Chemical composition of acid rains in the Venezuelan savannah region

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ABSTRACT

The chemical composition of rain events has been determined at 6 sites in the Venezuelan savannah region. The results indicate that precipitations are little affected by anthropogenic emissions and that rain concentrations of anions and cations are similar to those observed at "remote" continental sites. At each location, the rain is acidic with average pHs ranging from 4.4 to 5.4. Over 50% of the free acidity may be due to formic and acetic acids. HNO_3 and H_2SO_4 contribute only less than 36%. NH_3 plays a significant role as neutralizing compound; Ca and Mg carbonates may also, in some cases, reduce the acidity of the rain solution. A complete evaluation of the ions that take part in the acid-base equilibrium is given. The participation of organic acid is discussed in detail. The first rains of the season, during biomass burning periods, are heavily loaded with several compounds, showing that emissions and/or atmospheric production are enhanced during vegetation fires. No significant variation in rain acidity was observed; it is likely that the larger atmospheric photochemical formation of organic and inorganic acids during burning is neutralized by a large primary emission of NH_3. The study of these "particular" rains is useful in searching for pollutants emitted by fires and/or possible atmospheric processes that may occur in the associated haze layer.

1. Introduction

As part of a research program oriented to characterize the atmospheric chemistry of the Venezuelan savannah climatic region, and its possible relation to the acidification processes occurring in this ecosystem, over the last few years, the chemical composition of rainfall has been measured at several sites in the savannah region of Venezuela.

It is well established that in the rural regions of Venezuela, rainfall is acidic (Sanhueza et al., 1987, 1988 and 1989). On the other hand, a characterization of the Venezuelan environment (Sanhueza et al., 1988) indicates that terrestrial and aquatic ecosystems of the Orinoco River basin are sensitive to acid deposition; most of the soils are acidic, with a high exchangeable Al content; surface water has low alkalinity and extremely low buffer capacity. Therefore, in order to evaluate the possible future impact of an increase in rain acidity due to an increase in anthropogenic activities in the region, it is important to determine the chemical composition of rainfall at the present time, when "natural" conditions still prevail throughout most of the Venezuelan savannah region.

2. Field measurements

The map in Fig. 1 shows the savannah climatic region of Venezuela, which is located between the Amazon forest and the Caribbean Sea, and indicates the position of the sampling sites: Camburito (Portuguesa State), Chaguarama (Guárico State), Joaquín del Tigre (Monagas State), Guri and La Paragua (Bolívar State). Two well-defined climatic periods occur in the area: a dry season for December to April, and a rainy season from May to November. The annual rainfall at the monitoring sites is given in Table 1. No important variation in average temperature is observed
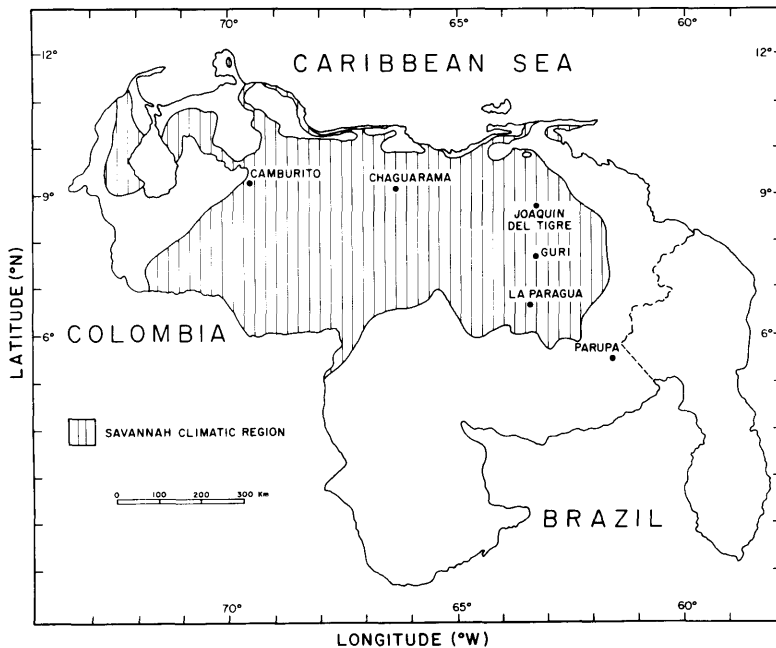
Fig. 1. Venezuelan savannah region and monitoring sites.

between the seasons. The vegetation is diverse, ranging from grassland to open forest (Medina, 1980). During the second half of the dry season, a vegetation burning period takes place, mostly due to agricultural practices. On a regional scale, the wind system shows that northeast and east-northeast (northeast trades) are most frequent. Wind speeds are lower during the wet season, espe-

cially in the region south of the Orinoco river, when the ITCZ is over the central part of Venezuela.

Samples were also collected in Parupa in the "Gran Sabana" region (Bolívar State). According to the Koeppen climatic classification, this region is classified as tropical humic monsoonic, that is a transition between savannah and rainforest

Table 1. *Rainfall collection periods*

Site	Type of collector	Recollection period	No. events[a]	Annual rainfall (mm)
Camburito	wet-only	Nov. 83/Aug. 84	18	1600
Chaguaramas	wet/dry	April/Dec. 87	12 (1)	920
J. del Tigre	wet-only	Feb./Sept. 85	12 (1)	1000
Guri	wet/dry	Oct./Nov. 88 and May 89	10 (1)	1300
La Paragua	wet-only	April 85 and Oct./Nov. 85	12 (2)	1600
Parupa	wet-only	May/Sept. 85	8	2000

[a] In parentheses are the samples collected during vegetation burning.

(without a marked dry season and less rainy than the rainforest ecosystem). Due to paleoclimatic sequence and agricultural practices of indigenous people, grassland vegetation predominate (Folster, 1986).

Samples were collected by event; two different types of collectors were used: (i) wet-only collector, which consists of a large plexiglass funnel, with a collecting area of 0.25 m^2, and a 2 l polyethylene bottle connected to the funnel by a 30 cm latex tubing. The system was kept closed during dry periods, and was opened manually at the beginning of a rainfall event. Other details are given by Sanhueza et al. (1987); (ii) an Aerochem Metric Inc., Model 301, wet and dry automatic collector. All the material was prepared in the laboratory following the direction given by Galloway and Likens (1976, 1978). Table 1 summarizes the collection periods, the type of collector used and some additional observations.

The pH was measured within 2 h of the end of the rain event. A fraction of the sample was preserved with chloroform (3 ml/0.5 l of rain) for the analysis of anions and NH_4^+ (Galloway et al., 1982); another fraction was preserved with nitric acid for the analysis of cations. At the Joaquín del Tigre, Chaguarama, Guri and Parupa sites, analysis of nitrate and phosphate were made, immediately, in the field.

Cations Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} were analyzed by atomic absorption spectroscopy and NH_4^+ with a selective ion electrode. Phosphate was determined by the ascorbic acid method, and the other anions by either ion exchange or ion exclusion chromatography; NO_3^- and Cl$^-$ were also determined colorimetrically (Gries reaction) and by mercury titration, respectively. For details (i.e., La Paragua site) see Sanhueza et al. (1989).

3. Results and discussion

A separate presentation will be made for burning and non-burning periods. Most of the discussion (Subsects. 3.1 and 3.2) will deal with the non-burning period results; Subsect. (3.3) is dedicated to discussion of the results during burning periods.

3.1. Chemical composition and rain acidity

The results of the volume-weighted pH and ions concentrations obtained at the six sites

are summarized in Table 2. Excess concentrations with respect to sea salt (X^*) of sulphate, chloride, potassium, calcium and magnesium were calculated using Na$^+$ as reference and ratios of 0.12, 1.16, 0.021, 0.044 and 0.227 (in eq l^{-1}) for the seawater composition, respectively. Concentrations of total (RCOOH$_T$) and dissociated (RCOO$^-$) acids are also given in Table 2 for formic and acetic acids. The dissociated concentrations were calculated as indicated by Sanhueza et al. (1989).

Compared to the other sites, larger concentrations of NO_3^- and SO_4^{2-} were observed in Camburito, suggesting that this site is affected by significant air pollution, therefore, this site is excluded from the general discussion, and is presented separately at the end of this section.

As is shown in Table 3 the concentration of ions associated with anthropogenic activity (i.e., SO_4^{2-}, NO_3^-, NH_4^+) are much lower at the Venezuelan sites than in rural areas of North America and Europe, and with the exception of NH_4^+ in Chaguarama, they are of the same order of magnitude as concentrations observed in "remote" continental rains (i.e., Northern Australia and Amazon forest). The relatively higher concentrations of NH_4^+ found in the Chaguarama rains are likely due to farming activity in this area.

The anions and cations that take part in the acid-base equilibrium in the Venezuelan savannah rainwater solution, are presented in Fig. 2. The results show that at Chaguarama, Joaquín del Tigre, Guri and La Paragua sites, dissociated organic acids (formate plus acetate) contribute with more than 50% to the acid anions equivalent. Organic acids were not measured in Parupa; however, from the ion concentrations (anions and cations that contribute to the acid-base equilibrium) (Table 2), it is possible to estimate that at this site, formic and acetic acids should also contribute with more than 50% to the acid-base equilibrium. The total water soluble organic carbon measured at this site, with a volume weighted average of 1.5 mg l^{-1} (TOC-Analyzer, Beckman Model 951A) indicates that rainwater is relatively loaded with organic compounds.

In Europe and North America, sulphuric and nitric acids, formed by the oxidation of anthropogenic SO_2 and NO_x, are the main contributors to the acid rain observed. As is shown in Fig. 2, in the Venezuelan savannah region, H_2SO_4 plus

Table 2. *Volume-weighted mean concentrations ($\mu eq/l$)*

Ion	Camburito $n = 18$[a]	La Paragua $n = 10$	J. del Tigre $n = 11$	Chaguarama $n = 11$	Guri $n = 9$	Parupa $n = 8$
pH	4.4	4.7	5.1	5.4	4.6	5.0
NO_3^-	13.5	3.2	3.67	4.64	2.68	2.34
$SO_4^=$	13.3	4.9	2.75	5.60	3.01	3.12[b]
SO_4^{*}[c]	9.09	4.4	2.06	4.62	2.85	2.81
Cl^-	50.1	7.7	9.90	11.8	3.45	7.19
Cl^*	9.07	3.2	3.2	2.35	1.90	4.05
PO_4^{3-}	0.58	<1.5	3.0	7.23	1.36	0.32
$HCOOH_T$	—	9.3	8.25	8.47	6.6	—
$HCOO^-$	—	8.4	7.90	8.27	5.89	—
CH_3COOH_T	—	9.5	8.5	7.8	4.31	—
CH_3COO^-	—	4.5	5.88	6.28	2.08	—
H^+	42.5	19.5	7.90	4.29	23.6	9.56
NH_4^+		<1.9	2.56	13.4	3.06	~6.70[d]
Na^+		3.5	5.51	8.14	1.34	2.71
K^+	9.35	1.1	1.30	7.24	0.26	1.11
K^*		1.03	1.18	7.07	0.23	1.05
Ca^{2+}	15.5	1.4	4.59	14.6	0.94	3.24
Ca^*		1.25	4.35	14.2	0.88	3.12
Mg^{2+}	3.19	0.9	2.46	4.01	0.48	1.56
Mg^*		0.11	1.21	2.17	0.25	0.94

[a] Number of events; [b] Determined by turbidimetry after 8 times preconcentration; [c] SO_4^*, Cl^*, K^* and Mg^* are the non-sea salt concentrations. [d] Estimated from analysis made with the Nessler reactant, recalibrated with the selective electrode.

Table 3. *Concentrations in rain of non-sea salt sulphate, nitrate and ammonium in various "rural" areas of the world (unit of $\mu eq\ l^{-1}$)*

	SO_4^*	NO_3^-	NH_4^+	Ref.
Venezuelan savannah[a]	2.1–4.6	2.3–4.6	1–13	Present work
Amazon Forest[b]	1–8.6	1–5.5	2–12	Andreae et al. (1988, 1990)
Jabiru, Australia	4.7	3.2	1.7	Gillett et al. (1990)
Katherine, Australia	4.0	3.6	2.9	Likens et al. (1987)
Northern Europe	69	31	31	Granat (1978)
Central Europe	90	39	—	Elbert and Andreae (1989)
Eastern North America	40–80	20–50	10–40	Stensland et al. (1986)
Western North America	6–75	2–23	12–20	Roth et al. (1985)

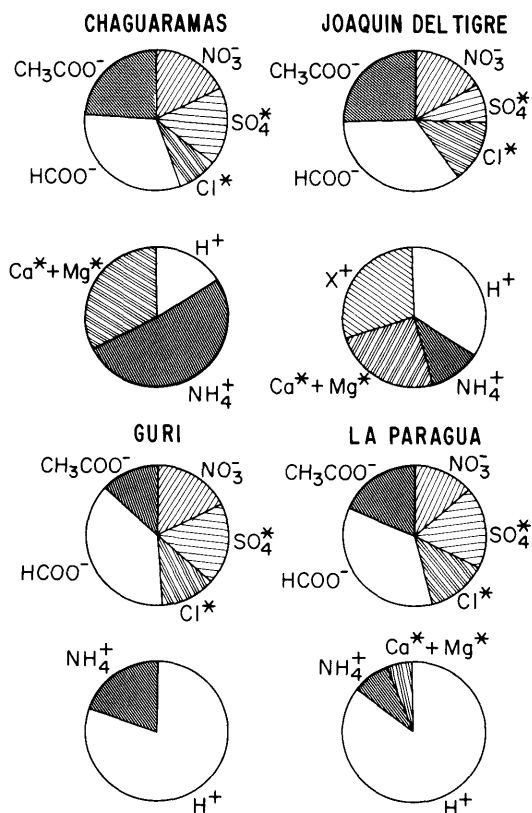[a] Camburito site is not included; [b] lower values are for the rainy season and larger values for the "dry" season.
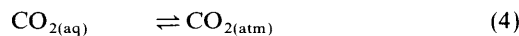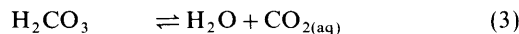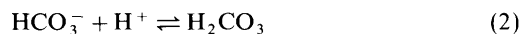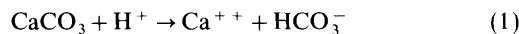
Fig. 2. Contributions (%) of acid anions and basic cations to the acid-base equilibrium in Chaguaramas, J. del Tigre, Guri and La Paragua sites.

HNO_3 only contribute less than 36% to the rain water acidity. Since, during non-burning periods most of the Venezuelan savannah region is unaffected by significant anthropogenic emissions (Sanhueza et al., 1988), the NO_3^- and SO_4^{2-} found in rain must be mostly produced through the oxidation of NO_x and reduced sulphur compounds emitted by natural sources. It is interesting to note that soil emissions of NO are highly variable from site to site in the Venezuelan savannah region; the NO soil emissions observed in Chaguaramas (Johansson et al., 1988; Johansson and Sanhueza, 1988) are around $10 \times$ larger than the emissions measured at Guri (Sanhueza et al., 1990). However, the NO_3^- concentrations in rain are quite similar (with a variation of less than a factor of 2 among sites), indicating that a good redistribution of NO_y must be produced in the atmosphere, or

that soil emission is not the main source of NO_y in the region.

Hydrochloric acid, measured as excess chloride in rain (Cl^*), represents a potential contribution to the free acidity that ranges between 9 and 14% (Fig. 2). Gaseous HCl is likely released from the reaction of seasalt aerosol with strong acids. The suspended particles in the atmosphere of the Venezuelan savannah region have a clear deficit of Cl^- that ranges between 0.5 and $1\ \mu g\ m^{-3}$ (Sanhueza and Rondón, 1988). It is still not known how the separation of HCl and HCl-depleted aerosols occurs; it is likely that HCl-depleted aerosols have a larger dry deposition velocity than HCl, and are therefore removed from the atmosphere faster than gaseous HCl (unpublished results).

As expected, NH_3 plays a significant role as a neutralizing compound; however, as is shown in Fig. 2, calcium or magnesium carbonate could also contribute to a reduction in the potential acidity of the rain solution. It is likely that the Ca* and Mg* found in rainfall is, in part, produced in the clouds by the following reactions:

$$CaCO_3 + H^+ \rightarrow Ca^{++} + HCO_3^- \qquad (1)$$

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \qquad (2)$$

$$H_2CO_3 \rightleftharpoons H_2O + CO_{2(aq)} \qquad (3)$$

$$CO_{2(aq)} \rightleftharpoons CO_{2(atm)} \qquad (4)$$

At $pH < 5$, reaction (2) is biased toward. the production of H_2CO_3 and CO_2 is released to the atmospheric through reactions (3) and (4).

Camburito-site. In comparison with the other sites, much higher concentrations of nitrate and sulphate were found at Camburito. Also, rainwater pH is the lowest in the Venezuelan savannah region (Table 2). Camburito is located downwind of the largest urban-industrial area of Venezuela (Caracas-Maracay-Valencia). The large anthropogenic emissions of NO_x and SO_2 in this region (Sanhueza et al., 1988) are probably oxidized to nitric and sulphuric acids during transport, producing acidification of the atmosphere. Therefore, in Venezuela, "regional" acid rain is already being produced by anthropogenic activity. It is important to evaluate the regional impact (natural ecosystems and agricultural lands) of this anthropogenic acidification. It is worth mentioning that

the concentrations of NO_3^- and SO_4^{2-} found in Camburito are significantly lower than the levels observed in rural North America and Europe (Table 3).

3.2. Formic and acetic acids

As we saw in Subsection 3.1, formic and acetic acids are major contributors to the rain acidity observed in the Venezuelan savannah region. This is in agreement with other measurements made in the tropics that show that precipitation acidity is dominated by HCOOH and CH_3COOH (Galloway et al., 1982; Keene and Galloway, 1986; Andreae et al., 1988; Ayers and Gillett, 1988; Sanhueza et al., 1989; Andreae et al., 1990; Gillett et al., 1990). The atmospheric sources of HCOOH and CH_3COOH in rain have not yet been properly identified. Likely sources include scavenging of gaseous acid by cloud or rain and in-cloud oxidation of aldehydes. Relatively large concentrations of gaseous HCOOH (1.3 ± 0.4 ppbv) and CH_3COOH (0.7 ± 0.3 ppbv) are present in the Venezuelan savannah atmosphere (Hartmann et al., 1991) and scavenging of these acids during rainfall could be a significant source of the formate and acetate ions found in the Venezuelan savannah rains. On the other hand, a statistically significant correlation between HCHO and HCOOH concentrations was found in Venezuelan rains (including the savannah region) (Sanhueza et al., 1991). The HCOOH/HCHO ratios found in heavy rains (> 10 mm) were close to one, in good agreement with predictions of theoretical models (Chameides and Davis, 1983; Jacob, 1986), suggesting that in cloud, oxidation of formaldehyde plays a major role in controlling the concentration of formic acid in tropical rains. As far as we know, acetic acid does not have a known source in cloud water.

In the literature, emphasis has been given to the high correlation of HCOOH and CH_3COOH in rainwater (Keene and Galloway, 1986 and 1988). A correlation also exist in our savannah rains, with an overall average of 2.07 ± 0.7 ($n = 45$), quite similar to the value of 2.25 calculated with data from several sites across the world (Keene and Galloway, 1988). However, a detailed analysis of our savannah data shows that a significant trend exists between the HCOOH/CH_3COOH ratios and the amount of rainfall; if we only consider heavy rain events (i.e., larger than 8 mm), we

obtain a HCOOH/CH_3COOH ratio of 1.2 ± 0.67 ($n = 19$). It is interesting to note that the ratio (calculated with the volume-weighted average, to avoid, in part, the bias produced by small showers) during the rainy season in the Amazon forest is 1.40 (Andreae et al., 1990). Therefore, since for pH's between 4.6 and 5.4, formic acid is more soluble than acetic acid (Winiwarter et al., 1988) and higher gas-phase concentrations of HCOOH are present in the savannah atmosphere (Hartmann et al., 1991), it is likely that below-cloud scavenging during rainfall biases the HCOOH/CH_3COOH ratios to higher values.

Assuming that HCOOH and CH_3COOH recorded in rains are representative of cloud-water conditions, and that the gas and the liquid phase concentrations are in equilibrium, the predicted gas phase concentrations in the cloud layer air, calculated from the pseudo Henry's Law constant (Winiwarter et al., 1988):

$$A_{aq}/A_{gas} = K_H^* = K_H(1 + K_a/[H^+])$$

are much lower than the levels measured in the boundary layer of the Venezuelan savannah (Hartmann et al., 1991). Therefore, it is likely that the HCOOH and CH_3COOH found in the savannah rain are the result of the following processes: (i) in-cloud scavenging of both acids followed by their fast consumption of OH radicals in the aqueous phase, and (ii) below-cloud scavenging of gaseous acids (whose contribution is relatively greater during light rains). In the case of HCOOH, however, in-cloud oxidation of formaldehyde seems to play a significant (perhaps a major) role in controlling the concentration of formic acid in tropical rains (Sanhueza et al., 1991).

3.3. Chemical composition of rain during vegetation burning

The first rains of the season, towards the end of the dry period, when vegetation burning still occurs throughout the savannah region, are heavily loaded with several compounds. The concentration ratios between burning and non-burning periods (BP/NBP) are given in Table 4. Clearly, the atmospheric budget of water-soluble ions is enhanced during the burning period. These results are consistent with the higher concentrations of water-soluble ions observed in the airborne particles

Table 4. *Burning to non-burning periods ion concentration ratios*

Ion	La Paragua	J. del Tigre	Chaguaramas	Guri
NO_3^-	4.6	2.8	3.5	7.4
SO_4^{2-}	2.6	1.1	3.6	8.9
$SO_4^{*\,a)}$	2.3	—	3.7	9.1
Cl^-	7.4	9.6	2.9	14.7
PO_4^{3-}	17.2	4.5	~ 1	~ 1
$HCOOH_T$	3.2	3.7	5.5	3.8
CH_3COOH_T	2.0	0.20	4.4	4.0
H^+	0.14	2.6	2.3	0.95
NH_4^+	63	3.8	6.1	13.9
Na^+	6.9	8.5	3.2	—
K^+	8.8	11.3	1.2	—
Ca^{2+}	16.5	3.2	2.1	—
Mg^{2+}	10.6	5.2	3.1	—

[a)] SO_4^* is the non-sea salt sulphate.

during vegetation burning periods (Sanhueza and Rondón, 1988). It is likely that a large proportion of these ions are incorporated in the rainwater by below-cloud scavenging processes. NO_3^-, SO_4^{2-}, and NH_4^+ must be produced in the atmosphere as final products of reactions of NO_x, SO_2, and NH_3 emitted during burning. Primary emissions of K^+ and Ca^{2+} (mainly as fine particles) seem to be produced in the fires. It is not clear whether, phosphate is directly emitted by fires or formed in the atmosphere from the oxidation of a reduced phosphorous compound (Sanhueza and Rondón, 1988).

Higher concentrations of HCOOH and CH_3COOH were observed during burning periods. According to Talbot et al., (1988), biomass burning emits $10 \times$ more acetic than formic acid; however, the ratio of formic to acetic acid in the Venezuelan savannah rains during burning periods is larger than 1. Therefore, it seems that the relative amount of these acids in rain is controlled by atmospheric processes, rather than by direct emission from fires. A good correlation has been observed between HCHO and HCOOH in Venezuelan rains (Sanhueza et al., 1991), suggesting that the increase of HCOOH is mainly related to a larger concentration of HCHO during this period, whose in-cloud oxidation produced formic acid (Chameides and Davis, 1983; Jacob, 1986; Lelieveld and Crutzen, 1990). Madronich and Calvert (1990) suggested that peroxy radical permutation reactions could be a significant source of gaseous formic and acetic acids. Since,

during vegetation burning, the reactivity of the savannah atmosphere is enhanced (Sanhueza, 1990), the production of peroxy radicals should increase and a larger production of organic acid is expected.

No significant difference is observed in the rain acidity between both periods. The greater formation of HNO_3 and H_2SO_4 from photo-oxidation of NO_x and SO_2 emitted by the fires, seems to be over-compensated by a large direct emission of NH_3; i.e., NH_4^+/SO_4^* ratios in the rainy season range between 0.22 and 2.9, whereas during burning periods, larger ratios are measured, ranging from 1.6 to 6.0. As in the case of the rainy season, free acidity is dominated by organic acids. It is interesting to note that our results contrast with the results obtained in the Ecuatorial forest of Africa (Lacaux et al., 1990), where an increase of rain acidity has been observed during upwind savannah fires. It is likely that in the present case (savannah rains), primary emissions from fires predominate, and the impact of the formation of secondary inorganic and organic acids is relatively less important than in downwind forest rains.

4. Conclusions

The chemical composition of rain recorded in Chaguarama, J. del Tigre, Guri, La Paragua and Parupa shows that with only few exceptions, the concentration of the majority of the ions (i.e.,

NO_3^-, $SO_4^=$, $HCOO^-$, CH_3COO^-, NH_4^+ and K^+) is very homogeneous in most of the Venezuelan savannah region. This suggests that primary or secondary sources are relatively well distributed. A comparison with the chemical composition of rains in Europe and North America indicates that savannah rains are little affected by anthropogenic emissions, and that they are of the same order as concentrations observed in "remote" continental sites.

The rain is acidic with average pH's ranging from 4.4 to 5.4; around 60% of the free acidity is due to formic and acetic acids, and 40% to sulphuric, nitric and hydrochloric acids. Ammonia plays a significant rôle as neutralizing compound; Ca and Mg carbonates may also, in some cases, reduce the acidity of the rain solution. Atmospheric reactions of NO_x, reduced sulphur compounds and ammonia naturally emitted should be the main sources of NO_3^-, $SO_4^=$ and NH_4^+, respectively. Gaseous HCl is likely released from the reaction of sea salt aerosol with strong acids and then incorporated to the rain solution. The concentration of HCOOH and CH_3COOH is most likely the results of chemical reactions in cloud droplets (i.e., oxidation of HCHO to produce HCOOH) and scavenging of the gaseous acids by rain processes.

At the Camburito site, located downwind of the largest urban-industrial area of Venezuela, the rain-water pH is the lowest in the region and higher concentrations of nitrate and sulphate were recorded. This indicates that acidification of rain by anthropogenic activities is already being produced in part of the Venezuelan savannah region.

The first rains of the season, towards the end of the dry season, when vegetation burning still occurs throughout the savannah region, are heavily loaded with several compounds. Primary emissions from fires (i.e., K^+ and Ca^{2+}), and secondary production (i.e., NO_3^-, NH_4^+, $SO_4^=$, $HCOO^-$ and CH_3COO^-) from gases emitted during burning explain the higher concentrations observed. Compared with the non-burning period, no significant variation in rain acidity was observed; it is likely that the larger atmospheric photochemical formation of inorganic and organic acids during burning is neutralized by a large primary emission of NH_3.

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