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SHORT CONTRIBUTION

Rainfall pH in the Venezuelan savannah

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ABSTRACT

The pH of rainfall samples collected by event were measured at three sites in the Venezuelan Savannah. The volume-weighted average pH values at Camburito, Joaquín del Tigre and La Paragua were 4.4, 5.1 and 4.8, respectively. These low pH values are in agreement with the reported values for other rural areas of tropical America.

1. Introduction

Due to anthropogenic acid rain production, measurements of rain pH have been intensively carried out in the industrial regions of the world. However, very little information exists for rural developing regions.

In general, rural areas of tropical America are little affected by industrial air pollution, and rainfall pH should be, mainly, controlled by natural factors (Sanhueza, 1985). At present, only a few measurements of rain pH have been made in the different ecosystems of tropical America.

1.1. Rain forest sites

(i) During the period 1966 to 1968, 53 rain samples were collected in the city of Manaus, giving an arithmetic mean pH of 4.6 (Anonymous, 1972). It is possible that the acidity of these samples was affected by local activities; however, in the same work, 2 samples were measured in the forest-reserve Adolfo Ducke, 20 km from Manaus, with an average pH even lower of 4.38.

(ii) In 1973, samples collected at La Selva, Costa Rica, ranged from 4.40 to 4.90 with an arithmetic mean of 4.66 (Johnson et al., 1979). It is important to point out that during the study, the site was affected by SO_2 emissions from the Volcano Irazu. Unfortunately, the authors do not report the $SO_4^=$ excess, and the contribution of H_2SO_4 to the free H^+ cannot be estimated.

(iii) In 1977 to 1978, during a trip along the Orinoco River, 31 samples were taken by Stallard and Edmond (1981); the pH ranged from 4.70 to 5.70 with an arithmetic mean of 5.03.

(iv) More recently, two groups reported values for San Carlos de Río Negro, Venezuela; Haines et al. (1983) got a volume-weighted mean of 4.7 for 70 rain events (range 4.0 to 6.7), and Galloway et al. (1982) for 19 events obtained a volume-weighted mean of 4.8 (range 4.0 to 5.4).

1.2. Cloud forest sites

(i) Steinhardt and Fassberger (1979) measured the pH of rain at San Eusebio (Estado Mérida), a cloud forest of the Venezuelan Andes region; pH ranged from 3.82 to 6.21 with an arithmetic mean of 4.55.

(ii) Núñez (1983) reported pH values of bulk precipitation at Altos de Pipe, Estado Miranda, Venezuela, with an arithmetic mean of 5.03 (19 samples ranging from 4.21 to 5.90). However, this cloud forest is near Caracas and the atmospheric depositions are affected (as was shown by the high $SO_4^=$ excess deposition rate) by nearby anthropogenic emissions.

1.3. Savannah sites

The only values reported for a savannah site correspond to bulk deposition samples collected at Calabozo, Venezuela (Montes et al., 1985). The volume-weighted mean pH's reported were 5.8, 5.6 and 5.8 for 1981, 1982 and 1983, respectively.

Therefore, with the exception of values given by Montes et al. (1985) for a savannah site, rainfall pH in rural sites of tropical America is around or below 5.0. In the present paper, in samples strictly collected by events, rainfall pH values are reported for three sites of the Venezuelan savannah.

2. Field measurements

As part of a research program oriented at characterizing the Venezuelan environment in relation to acidification processes, rainfall samples were collected during 1984 and 1985 at three savannah-sites. The map of Fig. 1 shows the area of Venezuela that is covered by savannah and indicates the position of the sampling sites: Camburito (Estado Portuguesa), Joaquín del Tigre (Estado Monagas) and La Paragua (Estado Bolivar). These sites are not affected by significant local (50 km) anthopogenic source of air pollution. However at the end of the dry season, the three sites are affected by the emissions produced by vegetation burning.

All year around, the prevailing wind directions in the Venezuelan savannah are NE and ENE (northeast trades) (F.A.V., 1984); therefore with the exception of Camburito, which is more-or-less down-wind ($\sim$150 km) of the emissions of the Caracas-Maracay-Valencia area source, the other two sites are not affected by important upwind sources of air pollution.

The sample-collector units consist of a large plexiglass funnel, with a collecting area of 0.25 m^2, mounted 2 m from the surface, and a 2 l polyethylene bottle connected to the funnel by a 30 cm latex tubing. The system was kept closed and completely dry during the dry period, and was opened at the beginning of a rainfall event. All the material was prepared in the laboratory following the directions given by Galloway and Likens (1976, 1978). After each rain, the collectors were rinsed with distilled-deionized water, dried with cellulose filter paper and then a new bottle was connected. Several blanks were

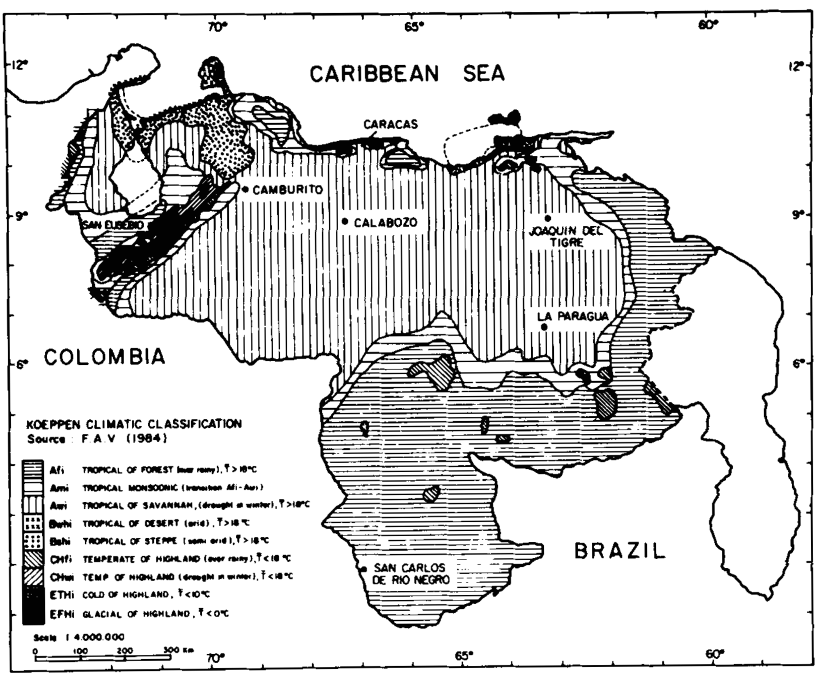

Fig. 1. Climatic regions of Venezuela and locations of monitoring sites.

Table 1. *Rainfall pH at three sites of the Venezuela savannah*

Site	Period	No. of events	pH Range	pH Volume-weighted average
Camburito (end 1983 wet season)	Nov.–Dec. 1983	6	4.0–4.8	4.3
Camburito (end 1984 dry season)	April/84	2	4.0–4.5	4.2
Camburito (1984 wet season)	May–August 1984	10	4.2–5.2	4.4
Camburito (total)	Nov./83–August/84	18	4.0–5.2	4.4
Joaquín del Tigre (1985 dry season)	Feb./84	1	5.3	5.3
Joaquín del Tigre (1985 wet season)	June–Sept. 1985	16	4.2–5.8	5.1
Joaquín del Tigre (total)	Feb.–Sept. 1985	17	4.2–5.8	5.1
La Paragua (end 1985 dry season)	April/85	2	5.3–5.6	5.6
La Paragua (1985 wet season)	Oct.–Nov. 1985	12	4.0–5.0	4.7
La Paragua (total)	April–Nov. 1985	14	4.0–5.6	4.8

performed, in the laboratory and at the field sites, to check that the collector does not change the pH of the dionized water.

The pH of rain water were measured, within 2 hours of the end of the rain event, with a Metrohm (Model E-250), a Fisher Accumet (Model 320) and a Beckman (Model 4500) pH meter in Camburito, Joaquín del Tigre and La Paragua, respectively. The pH meters were calibrated with standard buffer solution, from Fisher or Beckman, of pH 4.01 and pH 7.41, before and after each measurement. A fraction of the samples was preserved with chloroform (Galloway and Likens, 1978; Galloway et al., 1982) and transported to our central laboratory, where independent pH measurements were carried out, giving similar pH values to those obtained at the field sites.

At Camburito, the sampling was from November 1983 to July 1984. No attempt was made to collect all the events, but rather few of them were in the best clean condition. Every month the sample-collector was replaced by a new one, prepared at the central laboratory. One-week field trips were carried out in February, June, August and September, 1985, to the Joaquín del Tigre site. Two one-month field trips to La Paragua were carried out first during the dry period from 26 March to 26 April 1985, and second, in the rainy season from 8 October to 8 November 1985. At Joaquín del Tigre and La Paragua all the rain events that occurred during the field work, were collected.

3. Results and discussion

Table 1 summarizes the results. The values show that at the three sites, the pH values are similar to those reported by most authors for other sites in tropical America cited in the introduction.

The results show that our samples were around ten times more acidic than those reported for Calabozo by Montes et al. (1985) (see Fig. 1 for location). We think that the difference must be due to the contribution of dry deposition to the bulk precipitation samples collected by these authors (Montes et al., 1985). Even during the rainy season, the savannah region is relatively dry and windy, and the contribution of dry deposition to the total (bulk) deposition is important (i.e., at Camburito, 60% of total Ca^{++} deposition was produced by dry processes, calculated from the total depositions less the only wet depositions (Graterol, 1984)).

Considering that the Joaquín del Tigre and La Paragua sites, and most of the savannah region are relatively free of anthropogenic air pollution different from vegetation burning that occurs at the end of the dry season (Sanhueza, 1986), the low pH observed at those sites should be mainly from natural origin. According to Charlson and Rodhe (1982), "natural factors exist which can cause variable and significant decrease of pH from that expected from pure carbonic acid equilibrium". These authors theoretically estimated the possible contribution of H_2SO_4 from the natural portion of the sulphur cycle to produce rain pH ranging from 4.5 to 5.6. On the other hand, detailed analysis of the chemical composition of rain samples collected at remote areas of the world (Galloway et al., 1982; Keene et al., 1983; Galloway, 1985) shows that much of the acidity is contributed to by weak organic acid. The source of these organic acids is not known yet, but is most likely to be of natural origin.

At present, no further speculations will be made to explain which acids (and their origin) are responsible for the low pH observed in the Venezuelan savannah rainfall. We hope in the future, based on the emission inventory of the region and the chemical composition of atmospheric suspended particles and rainfall, to be able to answer these questions.

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