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Chemical composition of rainwater in western Amazonia — Brazil

B.A.D Honório [a], A.M.C. Horbe [b,*], P. Seyler [c]

[a] Programa de Pós-Graduação em Geociências, Universidade Federal do Amazonas, Av. General Rodrigo Otávio Jordão Ramos, 3000, Coroado, 69077-000, Manaus-AM, Brazil
[b] Departamento de Geociências, Universidade Federal do Amazonas, Av. General Rodrigo Otávio Jordão Ramos, 3000, Coroado, 69077-000, Manaus-AM, Brazil
[c] IRD; LMTG; UT3, (OMP), 14 Av Edouard Belin, F-31400 Toulouse, France

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ABSTRACT

An extensive sample study in western Amazonia, Brazil was performed over the course of one year to i) establish the natural influence of the forest, ii) determine the contribution of the vegetation and fossil fuel burning and iii) detect the geographical and temporal influences on the rainwater composition. Six sampling stations were chosen on two 1000 km-long orthogonal axes. Parintins, Itapiranga, Manaus, Tabatinga were the stations from East to West, and Boa Vista, Manaus, and Apui were the stations from North to South. The results indicate a complex control of the chemical composition of the rainwater and a rather high heterogeneity among the stations. This heterogeneity can be explained by the influence of biogenic, terrestrial dust, agriculture activities and biomass-burning aerosols, and the urban development of Manaus City with its rapid increase in the use of fossil fuel. The isotopic composition of the rainwater indicates that from the north and west sides to the south and east sides, a slight geographical and temporal gradient exists, and more $\delta^{18}0$ enriched rainwater tends to be present in the west (Tabatinga) and in the North (Boa Vista). During the dry season a more negative $\delta^{18}0$ rainwater was observed in Manaus and Boa Vista stations, as compared to others stations. This observation indicates the more intense evaporative contribution of rainwater as a consequence of a rapid deforestation (savannization) process in the Manaus region.

1. Introduction

Chemical elements are transported in the atmosphere in the form of wind-blown soil particles, fine volcanic products, sea salts, ashes from forest fires and biogenic aerosols; these chemicals contribute to the atmospheric input of trace elements in rainwater. Because aerosols can travel long distances in the atmosphere, the natural background concentrations of elements in rainwater and aerosols are difficult to determine. Several studies found high contributions of atmospherically derived components to the soil budget for several elements, including both major and trace elements (Al-Momani et al. 2000; Atteia, 1994; Galloway et al., 1984; Heaton et al., 1990). This input plays an important role in tropical regions where soils are depleted of base-cations. In Niger and the Ivory Coast, the emission of terrigeneous particles of crustal composition is the main source of trace elements in atmospheric dust (Freydier et al., 2002). In both places a 50-fold enrichment of continental-crust-related zinc was found in rainwater and was due to remote industrial sources. The impact of human activity on the rainwater chemistry has been demonstrated in large cities and in regions far from industrial centers (Al-Momani 2003; Berg et al., 1994; Hontoria et al. 2003; Jaradat et al. 1999; Őzsoy and Saydam, 2000).

In Amazonia, evapotranspiration of the extensive forest cover, and the evaporation of water from lakes and rivers are the main sources of water vapor in the atmosphere (Marques et al., 1977; Forti and Moreira-Nordemann, 1991; Martinelli

* Corresponding author.
E-mail addresses: benicia_1@hotmail.com (B.A.D. Honório), ahorbe@ufam.edu.br (A.M.C. Horbe), patrick.seyler@ird.fr (P. Seyler).

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et al., 1996). The rainforest is the main source of natural aerosols (Cornu et al., 1998) but deforestation, the burning of vegetation, and the increase in the use of fossil fuel in large cities (e.g. Manaus and Boa Vista in western Amazonia) are also sources of aerosols that alter the rainwater composition (Yamasoe et al., 2000).

We monitored six rainfall stations in western Brazilian Amazonia over the course of one year to (i) measure the chemical composition of rainwater in Amazonia, (ii) establish the natural influence of the forest, (iii) evaluate the contribution of vegetation and fossil fuel burning and (iv) detect geographical and temporal influences in the rainwater compositions.

2. Sampling locations, material and methods

Eighty-two rainwater samples were collected from January to December of 2006 in open areas in six cities in western Amazonia: Manaus, with a population size of 1,700,000; Boa Vista, with 250,000; and Tabatinga, Itapiranga, Parintins and Apuí, each with fewer than 100,000 inhabitants (Fig. 1). Apuí, in southern Amazonas, has 17,500 inhabitants and is located in region where intensive forest burning is common in the dry season from May to October. Two sites (one under forest canopy, one in an open area) in Manaus were chosen to estimate the material trapped by the vegetation.

Manaus, Apuí, Tabatinga, Itapiranga and Parintins are south of the Equator in western Amazonia where the average temperature between 24° and 31 °C, and the average precipitation between 1650 and 2500 mm year^{-1}. Seasonality is marked by rainfall, with the rainy season from December to May and the dry season from June to October.

During June and August almost no rain falls in Apuí (2–2.9 mm month^{-1}) and in August and October very little rain falls in Itapiranga (13–21 mm month^{-1}) (Table 1). Boa Vista, north of the Equator, has similar temperatures with an average precipitation of 1783 mm year^{-1}, with the rainy season from October to April. During 2006, the most rainfall was in Parintins (2452 mm year^{-1}) and Apuí (2081 mm year^{-1}). Tabatinga, in the west on the border of Brazil, Colombia and Peru, has less rainfall (1737 mm year^{-1}) that is distributed fairly uniformly throughout the year. Atmospheric circulation in Amazonia is dominated by east-west trade winds, and the region is far from the sea (between 1000 km for Parintins and 3000 km for Tabatinga).

Fig. 1. Map of Brazil with the samples sites location.

Rainwater samples were collected manually with a wet-only collector (funnel-type) at approximately 1.5 m above the ground. In order to avoid trace element contamination, the funnel and bottles used for storing the water were cleaned with 3 parts of HCl to 1 part of HNO_3, then filled with HNO_3 (2.5%) for 24 h. The bottles were then rinsed five times with Milli-Q water (0.2 µS cm^{-1}) and filled with Milli-Q water until the collection. To avoid dry deposition, the rainwater sampler was fixed to the ground before the onset of rainfall and removed after each rain event. After collection, samples were filtered through a 0.45 µm Millipore® membrane filter. The filtration process separated the rainwater into three aliquots. Two aliquots were used to measure anions and the O and H isotopes, and one aliquot was acidified with bi-distilled HNO_3 to measure cations and trace elements.

Conductivity and pH of the Manaus samples were measured instantaneously at the end of each rain event. Elsewhere, these were measured in the Universidade Federal do Amazonas laboratory in Manaus within 10 days of rainfall. The pH was measured using a combined "Schott-Geräte" electrode calibrated using NIST standard buffer solutions (pH 4.00 and 6.86 at 25 °C). The accuracy of the pH and conductivity measurements were ±0.05 units and ±1 µS cm^{-1} respectively. The major anions (Cl, NO_3, and SO_4) and cations (Ca, Mg, Na, and K) were determined using ion chromatography (Dionex ICS-900) and SiO_2 (as H_4SiO_4) by colorimetry. Trace element concentrations were measured using a quadrupole-based ICP-MS (Elan 6000, Perkin Elmer SCIEX), using the Internal Standard method with indium. The international geostandard SLRS-4 (certified by the National Research Council of Canada) was used to check the accuracy of the ICP-MS analyses. The analytical precision, evaluated using repeated standard reference materials analysis, is generally better than 10% while reproducibility, determined using replicate sample analysis is better than 5%. The O and H isotopes were measured within two months at the facilities of the Universidade Federal da Bahia in Brazil on a mass spectrometer Thermo Finnigan Delta Plus XL More information about the analytical procedure will be found in Seyler and Boaventura (2003); Hagemann et al. (1970).

The H^+ concentration was calculated from the pH, and concentrations of the elements are standardized by rainwater volume as volume-weighted mean concentrations (VWM) according to the formula: $C_{VWM} = [(C_x x V_x) / \Sigma V_x]$ where Cx is the element concentration and Vx the rainwater volume of a collected rain event x. The marine contribution (M) for a given element x was calculated according $M_x = [(C_{Na})_{rainwater} - (C_x/C_{Na})_{sea}]$ and the terrestrial influences (TI) according to $TI = [(C_x)_{rainwater} x (C_{Al})_{crustal}] / [(C_x)_{crustal} x (C_{Al})_{rainwater}]$ (Duce et al., 1975).

3. Results and discussion

3.1. Chemical and isotopic characteristics of western Amazon rainwater

We report the volume-weighted mean concentrations (VWM), of cations (H^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (Cl−, NO_3, and SO_4) in Table 1. The concentrations of bicarbonates were close to the detection limit of the titration method (detection limit was 0.2 µmol L^{-1}, using the Gran method with a 10 ml sample volume) and therefore we do not report the bicarbonate concentrations. These low concentrations, common in rainwater are the expected concentrations given by the equilibrium of bicarbonates system at temperature and pressure conditions of the atmosphere (Drever, 1997).

The ionic charge balance reveals a systematic anion deficit at all sites sampled which does not ascribe to the bicarbonates owing to the pH values measured in the rainwater samples (mean value close to 4.2). This anion deficit, almost always observed in tropical and subtropical rainwater, is well-documented.(Lesack and Melack, 1995; Willians et al., 1997; Lara et al., 2001; Freydier et al., 2002; Artaxo et al., 2005) and it is mainly due to the presence of organic compounds such as acetate, formate, and oxalate. No analyses of these compounds were made, but they could represent up to 73% of the fine particular matter emitted by the biomass (Cachier et al., 1995; Yamasoe et al., 2000).

The pH and conductivity are heterogeneous in rainwater. The dry season is usually more acidic except in Boa Vista and Itapiranga. Rainwater conductivity is higher in the dry season for the Manaus under-canopy station, Itapiranga, and Parintins. The Manaus open-area station, Apuí and Tabatinga have similar conductivities between the seasons (Table 1 and Fig. 2).

Among the seven sampling stations, Manaus under-canopy samples have the most concentrated rainwater that is 3 to 4 times more concentrated than the Manaus open-area samples and the Tabatinga samples are the most dilute (Fig. 3). Higher ion concentrations occurred in the dry season except at Boa Vista and Itapiranga (Figs. 3, 4). In general, H^+, Ca^{2+} and Na^+ are the most abundant cations, and anion concentrations are much more variable (Table 1, Fig. 4).

For all stations, Al, Zn and Fe are the most concentrated elements while Pb, Rb and Mo are the least concentrated. Among the stations, trace element concentrations are lowest in Tabatinga, Itapiranga and Parintins, and highest in Manaus under-canopy. For the Manaus open-area and Manaus under-canopy stations, higher concentrations occur during the dry season and under-canopy samples are more than twice as concentrated as the Manaus open-area samples for most of the elements (Table 1, Fig. 4).

Concerning the stable isotopic compositions of Amazon rainwater, the stations Tabatinga (the western station) and Boa Vista (the northern station) have the highest fractionated rainwater (Table 2, Fig. 5). Manaus open-area and under-canopy stations are isotopically similar and have the least fractionated rainwater in the wet season and Itapiranga, Patintins and Apuí in the dry season. A slight regional gradient exists with rainwater more fractionated on the west side (Tabatinga) and on the north side (Boa Vista) than in the east (Parintins) and south side (Apuí) of the Amazon region (Fig. 5).

Greater negative $\delta^{18}O$ values at most stations during the dry season are in agreement with Salati et al. (1979). This trend occurred from the south (Apuí) to the northern Amazonia (Boa Vista) and from the east (Parintins) to western (Tabatinga) in the dry and wet season (Fig. 6). The mean rainwater regression line for all of the stations ($\delta D = 7.9\ \delta^{18}O + 8.4$) is similar to that of the global rainwater regression line ($\delta D = 8\ \delta^{18}O + 10$) with no difference between seasons ($\delta D = 7.9\ \delta^{18}O + 9.9$ for the wet season and $\delta D = 7.6\ \delta^{18}O + 9.9$ for the dry season) (Fig. 6). However, in Manaus, the rainwater regression line indicates a slight deviation to a lower δD ($6.13\ \delta^{18}O + 0.85$) with a minor difference in the slope for the Manaus under-canopy station ($\delta D = 6.98\ \delta^{18}O + 4.1$).

At all stations, the d values (calculated by $d = \delta D - 8\delta^{18}O$) are in agreement with those estimated by Craig (1961) ($d = 10$) for many stations around the world. Deuterium excess is typical for lower humidity conditions and for higher altitudes or short distances from the coast, and depletion is a consequence of the evaporative contribution (Dincer and Paine, 1971). Our d values indicate higher evaporative contribution for the wet season in all stations and lower humidity conditions for Manaus (Table 2).

The evaporative process indicate by the deviation of the rainwater regression line to the lower δD and the d values, was probably enhanced by the very intensive local deforestation around Manaus. The tendency for rainwater to be more fractionated in the west (Tabatinga) indicates a continental effect caused by the eastern-western trade winds, but these winds do not explain the south to north gradient.

3.2. Origin of the elements

The rainwater from western Amazonia is chemically heterogeneous and reveals a complex control of the chemistry of the Amazonia rainwater. The chemistry is driven primarily by the continuous cycle of evaporation and precipitation during the westerly trajectory from the Atlantic Ocean. We consider Tabatinga, Itapiranga and Parintins with a low chemical load, as having the most pristine rainwater environment in western Amazonia. They have the same range of chemical concentrations as the previously studied Amazon forest remote stations (Lesack and Melack, 1995; Willians et al., 1997), and remote areas in an African tropical forest (Freydier et al., 2002) (Table 3). Conversely the rainwater from Apuí, Boa Vista and Manaus are clearly impacted by human activities. The low pH (3.7 - 4.5) indicates anthropogenic influence but is lower than other urban agricultural regions (Lara et al., 2001; Xu and Han, 2009).

Since the Al in most of the rainwater samples has a terrestrial origin, at least some of the elements come from the upper continental crust. A value of 10 is generally used to indicate enrichment (Berg et al., 1994). Zn, Mo, Cu, Ni and Pb have enrichment greater than 10 in almost all stations, and Sr, Rb, V, Mn and Ba are 1 – 10 (Fig. 7A). We also calculated the marine contribution for each element. For all sampling stations the marine contribution is negligible compared to biogenic sources (Fig. 7B).

Table 1
Rainwater composition at the six stations in western Brazilian Amazon region: precipitation (ppt in mm), conductivity (C in μScm^{-1}), major ionic composition in μmol L^{-1} and trace elements concentration in nmol L^{-1}, VWM-Volume-weight mean, VWMW in the wet season, VWMD in the drier season. Mean, Min- minimum, Max- maximum and Sd2- standard deviation are no standardized by volume-weight.

	Ppt	pH	C	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	SiO_2	Al	Zn	Fe	Sr	Cu	Mn	Ba	Ni	Pb	Rb	Mo	V
Boa Vista																								
VWM		4.5	4.6	63.0	55.9	4.5	52.4	4.4	1.6	4.7	10.2	1.2	1952	655	426	141	77	93	15	23	4	4	2	3
VWMW		4.5	4.7	64.3	61.5	4.8	58.8	4.9	1.6	4.5	10.2	1.2	2147	616	461	157	84	103	15	24	4	4	1	4
VWMD		4.4	3.6	53.6	14.4	2.0	6.2	0.6	1.9	6.3	10.5	0.7	522	938	173	18	26	18	14	15	1	2	7	1
Mean	166.0	4.7	4.4	38.9	37.0	3.9	24.5	2.2	2.3	10.7	16.5	1.6	1016	487	237	70	70	48	15	27	2	4	3	2
Min	0.0	4.0	2.9	1.6	6.0	0.8	1.7	0.2	<DL	1.0	1.4	0.02	124	45	50	1	16	3	2	3	1	1	<DL	<DL
Max	562.3	5.8	5.9	100.0	207.1	12.7	213.0	16.2	7.0	39.6	113.1	6.2	7077	1917	1476	579	162	363	47	135	11	12	16	12
Sd2	196.8	0.6	1.2	39.4	61.2	4.0	62.7	4.8	2.0	12.3	32.4	2.3	2017	673	417	172	59	106	17	38	3	4	5	4
Manaus open-area																								
VWM		4.1	8.3	114.7	15.4	3.2	17.1	2.1	9.5	12.3	10.1	0.7	951	309	312	44	55	40	5	37	1	4	8	24
VWMW		4.2	8.5	117.8	13.2	2.4	11.7	1.6	5.5	9.6	7.6	0.6	781	235	237	31	41	33	5	27	1	3	8	19
VWMD		4.1	7.1	93.6	30.0	8.9	53.7	5.2	36.3	30.8	27.1	1.7	2088	807	809	131	152	85	5	101	1	9	2	54
Mean	204.4	4.1	7.9	104.5	21.6	5.2	29.7	3.2	18.7	19.3	18.0	1.1	1371	486	489	93	91	56	5	58	1	6	6	35
Min	38.7	3.4	4.9	12.6	1.3	0.6	3.4	0.3	2.6	0.0	1.9	0.3	384	62	84	2	11	5	<DL	11	<DL	1	<DL	4
Max	437.2	4.9	14.3	398.1	80.8	14.3	82.2	9.2	46.4	51.4	82.9	2.7	2914	1221	1233	677	256	120	24	199	2	16	26	77
Sd2	137.4	0.4	2.8	101.5	20.3	4.4	27.8	2.6	19.4	17.3	22.0	0.7	876	436	392	187	89	36	8	60	1	5	9	29
Manaus under-canopy																								
VWM		4.1	17.4	81.9	31.7	20.0	111.4	11.4	30.7	17.4	19.3	2.8	1457	318	402	201	50	211	29	29	5	26	4	26
VWMW		4.2	17.3	73.1	24.4	17.2	41.7	9.1	25.6	13.0	15.6	2.4	1074	240	354	76	37	178	21	22	4	22	5	18
VWMD		3.8	19.4	162.5	95.5	43.4	673.8	31.8	79.1	61.3	58.0	6.7	4917	969	729	1189	169	489	101	89	12	55	2	97
Mean	204.4	4.0	17.9	105.4	51.9	27.6	286.6	18.5	46.3	32.0	31.8	4.3	2659	530	559	521	89	305	54	50	7	36	3	51
Min	38.7	3.7	11.4	31.6	9.3	10.2	16.4	4.4	13.0	3.9	2.8	0.9	622	111	200	25	17	57	11	11	2	12	<DL	9
Max	437.2	4.5	21.8	199.5	117.5	53.1	1218.4	40.9	84.9	76.8	79.5	9.2	6515	1348	1335	2131	208	697	137	117	16	63	16	134
Sd2	137.4	0.3	3.0	54.8	40.1	15.3	418.8	14.5	31.0	30.2	27.0	3.4	2277	415	367	787	75	235	50	39	4	20	5	51
Apuí																								
VWM		5.5	12.8	31.8	80.5	3.4	11.5	1.2	16.8	4.1	11.4	0.6	558	406	205	31	62	64	4	61	6	3	2	2
VWMW		4.8	9.1	19.6	52.2	2.7	11.2	0.8	9.0	1.6	9.6	0.6	674	421	205	33	59	48	4	63	5	2	2	2

(continued on next page)

Table 1 *(continued)*

	Ppt	pH	C	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	NO_3^-	Cl^-	SiO_2	Al	Zn	Fe	Sr	Cu	Mn	Ba	Ni	Pb	Rb	Mo	V
VWMD		4.4	17.2	52.3	129.2	3.8	5.6	1.8	31.8	9.5	10.6	0.2	601	451	164	7	40	81	4	22	5	4	<DL	1
Mean	189.0	4.5	12.1	44.0	74.4	3.1	8.8	1.0	15.2	4.7	9.1	0.4	562	369	173	19	45	52	4	41	4	3	1	1
Min	2.0	4.0	2.1	6.3	5.4	0.7	3.0	0.2	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Max	379.6	5.2	18.7	100.0	210.5	6.0	24.4	3.3	39.9	16.6	23.0	2.6	1021	1028	554	70	143	118	9	152	11	8	4	5
Sd2	116.2	0.5	6.5	36.9	71.2	2.0	7.8	0.8	14.0	5.9	5.9	0.7	375	354	139	27	39	41	3	55	3	2	1	1
Tabatinga																								
VWM		6.1	5.8	20.2	8.7	2.0	4.6	0.6	1.9	11.1	4.9	0.4	361	117	358	15	20	12	5	10	1	2	5	1
VWMW		5.6	5.1	2.7	8.1	1.5	3.1	0.5	1.6	13.8	5.0	0.3	308	107	353	10	19	11	5	10	1	2	1	1
VWMD		3.4	3.9	37.2	7.0	2.0	5.8	0.8	1.5	3.8	1.2	0.8	218	78	123	21	11	6	2	6	1	2	16	1
Mean	144.8	5.1	4.8	28.3	7.0	1.8	4.4	0.6	1.7	8.1	3.7	0.4	327	117	261	13	16	11	4	8	1	2	6	1
Min	56.1	3.9	2.9	1.3	0.7	0.2	0.8	0.1	<DL	<DL	<DL	<DL	68	49	17	1	2	2	1	1	1	<DL	<DL	<DL
Max	261.2	5.9	6.0	125.9	19.2	3.4	13.1	1.0	3.0	55.7	13.3	1.5	651	235	730	55	37	18	13	16	2	2	49	3
Sd2	70.0	0.7	0.9	43.4	6.9	0.8	3.0	0.2	0.9	15.7	3.6	0.5	226	57	284	15	13	4	4	5	<DL	1	14	1
Itapiranga																								
VWM		4.0	4.7	122.8	12.3	6.2	6.6	1.6	2.1	6.4	7.7	6.8	296	149	149	24	24	24	13	17	1	7	1	2
VWMW		3.9	4.3	148.7	14.4	4.8	7.7	1.8	2.0	7.1	7.3	3.0	308	126	186	30	24	27	9	20	1	5	2	2
VWMD		3.2	4.0	21.3	2.7	8.9	3.4	1.2	1.7	2.3	5.7	12.7	237	187	45	7	6	10	25	2	1	12	<DL	1
Mean	157.1	4.2	5.2	90.1	10.1	10.9	6.0	1.6	2.2	5.8	7.4	15.0	372	269	116	19	23	33	30	12	1	14	1	2
Min	13.8	3.6	0.4	25.1	1.0	1.9	2.1	0.5	1.0	0.0	0.0	0.0	25	44	<DL	2	2	4	1	2	<DL	2	<DL	<DL
Max	325.3	4.6	12.2	251.2	36.3	44.1	18.3	3.5	3.3	24.2	18.0	72.1	1063	917	416	102	65	196	137	69	2	66	5	5
Sd2	119.4	0.3	2.7	69.0	9.1	15.6	5.0	1.2	0.9	6.6	5.1	27.2	363	278	156	29	20	53	48	19	1	24	2	2
Parintins																								
VWM		5.3	5.9	10.5	16.9	2.7	10.8	1.9	3.5	5.7	11.0	0.9	769	115	235	30	28	26	6	15	1	3	1	5
VWMW		5.5	5.6	4.7	18.9	2.9	10.7	2.0	3.3	5.9	10.4	0.9	853	116	266	33	31	27	7	17	1	3	1	5
VWMD		4.4	7.1	40.2	6.2	2.2	11.6	1.6	4.4	5.0	13.8	0.9	333	108	76	15	11	20	5	5	1	2	1	5
Mean	204.4	5.0	6.4	21.2	14.5	2.6	10.4	1.8	4.2	6.0	12.7	0.8	562	107	186	24	23	24	6	12	1	3	1	5
Min	29.7	4.2	4.0	1.6	4.4	1.7	5.0	0.9	0.5	2.2	3.5	0.1	156	56	54	4	5	10	2	1	<DL	1	<DL	1
Max	429.4	5.8	8.8	63.1	47.2	4.4	17.1	2.9	12.9	11.8	54.0	2.0	2683	191	770	78	85	40	13	68	2	4	4	26
Sd2	132.6	0.6	1.7	21.3	13.6	0.9	3.8	0.6	3.7	3.3	13.7	0.6	686	48	229	23	27	10	3	20	1	1	1	7

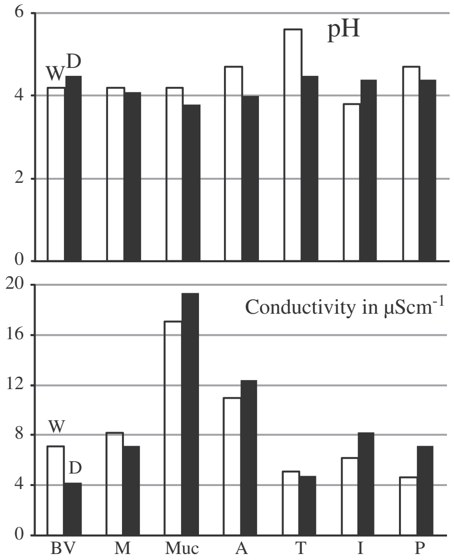

Fig. 2. pH and conductivity (µScm-1) variability standardized by the rainwater volume-weighted mean (VWM) (W- wet season, D- drier season, BV- Boa Vista, M- Manaus open-area, Muc- Manaus under-canopy, A- Apuí, T- Tabatinga, I- Itapiranga, P- Parintins).

At the two Manaus stations (the open-area and under-canopy stations), the washout of dry deposition on the vegetation and its subsequent dissolution by the rain enriched the throughfall in Sr, Rb, V, Mn and Ba. This enrichment can be attributed to a terrestrial or biogenic influence and can be related to the westwards Sahara dusts (Moreno et al., 2006). The local biomass-burning emissions, which can be 30 times greater in the dry season compared to the wet season (Artaxo et al., 2005), enrich the atmosphere in particulate aerosols. Because Apuí is heavily influenced by forest burning, the K^+ and Cl^- content and the Zn, Cu, Ni and Pb higher enriched at this station is probably a consequence of fires (Sequeira and Lai, 1998 and Yamasoe et al., 2000). In Manaus, the rapid urban development and the increase in the use of fossil fuel resulted in an increase in the chemical load of the rainwater. This increase explains the SO_4^{2-}, NO_3^- contents and the more acidic pH found at this station in the dry season.

4. Conclusion

The extensive study in western Amazonia, Brazil, performed over the course of one year, indicate a rather high heterogeneity throughout the Amazon and a complex control of the chemical composition of the rainwater. It is a product of a mixture of different local and distant sources that are influenced by the continuous cycle of evaporation and precipitation during the westerly trajectory from the Atlantic Ocean and by aerosols that were originate from biogenic and terrestrial dust (link to agricultural activities), biomass-burning aerosol and fossil fuel combustion with negligible marine contribution. We consider Manaus, Boa Vista and Apuí the most impacted by human activities, while Tabatinga, Itapiranga and Parintins with a low

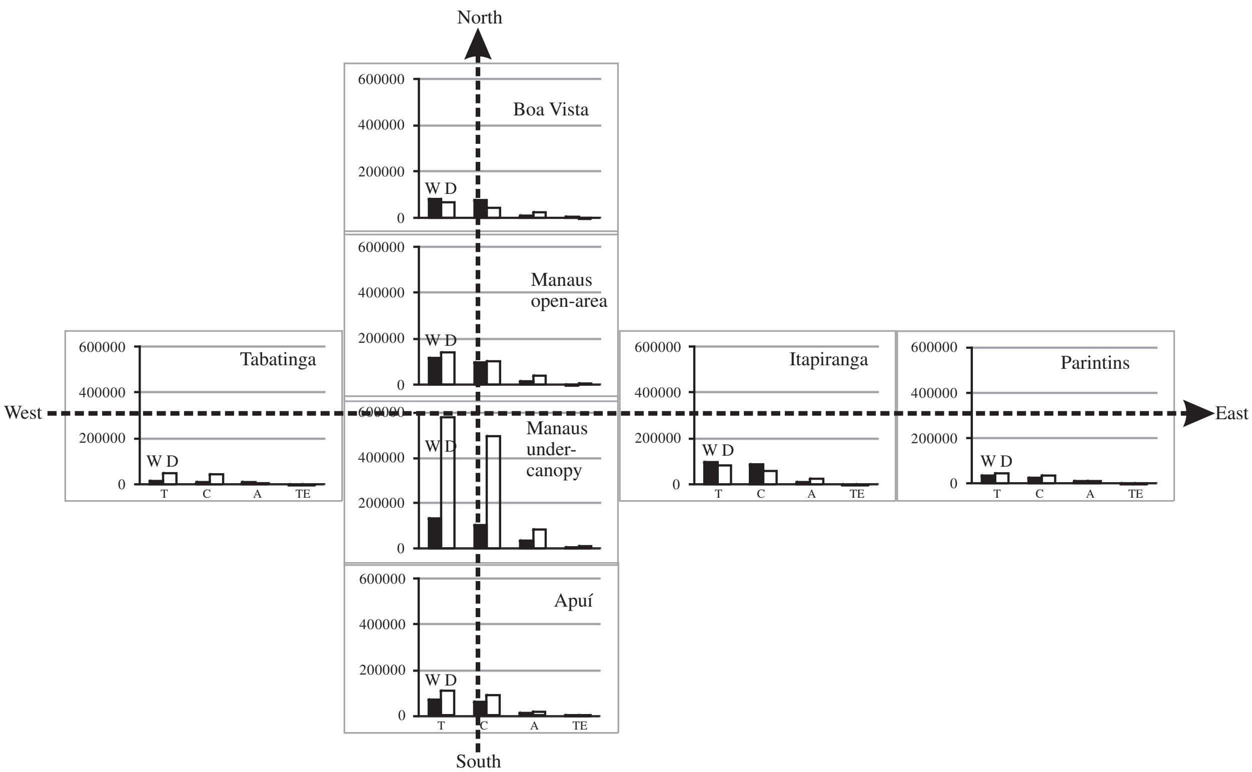

Fig. 3. The volume-weighted mean (VWM) calculated for the year of 2006 in µmol.L-1 for major ions and in nmol.L-1 for trace elements in the six stations (T- total load, C- cations load, A- anions plus SiO2 load, TE- trace elements load, W- wet season, D- dry season).

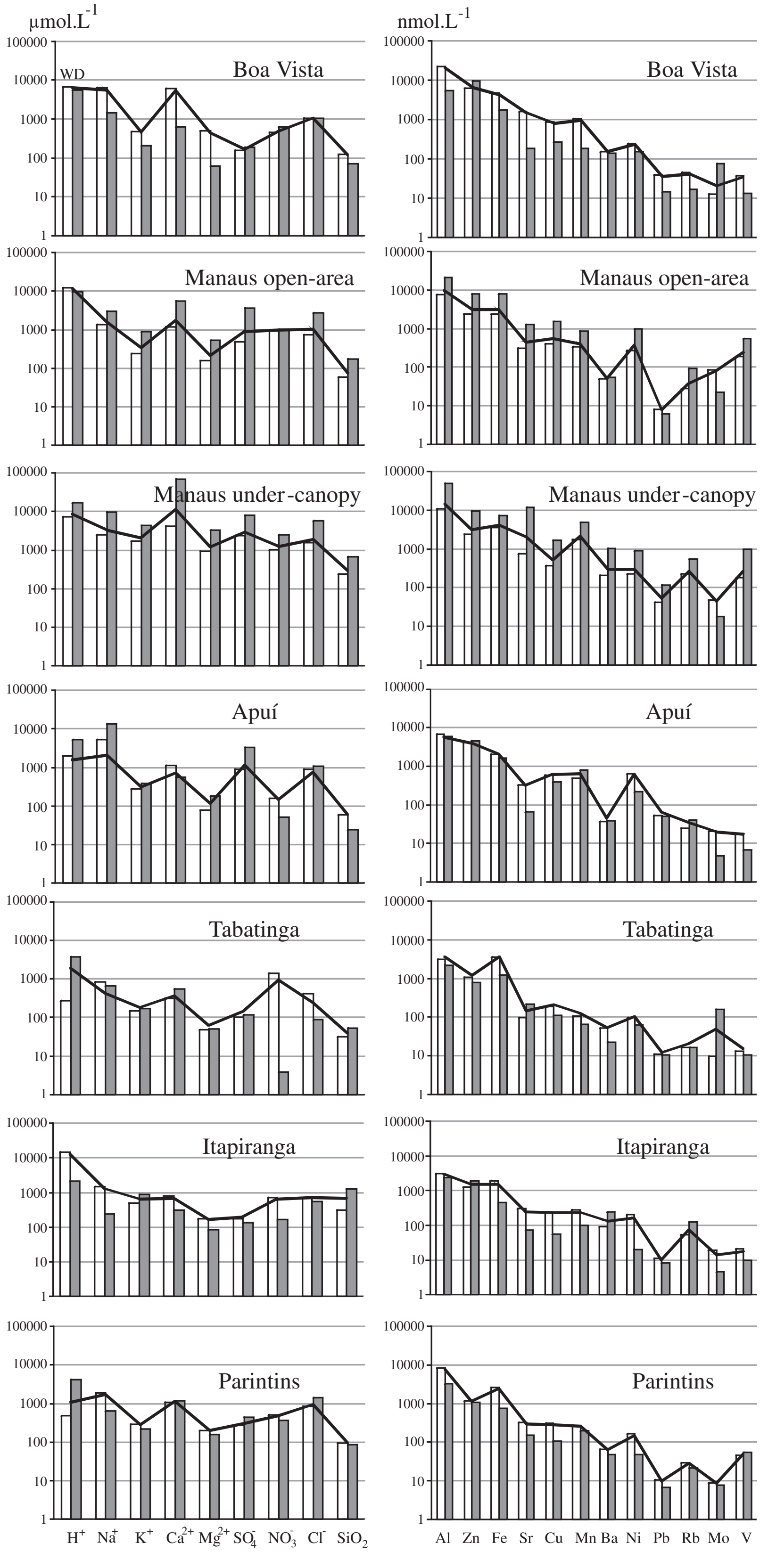

Fig. 4. Mean annual (black line) and seasonal chemical composition in logarithmic scale of μmol L^{-1} for major ions and in nmol L^{-1} for trace elements standardized by the rainwater volume-weighted mean (VWM) (white bar wet season - W, grey bar drier season - D) in the rainwater from western Amazonia.

Table 2
Compariron stable isotopic (‰) among sites from rainwater in the western Brazilian Amazon region.

Station	One year mean			Wet season				Dry season		
	$\delta^{18}O$	δD	Max	Min	$\delta^{18}O$	δD	d	$\delta^{18}O$	δD	d
Boa Vista	-5.6	-34	-1.3	-68	-5.5	-34	10	-6.1	-39	9.8
Manaus open-area	-1.4	-8	0.3	-34	-0.9	-5	2.2	-5.6	-32	12.8
Manaus under-canopy	-1.8	-8	-0.3	-34	-1.4	-6	5.2	-4.9	-29	10.2
Apuí	-4.4	-27	1.1	-48	-4.4	-27	8.2	-2	6	10
Tabatinga	-7.5	-49	0.1	-138	-11	-79	9	-3.2	-13	12.6
Itapiranga	-4.4	-27	-1.5	-98	-5.2	-35	6.6	-2.1	-5	11.8
Parintins	-5.1	-30	0.7	-66	-5.8	-36	10.4	-1.2	2	7.6

chemical load, as having the most pristine rainwater environment in western Amazonia.

A slight continental gradient exists with rainwater more fractionated on the west side and on the north side than in the east and in the south side of the Amazon region. There are also a higher evaporative contribution for the wet season in all stations and lower humidity conditions for Manaus region similar to the natural environment from Boa Vista. This indicates an intense evaporative contribution related to the rapid deforestation and urbanization of the Manaus and thus to a savannization processes of the region.

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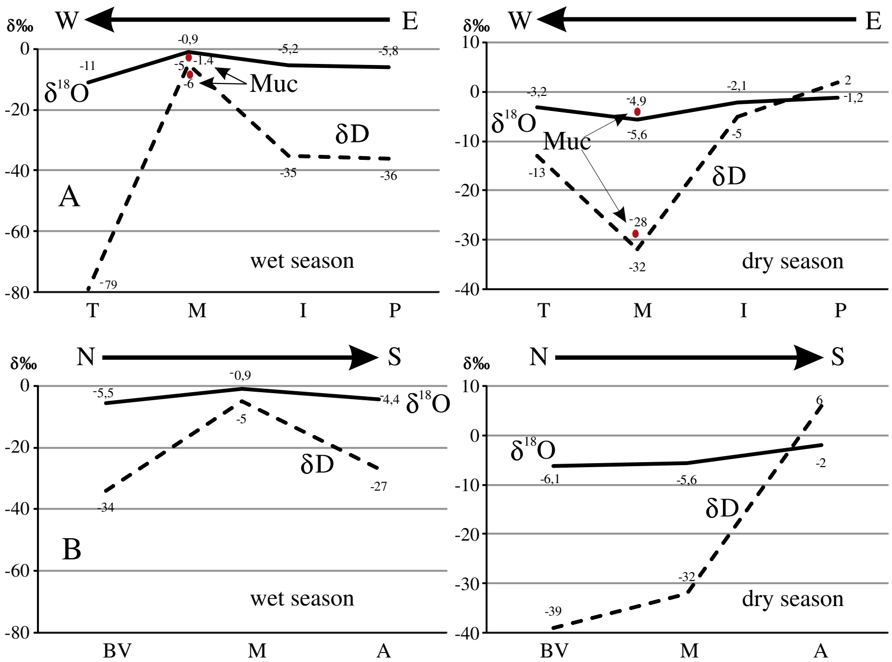

Fig. 5. Isotopic composition standarized by the rainwater volume-weighted mean (VWM) in east - west trend and north - south trend (T- Tabatinga, M- Manaus open-area, Muc- Manaus under-canopy, I- Itapiranga, P- Parintins, BV- Boa Vista, A- Apuí, N- north, S- south, W- west, E- east).

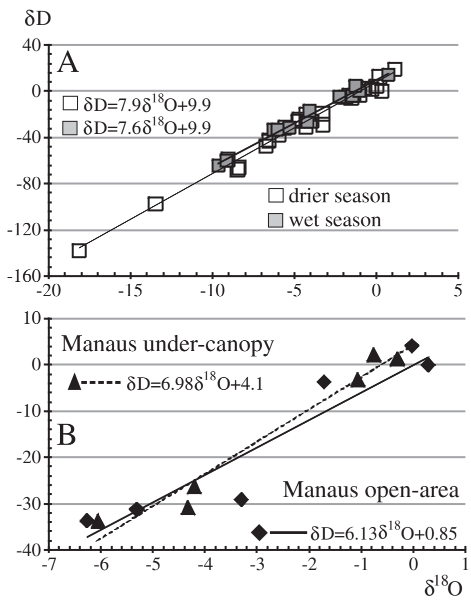

Fig. 6. Isotopic composition and rainwater regression line, A from all stations and B from Manaus stations.

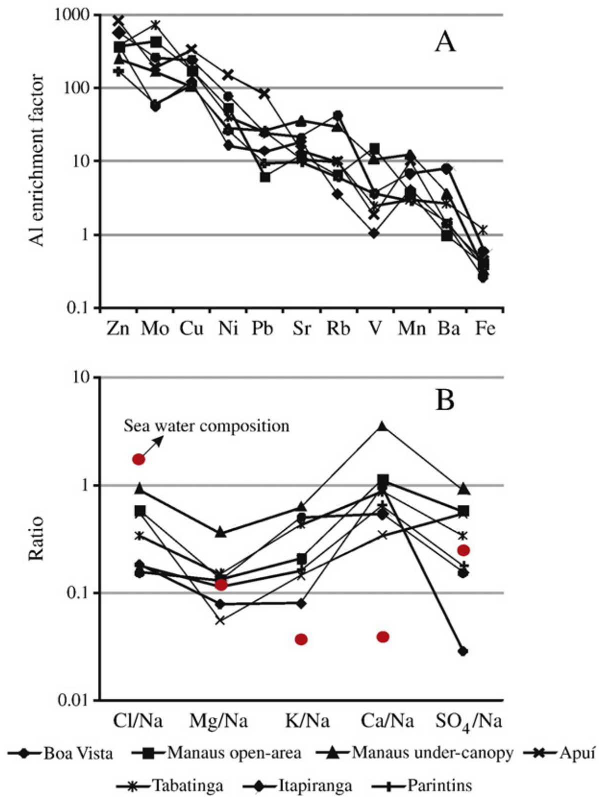

Fig. 7. A- aluminium enrichment factor in the rainwater and B- concentration of Cl^-, Mg^{2+}, K^+, Ca^{2+} and SO_4^{2-} relative for the concentration of Na^+ in sea water.

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Table 3
Comparison of the annual VWM concentration in μeq L^{-1} from the rainwater of western Amazonia in 2006 (this study) with the Lesack and Melack (1995) from 1984, Willians et al. (1997) from 1990, and Freydier et al. (2002).

Station	Boa Vista	Manaus	Manaus throughfall the Canopy	Apuí	Tabatinga	Itapiranga	Parintins	Lesack & Melack (1995)	Willians et al. (1997)	Freydier et al. (2002)[a]	
pH	4.2	3.9	4.1	4.6	4.8	3.5	5.0			4.7	5.0
Cond.	6.2	8.3	17.4	11.0	5.0	6.2	5.9				
H^+	63.0	115	81.9	27.3	17.5	335	10.4	13	17	19	11
Ca^{2+}	52.5	17.2	111.4	9.9	4.1	6.7	10.8	2.1	2.4	5.0	2.8
Na^+	55.8	15.4	31.7	70.5	7.7	12.3	16.9	2.5	2.4	1.1	1.0
K^+	4.4	3.2	20.0	2.9	1.7	6.2	2.7	0.7	0.8	1.9	2.2
Mg^{2+}	4.4	2.1	11.5	1.0	0.6	1.6	2.0	1.5	0.9	1.1	1.2
Σ^+	180.0	152.8	256.5	111.6	31.5	361.8	42.8	26	26	28.1	18.2
SO_4^{2-}	1.6	9.5	30.7	14.4	1.7	2.1	3.5	4.5	2.0	6.9	2.1
NO_3^-	4.3	12.3	17.4	3.5	9.6	6.4	5.7	3.5	4.2	30	12
Cl^-	10.2	10.1	19.3	9.8	4.3	7.7	11.0	4.7	4.6	1.9	1.4
Σ^-	31.9	67.4	27.7	15.6	16.2	20.2	31.9	13	11	38.8	15.5

[a] In tropical forest environment in Africa, DL – detection limit.

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