performed using the CRAN R free software, version 4.2.1 (R Team Core 2019).

RESULTS

Rainfall, pH, conductivity and rainwater composition

A total of 3,258 mm of precipitation occurred during the sampling period, with 2,345 mm (72%) in the wet and 913 mm (18%) in the dry season (Table 1). The mean and range of the conductivity values were 3.8 ± 2.4 µS cm^{-1} (0.72–13 µS cm^{-1}) and 2.9 ± 2.1 µS cm^{-1} (0.22–12 µS cm^{-1}) during the dry and wet season, respectively. Statistically significant differences for mean conductivity were found between both seasons. Mean and range of pH values were 5.17 ± 0.50 (4.20–6.50) and 5.22 ± 0.47 (3.90–6.80) during the dry and wet season, respectively (Table 1). Organic carbon (TOC) represented 77% of total carbon (TC), being slightly higher in the dry (80 %) than in the wet period (72%) (Table 1). The concentrations of ionic species in rainfall followed the sequence NH_4^+ > Na^+ > Cl^- > NO_3^- > SO_4^{2-} > K^+ > Ca^{2+} > $HCOO^-$ > Mg^{2+}. Ammonium and Cl^- were the most dominant cation and anion, respectively. The overall contribution of cations and anions to the ionic strength in the rainwater was 58% and 42%, respectively.

The highest values of ions were recorded in the dry season (Table 1). There was a statistically significant difference in the concentration of NH_4^+ and NO_3^- between seasons, while the other ions did not differ significantly between seasons. Only Ca^{2+} and Mg^{2+} showed a slight, statistically non-significant increase in concentration throughout the study period, while the other ions showed no incremental trend. K^+, NH_4^+, NO_3^-, and SO_4^{2-}, which originate from combustion processes, showed a similar behavior during the dry season.

Many elements were below the detection limit and were therefore not reported. Among the thirteen elements detected (Al, V, Mn, Fe, Co, Cu, Zn, Rb, Sr, Cd, Sb, Ba and Pb), nine (Al, Mn, Co, Cu, Rb, Cd, Sb, Ba and Pb) had higher concentrations during the dry period (Table 1). The elements did not show a clear trend over the years of study.

Wet deposition fluxes

The wet deposition fluxes showed acidic characteristics (H^++NO_3^-+SO_4^{2-} = 473 µmol m^{-2}) due to high concentrations of H^+. The pooled concentration of the basic elements, which have nutrient properties, such as Na^+, K^+, Ca^{2+}, and Mg^{2+} was not enough (221 µmol m^{-2}) to neutralize the acidity. Na^+ and Cl^- represented an important fraction (266 µmol m^{-2}) of ion deposition of marine influence. Nitrogen fluxes (272 µmol m^{-2}) were high due to the high flux of ammonia (170 µmol m^{-2}), one of the highest found in the study (Table 1). Soluble trace element concentrations appeared in the following order: Al > Fe > Zn > Mn > Cu > Sr > Rb > Ba > V > Co > Pb > Cd > Sb (Table 1).

Table 1. Amount, pH, conductivity and composition of rainwater in the Cuieiras Biological Reserve, central Brazilian Amazon during the dry and wet season. Values are the average ± standard deviation, followed by the range, for annual measurements from 2008 to 2010.

Parameter	Dry season (n = 47)	Wet season (n = 67)	Overall average (n = 47)
Total rainfall (mm)	913a	2345b	1629
Daily rainfall (mm)	20 ± 21 [0.1–69] a	35 ± 25 [1–100] b	28
Conductivity (µS cm^{-1})	3.8 ± 2.4 [0.7–13.0] a	2.9 ± 2.1 [0.2–12.0] b	3.4
pH	5.2 ± 0.5 [4.0–7.0] a	5.2 ± 0.5 [4.0–7.0] a	5.2
TC (mg L^{-1})	7.6 ± 4.0 [3–18.0] a	5.5 ± 3.5 [0.3–17.0] b	6.6
IC (mg L^{-1})	1.5 ± 0.8 [0.3–2.5]	1.5 ± 0.9 [0.1–3.0]	1.6
TOC (mg L^{-1})	6.1 ± 4.7 [0.2–17.0] a	4.0 ± 3.3 [0.1–15.0] b	5.1
H^+	12 ± 13 [0.3–71]	12 ± 19 [0.3–102]	12
NH_4^+	9.5 ± 7.3 [0.2–33.0] a	4.8 ± 7.1 [0.1–51.0] b	7.2
Na^+	8.3 ± 8.8 [0.1–46.0] a	5.2 ± 6.7 [0.1–36.0] b	6.8
K^+	2.6 ± 2.7 [0.1–100.0] a	1.2 ± 1.4 [0.1–100.0] b	1.9
Mg^{2+}	1.2 ± 0.9 [0.1–15.0] a	0.7 ± 0.6 [0.1–8.0] b	1.0
Ca^{2+}	2.0 ± 1.7 [0.1–8.0] a	1.4 ± 1.5 [0.1–9.0] a	1.7
SO_4^{2-}	2.3 ± 2.7 [0.2–15.0] a	1.5 ± 1.9 [0.1–11.0] b	1.9
NO_3^-	6.0 ± 5.3 [0.8–23.6] a	3.1 ± 4.5 [0.1–30.0] b	4.6
Cl^-	6.7 ± 7.2 [0.6–39.0] a	4.2 ± 4.4 [0.1–20.0] b	5.5
$HCOO^-$	1.2 ± 1.5 [0.13–8.0] a	1.1 ± 1.6 [0.1–7.0] a	1.2
Al	203 ± 253 [18–1587] a	164 ± 228 [12–100] b	184
V	1.1 ± 0.9 [0.1–3.7] a	1.0 ± 1.5 [0.1–9.0] a	1.1
Mn	15.0 ± 13.0 [1.6–65.0] a	7.8 ± 8.6 [0.3–45.0] b	11.4
Fe	47 ± 40 [9–184] a	45 ± 58 [4–352] a	46
Co	1.3 ± 3.2 [0.03–19.0] a	0.8 ± 1.6 [0.03–9.0] b	1.05
Cu	13.0 ± 19.0 [1.5–101.0] a	7.9 ± 9.2 [0.3–43.0] b	10.5
Zn	35 ± 34 [4–179] a	37 ± 98 [1.7–795] a	36
Rb	2.3 ± 2.1 [0.3–10.0] a	0.9 ± 1.3 [0.1–8.0] b	1.6
Sr	2.8 ± 2.1 [0.6–10.0] a	2.3 ± 2.8 [0.1–17.0] a	2.6
Cd	0.6 ± 0.6 [0.1–2.2] a	0.4 ± 0.6 [0.02–3.0] a	0.5
Sb	0.2 ± 0.1 [0.04–0.7] a	0.1 ± 0.2 [0.03–1.2] a	0.2
Ba	2.2 ± 1.9 [0.6–13.0] a	2.0 ± 2.0 [0.2–13.0] a	2.1
Pb	0.7 ± 0.6 [0.1–3.0] a	0.6 ± 1.1 [0.03–6.0] a	0.7

Different letters in the same line indicate significant difference ($p < 0.05$) according to a t-test. The absence of letters indicates that the statistical test was not performed. N = number of samples. Trace elements in (nmol L^{-1}); anions and cations in (µmol L^{-1}).

Origin of the pollutants

To infer the possible sources of the studied species, the enrichment factor and PMF analysis were used. The average EF for marine sources ranged from 0.69 to 15.90 and from 0.69 to 13.80 for the dry and wet season, respectively (Table 2). Average EF_{soil} in the dry season ranged from 0.02 to 9.409, and from 0.02 to 9.881 in the rainy season. EF_{marine} for Cl^- and Mg^{2+} was <1, but EF_{soil} for Cl^- was >10 (Table 2). EF of Al, V, Fe, and Ba was <10. An EF >10 indicates enrichment (Zhang et al. 2007), which was the case of Mn, Co, Cu, Zn, Rb, Sr, Cd, Sb, and Pb. Overall, the marine contribution was negligible compared to biogenic sources (Table 2).

We identified six source factors in the PMF analysis. Factor 1 was characterized by the dominant portions of NO_3^-, SO_4^{2-} and V, with the two first species together indicating a significant source of secondary origin (Table 3; Figure 2). Factor 2 was characterized by the high loading of NH_4^+. Factor 3 had Ca^{2+} with the highest loading, followed by $HCOO^-$, indicating that Ca^{2+} was the dominant neutralizing ion at CBR. Factor 4 contributed with high loadings for Mg^{2+}, Sr, Ba and Rb, Cl^-, Cd, Mn, Co, Cu and Pb. Factor 5 had the highest loadings for Na^+ and K^+. Factor 6 accounted for 69.6%, 52.8%, 47.8%, 40.3%, 36.6%, and 31.2% of the total concentrations of TC, Fe, Co, Cu, Zn, and Al, respectively. The average contribution of sources from the PMF analysis was crustal (48%), followed by secondary aerosol (26%), biogenic (22%), and industrial emissions (4%).

Table 2. Enrichment factors for rainwater components of soil or sea-salt origin in the dry and wet season in the Cuieiras Biological Reserve, central Brazilian Amazon from 2008 to 2010.

Element	Dry season		Wet season	
	EF_{soil}	EF_{marine}	EF_{soil}	EF_{marine}
Na^+	0.14a	dna	0.11a	dna
Mg^{2+}	0.02a	1.07A	0.02a	1.18A
K^+	0.05a	12.56A	0.04a	10.60B
Ca^{2+}	0.05a	15.90A	0.03a	13.80B
Cl^-	24a	0.69A	19a	0.69A
NO_3^-	4.75a	dna	3.59b	dna
SO_4^{2-}	3.16a	3.89	3.01a	4.74
Al	0.92a	dna	1.10a	dna
V	8.06a	dna	9.88b	dna
Mn	15.80a	dna	12.10b	dna
Fe	1.70a	dna	1.60a	dna
Co	48.40a	dna	44.50b	dna
Cu	274a	dna	180b	dna
Zn	618 a	dna	887 b	dna
Rb	33.80 a	dna	20 a	dna
Sr	16.20 a	dna	11.90 b	dna
Cd	9409	dna	9881	dna
Sb	1514	dna	2227	dna
Ba	7.13	dna	9.14	dna
Pb	145	dna	198	dna

dna = does not apply. Different letters in the same line indicate significant difference (p < 0.05) according to a t-test. Within each line, lowercase and capital letters refer, respectively, to the comparison of EFsoil and EFmarine between seasons.

Table 3. Factor profiles (% of species sum) of source species measured in rainwater collected in Cuieiras Biological Reserve from 2008 to 2010 according to EPA PMF 5.0 output.

| Species	Fossil fuel combustion	Natural sources	Crustal component	Sea salt/ anthropogenic emission	Fungal spores/ biomass burning	Car exhaust and dust
TC	0.0	13.8	16.7	0.0	0.3	69.6
Ca^{2+}	0.0	0.0	87.7	0.0	87.7	0.0
NH_4^+	0.0	84.9	5.0	0.0	10.2	0.0
COO	23.9	0.0	70.7	0.0	0.0	5.3
Cl^-	12.3	10.0	0.0	52.4	9.4	15.8
NO_3^-	66.9	27.9	0.4	0.0	0.0	4.7
SO_4^{2-}	53.8	17.7	9.2	14.3	5.1	0.0
Na	0.0	0.0	0.0	24.6	67.8	7.5
Mg	5.6	23.8	2.6	68.1	0.0	0.0
Al	17.2	12.0	5.3	15.3	13.6	36.6
K	8.7	27.8	2.1	0.0	61.4	0.0
V	51.5	2.7	0.0	10.9	9.2	25.8
Mn	0.2	12.6	6.4	46.3	17.9	16.6
Fe	12.8	7.1	6.2	18.6	2.4	52.8
Co	0.0	0.0	0.0	41.5	10.6	47.8
Cu	7.9	13.8	4.5	33.5	0.0	40.3
Zn	6.7	17.1	5.3	19.0	20.6	31.2
Rb	11.7	25.2	0.0	55.5	0.5	7.2
Sr	0.7	13.8	6.6	65.0	5.3	8.6
Cd	8.2	13.1	20.1	47.6	6.7	4.2
Ba	3.4	0.0	9.3	55.5	13.1	18.7
Pb	7.9	26.2	0.0	33.3	4.1	28.5
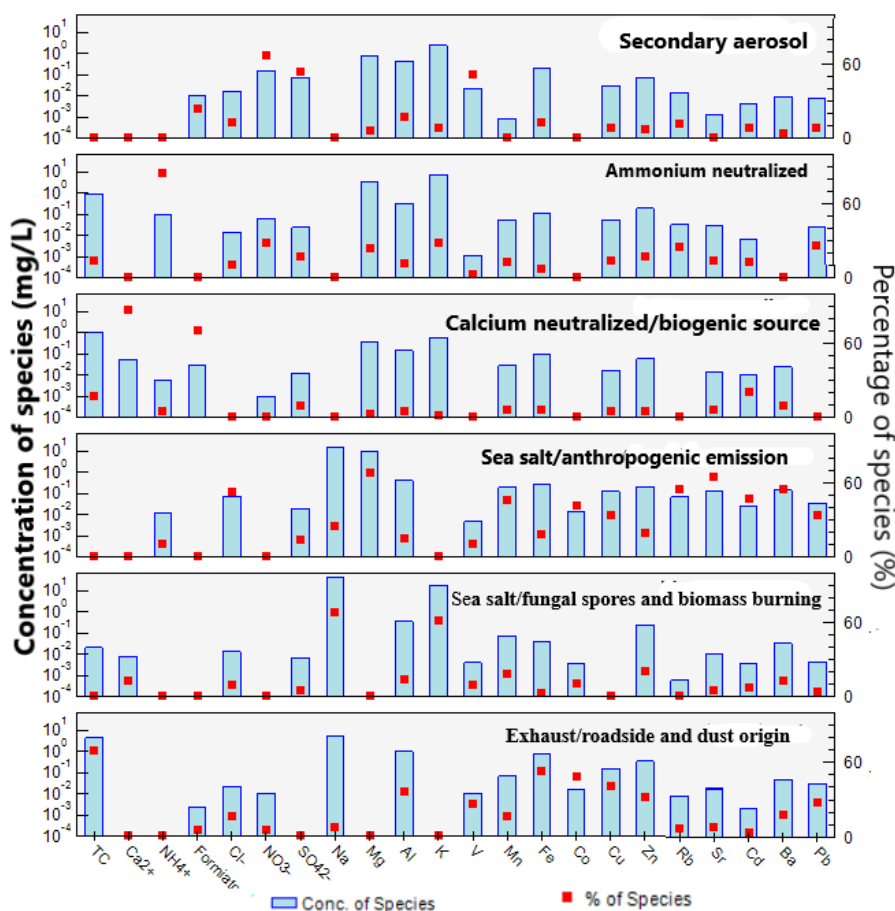
Figure 2. Source apportionment profiles of chemical components of rainwater collected in the Cuieiras Biological Reserve during 2008–2010.

DISCUSSION

Rainfall, pH, conductivity and rainwater composition

The conductivity reflects the total dissolved ions in rainfall (Gioda et al. 2013). Lower conductivity in the wet season may be ascribed to the dilution factor or higher water content in the rain droplets. The average conductivity in CRB (3.4 µS cm⁻¹) was lower than that in Lake Calado, located 80 km west of Manaus, in the 1990s (6.5 µS cm⁻¹) (Williams et al. 1997), and in an open area in Manaus city (7.9 µS cm⁻¹) (Honório et al. 2010). Rainfall samples from other Amazonian cities showed small variations in the mean conductivity such as in Boa Vista, in Roraima state (4.4), and in Apuí (4.5), Tabatinga (4.8), Itapiranga (5.2) and Paritins (6.4) in Amazonas state (Honório et al. 2010) and in Rio Branco, in Acre state (6.7) (Duarte et al. 2013).

Unpolluted rainfall normally has a pH between 5.0 and 5.5, which is considered slightly acidic (EPA 2020). Our samples showed pH within the normal range in both seasons, with no statistical difference between the seasons. This suggests that the anthropogenic influence is small in the study site.

Similarly to our study, an average TOC of 4.2 mg L⁻¹ was measured in rainwater collected from 2005 to 2010 in the southwestern state of Acre, with a higher concentration in the dry than in the wet season (Duarte et al. 2013). In Mato Grosso state (also in the southwest) an average TOC of 6.7 mg L⁻¹ (15.6 and 3.3 mg L⁻¹ at the beginning of the dry and rainy season, respectively) was reported 2007-2008 (Neu et al. 2016). Higher TOC concentrations in the dry season are due to the accumulation of carbon-rich PM in the atmosphere when there is minimal rainfall, while PM is depleted during rainfall events in the rainy, because a fraction of particulate organic matter (POM) is solubilized (Monteith et al. 2007). Correspondingly, our results suggest that TOC is accumulated during the dry season and depleted during subsequent rainfall events.

The overall contribution of cations and anions to the ionic strength in our samples indicate dominance of alkaline components, especially NH_4^+, Na^+, and K^+. The average concentrations of ions were of the same order of magnitude as those reported in Lake Calado, 80 km west of Manaus in 1984 (0.7 µmol L⁻¹ for K^+ to 9.0 µmol L⁻¹ for SO_4^{2-}) (Lesack and Melack 1991) and in 1990 (0.8 µmol L⁻¹ for K^+ to 4.6 µmol L⁻¹ for Cl⁻ (Williams et al. 1997). However,

the concentrations were two to three times higher than in this study when measured in an open area in Manaus city (2.1 µmol L⁻¹ for Mg²⁺ to 17 µmol L⁻¹ for 17.1 µmol L⁻¹ for Ca²⁺) (Honório et al. 2010). As expected, anthropogenically impacted areas present higher concentrations of some ions. The lack of more recent studies makes it difficult to assess the trend in concentrations.

NH_4^+ is present even in air considered to be unpolluted, because of natural chemical and biochemical processes (Spataru 2022). However, like NO_3^- and SO_4^{2-}, NH_4^+ is a main component of secondary aerosols and has a share coming from anthropic activities (Migliavacca et al. 2004). The presence of SO_4^{2-} and NO_3^- mainly indicates anthropogenic origin due to emissions of SO_2 and NO_x gases through the burning of fossil fuels and industries (contribution received from long distances by winds) (Sudalma et al. 2015). Furthermore, the association between these three ions shows that the aerosols NH_4NO_3 and $(NH_4)_2SO_4$ were generated through chemical reactions of NH_3 with HNO_3 and H_2SO_4.

We recorded an excess of cations relative to anions, which is compatible with other studies (Galloway et al. 1982; Williams et al. 1997) with an anion deficit of 14 µmol L⁻¹. It is worth highlighting the average contribution of acetic and formic acids with 2.7 µmol L⁻¹ and inorganic acids ($Cl^-+NO_3^- +SO_4^{2-}$) with 7.4 µmol L⁻¹. Overall, the mean concentration of major ions was in the same range as reported around the same period for a nearby location with influence of the plume from Manaus and road emissions (Pauliquevis et al. 2012), although some species such as acetic acid, Ca²⁺, and Mg²⁺ had higher concentrations. Because it is 1,200 km from the Atlantic coast, CBR has a low VWM for Na⁺ when compared to regions of direct marine influence, which is owed to the very high rainfall rate in the central Amazon, resulting in the efficient removal of the sea salt component (Pauliquevis et al. 2012).

Although there was no significant difference in VWM concentration for some ions, the deposition in the dry season was higher, differing from another study in the same region and similar to results from the southwestern Amazon state of Rondônia around the same period (Artaxo et al. 2009).

Wet deposition fluxes

A similar behavior to our wet deposition fluxes, with highest concentrations for Al, Fe and Zn, was observed in rainwater collected in six Amazonian cities (Honório et al. 2010). This is expected, since Al, Fe, and Zn are generally the most abundant metals worldwide in aerosols, which are responsible for raindrop formation (Li et al. 2017). However, the average concentrations found in our samples (30-100 nmol L⁻¹) were much lower than those in Honório et al. (2010) (300-950 nmol L⁻¹). This indicates that the region in this study is less affected in terms of atmospheric pollutants than the cities located in the central regions of the Amazon, where air quality is poorer.

For most elements higher concentrations occurred during the dry season, mainly Al, Mn, Co, Cu, Rb, Cd and Ba, which had ratios more than two times higher than in the wet season. Most of the metals were enriched in the rainfall, suggesting that their charges originate almost entirely from local and long-range anthropogenic sources (Da Silva et al. 2020). The degree of enrichment depends on the type, proximity, and extent of individual sources. Atmospheric Co can be attributed to coal combustion, mining activities, and automobile traffic, in a mix of crustal and anthropogenic factors (Uygur et al. 2010). Diesel powered machinery, manure, pesticide and fertilizer application in agriculture, and sewage wastes cause entry of Cd into the soil (Tabelin et al. 2018; Hocaoglu-ozyigit and Genc 2020). This metal in rainwater is a reliable fingerprint for evaluating aerial pollution (Adegunwa et al. 2019). No clear trend of increase or decrease in the concentration of these elements was observed over the years of study. EF values may result in metals, their pollution loads, as well as speciation forms of trace elements (Gopal et al. 2023).

Origin of pollutants

The rainwater in the Amazon has a chemically heterogeneous composition, which is driven primarily by the continuous cycle of rainfall and evaporation (Honório et al. 2010). Some íons such as Cl⁻ and Na⁺ are predominantly from the ocean, while Mg²⁺, K⁺, and Ca²⁺ may have marine, soil or anthropogenic origin. K⁺ and Ca²⁺ presented similar profiles, originated predominantly from anthropogenic sources (90%), followed by seawater (7%) and soil (3%). Sr, Rb, V, Mn, Co, and Ba enrichment may be ascribed to a terrestrial or biogenic influence related to the Sahara dust (Honório et al. 2010). A small fraction of Sr also could be related to seawater (Lebrato et al. 2020). The local biomass burning and forest fire emission during the dry season alters profoundly the composition of the atmosphere in most of the Amazon because higher amounts (until 30 times higher compared to the rainy season) of particles and gases are emitted (Artaxo et al. 2005). As the Amazon is heavily influenced by forest burning, K⁺ and Cl⁻ content, as well as higher enrichment of Cu, Pb, Zn, and Sb in our study, is probably influenced by fires (Yamasoe et al. 2000). As the city of Manaus lies 60 km away from CBR, its rapid urban development and major use of fossil fuel likely contributes to the increase in the chemical load of rainwater in the study area. The dominant species of fossil fuel originate from transformation of the precursors NO_x and SO_2 (Lin 2020). This increase may explain the NO_3^- and SO_4^{2-} content, as well as the more acidic pH in the dry season. The intensification of positive anthropogenic emission sources results in the acidification of the samples. However, SO_4^{2-} may have part of its origin in seawater, as this ion is found in the form of $CaSO_4$ and $MgSO_4$.

Regarding natural sources, neutralization occurs through the presence of alkaline species in the atmosphere such as Ca²⁺

and Mg^{2+}, derived mostly from soil dust and resuspension, and NH_4^+, mainly released from wastewater treatment, animal waste and fertilizers, and K^+ from biomass burning (Tiwari et al. 2016). Differently from SO_2 and NO_2, NH_3 reacts rapidly with acidic components to form NH_4^+ in the source area and is not transported over long distances (Asman et al. 1998). NH_4^+ acts as a basic agent neutralizing HNO_3 (Alves et al. 2007). Since the main economic activities in the region of CBR are agriculture (cassava, sugar cane, rice, beans, and fruits), livestock (cattle, equine, goats, and pigs), mineral extraction, and poultry farming (EcuRed 2017), ammonium sources in this area may be related to anaerobic digestion of animal and human waste and the use of agricultural fertilizers.

Finally, the biogenic factor was formed by $HCOO^-$, although these organic ions were underestimated. Some ions may have been more underestimated than others. Ca^{2+} and Mg^{2+} are markers of local calcareous soils and suspended road dust (Rao et al. 2016). Suspended soil dust, vegetation, and the metabolism of microorganisms constituted the main natural sources of these acids in the atmosphere.

The PMF analysis flagged six possible sources of the chemical species found in the rainwater. $Na^±$ and K^+ indicate the contribution of sea salt and/or fungal spores and biomass burning (factor 5) to the rainwater composition. Sodium salts in the Amazon Basin are mainly attributed to marine aerosols transported from the Atlantic Ocean (Moran-Zuloaga et al. 2018). However, it has been demonstrated that fungal spores can account for 69% of the total sodium mass during the wet season (China et al. 2018). The analysis managed to separate the part of $Na^±$ originating from sea salts (factor 4) from that originating from fungi (factor 5). The proportion of $Na^±$ in fungal spores coincided with that of the study (China et al. 2018). Besides, the Brazilian Amazon is yearly impacted by forest fires that produce large amounts of smoke particles that linger in the atmosphere and affect local health of the population, which, in small quantities, can contribute to $Na^±$ and $K^±$ levels (De Oliveira Alves et al. 2015).

The significant concentration of NH_4^+ and NO_3^- obtained are indicators of anthropic influence. Long-range transport likely increased the concentrations of these ions, as biomass fires are frequent during the dry season throughout Amazonia, and air masses from the city of Manaus may have reached the sampling site.

There are no recent studies published on the chemical composition of rainwater in the CBR, so it is difficult to draw a scenario. But, considering that the population in Manaus went from 1.8 million in 2010 (final collection period) to 2.1 million in 2024 and that the vehicle fleet went from 452 thousand vehicles (2010) to 855 thousand (2024), we can infer that pollution has increased considerably. Therefore, there is a tendency for the chemical composition of rainwater in CRB to also be influenced. Our findings corroborate the complex composition of rainwater in the Amazon, influenced by a mixture of different local and distant sources, and continuous cycles of rainfall and evaporation in this region.

CONCLUSIONS

The assessment of the chemical composition of rainwater from the Cueiras Biological Reserve, in central Amazonia, a primary forest 60 km from a large urban center, indicated a highly heterogeneous composition, reflecting the contribution mainly from crustal and biogenic emissions. However, sources such as biomass burning, as well as long-distance Saharan dust and fossil fuel combustion in the nearby urban center were also observed. The characteristic continuous cycles of evaporation and rainfall in the region also played a role. The high concentration of chemical components in the dry season were owed directly to the winds blowing from the interior of the country to the Amazon region between May and October, together with the intensification of the biomass burning. The concentration of elements of anthropogenic origin was detected even in places far from the Amazon. This is the longest monitoring of the chemical composition of rainfall ever carried out at CBR. Continuous monitoring of rainfall is essential for several reasons, including providing data to analyze weather patterns and changes in the climate, in addition to detecting the presence of pollutants in rainwater, which is important for public health and the environment.

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