

SHORT CONTRIBUTION

pH of bulk precipitation during 3 consecutive annual courses in the Trachypogon savannas of the Orinoco Llanos, Venezuela

By R. MONTES, *Departamento de Estudios Ambientales, Universidad Simón Bolívar, Apdo. 80659, Caracas 108, Venezuela*, J. J. SAN JOSÉ, J. GARCIA-MIRAGAYA, *Centro de Ecología, Instituto Venezolano de Investigaciones Científicas, Apdo. 1827, Caracas 101, Venezuela* and N. PARRA, *Estación Biológica de los Llanos, Sociedad Venezolana de Ciencias Naturales, Apdo. 5, Edo. Guárico, Venezuela*

(Manuscript received December 20, 1984; in final form August 21, 1985)

ABSTRACT

Bulk precipitation was daily collected and individual pH measured at the Trachypogon savannas, Venezuela, over a consecutive 3-year period. The volume-weighted mean pH as calculated, were 5.8, 5.6 and 5.8 for 1981, 1982 and 1983, respectively. The annual variation of pH ranged from 4.9 to 6.9; 4.8 to 6.3 and 5.4 to 6.8 units in 1981, 1982 and 1983, respectively. However, in this savanna area, which is relatively remote from heavy sources of industrial pollution, the annual proportion of daily rains with pH < 5.0, occurring mainly at the onset and end of the wet season, were 2.0, 3.0 and 0.0% for 1981, 1982 and 1983, respectively.

1. Introduction

Lowland Trachypogon savannas are a major ecosystem of northern South America, traditionally used for stock-raising activities (San José et al., 1985). Studies on photosynthetic functions of these savannas (San José and García-Miragaya, 1981) indicate the presence of strong environmental constraints, some referred to physical and chemical soil characteristics. Special emphasis has been laid on rainwater as an alternative source of mineral nutrients for this ecosystem.

A serious potential drawback has recently arisen as a result of the intensive petroleum activities carried out in the Trachypogon savannas, where the petroleum belt covers an area of 82,000 km² (25 % of the total area) of the Orinoco Llanos. As a result, studies on the environmental impact of these activities are now in course, with special attention paid to the acidity of precipitation, as previously reported for similar situations (ESSO Resources Canada Limited, 1979).

The present study involves daily measurements of precipitation pH in the Trachypogon savannas of the Orinoco Llanos, for 3 consecutive years. At present, the selected location is relatively remote from sources of heavy industrial pollution (~200 km to the nearest main industrial area).

2. Material and methods

A permanent plot (1 ha) was located at the Biological Station of the Plains (8°56'N; 67°25'W), at Calabozo, Venezuela (Blydenstein, 1962).

Rain was collected with polypropylene collector-devices designed as follows: a 2 l polypropylene bottle (NALGENE), 21.0 cm high, was cut 5.0 cm from the top. This portion was used as a funnel (9.0 cm Φ) and attached to the remaining 16 cm of the bottle to form a collector device. The neck of the funnel was stopped with a plug of glass wool to prevent the passage of large particles. 3 of these polypropylene devices were placed in an open field,

on posts 1.60 m above the surface of the grass and spaced at 10 m intervals, delimiting the vertices of an equilateral triangle. A standard rainwater gauge was placed in the centre of the same.

The containers were kept open throughout the study period and due to the low durability of the material under the savanna climate, they were changed twice; midway during the wet season and at the beginning of the following wet season. pH was measured in a suspension formed by rain and dry fallout; a mixture referred to as bulk precipitation (Whitehead and Feth, 1964), which was collected and measured in each of the 3 polypropylene collectors, on every rainy day from May 1981 to November 1983. In order to prevent build-up of a microbial coating on the walls of the vessels, these were scrupulously washed after each sampling, with iso-propyl alcohol, followed by 3 portions, 200 ml each, of distilled water. In addition, the glass wool plug was changed after each sampling, with no apparent effect on pH measurements, according to the laboratory test.

Daily, the 3 collected samples were taken to the laboratory, stirred, and on quiescent conditions, pH was measured in each (meter Broadley J. Corp. Model 5, accuracy ± 0.05 pH units) using an Ag-AgCl glass electrode. Before and after each set of measurements, the pH meter was standardized with pH 4.0 and pH 7.0 reference buffer solutions (Orion Research Inc.) and with a primary reference standard solution of acetic acid. It was also periodically checked with another pH meter, with 2 different pH electrodes (Orion Research model 20-digital with accuracy of ± 0.01 units). Quality control evaluations were performed with standard solutions poured into the collector and subsequently analysed.

Volume weight mean pH (VWMpH) of the three samples, was expressed as a concentration (μMl^{-1}) by weighted mean, after applying the equation:

$$\text{VWMpH} = \frac{\sum (H^+)(\text{vol})}{\sum (\text{vol})},$$

where: $H^+ = \mu\text{Ml}^{-1}$ of H^+ in the rain event; vol = volume of rainwater per event. The averaged values were then reconverted to pH units and these data were used for cyclical trends using Noether's (1956) test, a free distribution non-parametric test.

Precision was obtained by repeating the pH measurements on each of the 3 containers in field conditions, and accuracy was evaluated with the

dilute acetic acid solution of known concentration. The pH results indicate a precision and accuracy of less than $\pm 10\%$.

3. Results and discussion

During the measuring period (from May 1981 to the end of 1983), volume and pH of 453 rain samples (3 individual samples taken on each of the 151 rainy days) were measured in a Trachypogon savanna at the Orinoco Llanos. There were 74 days in which the precipitation volume was below 0.5 mm, and therefore pH measurements were impractical. Total annual precipitation for 1981, 1982 and 1983 was 1185, 1124 and 1380 mm, respectively. Rains were seasonally distributed between April and October (Fig. 1).

According to Noether's (1956) test, pH of the bulk precipitation, measured during the study period, did not show a cyclical trend ($P_{(2)} = 0.28$ at $\alpha = 0.05$). In addition, Pearson's correlation between daily precipitation pH and rain volume during the 3 consecutive years was not significant ($r = 0.03$) as calculated according to Conover (1980). The volume-weighted mean pH (VWMpH) of bulk precipitation, varied within and between years (Fig. 1). Thus, the annual VWMpH of bulk precipitation was more acidic during 1982 (pH = 5.6) than in 1981 (pH = 5.8) or 1983 (pH = 5.8).

Even though there is scarce global information on the natural pH of precipitation, a pH < 5.0 seems to be an indicator of the lower limits of the natural mean pH of precipitation (Galloway et al., 1982). Therefore, according to this pH reference value, the total number of rains in the Trachypogon savannas with pH < 5.0 was 2, 3 and 0% in 1981, 1982 and 1983, respectively. Nevertheless, although pH values within the years ranged from 6.9 (July 9) to 4.9 (October 27) in 1981; 6.3 (June 18) to 4.8 (April 6) in 1982 and 6.8 (May 26) to 5.4 (April 18) in 1983, a comparison between the VWMpH values obtained at the Trachypogon savanna and the information available for other Venezuelan areas, indicates that the acidity of the rains analysed in the present paper, was less than that reported for the cloud forest at Carbonera Mérida, ranging from 3.8 to 6.2 units of pH with an average of 4.6 (Steinhart and Fassbender, 1979); Lake Valencia basin, ranging from 3.5 to 7.0 units in 2

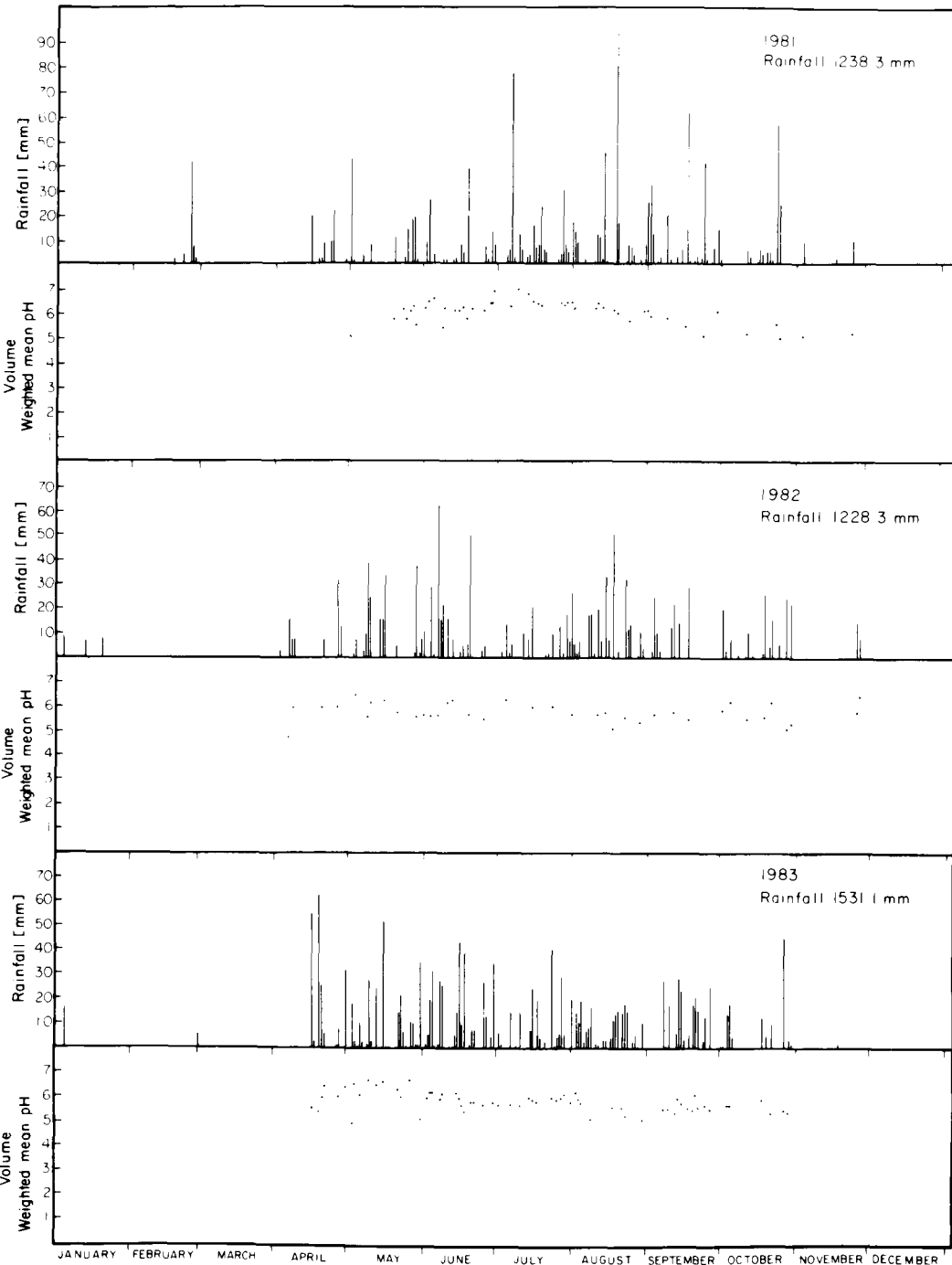


Fig. 1. Rainfall and volume-weighted mean pH in the Trachypogon savannas of the Orinoco Llanos, Venezuela.

years (no average was reported in this work) (Lewis and Weibezahn, 1981) and San Carlos de Rio Negro, Amazon Territory, from 4.0 to 6.7 and an average of 4.7 (Haines et al., 1983). Furthermore, the range of annual pH variation was also lower (1.6 units) in the Trachypogon savannas as

compared with the previously-mentioned localities (2.4 units in Carbonera; 3.5 units of Lake Valencia basin and 2.7 units in the Amazon Territory).

The high pH values found in this study are a possible indicator that carbonic acid, in equilibrium with the dissolved CO_2 , the latter released either by natural processes or burning of the vegetation, may be the major source of H^+ . In addition, neutralizing agents such as ammonia (Montes et al., unpublished data) could also be important. On the other hand, rains with $\text{pH} < 5.0$ may be a result of local vegetation burning, mainly at the onset of the wet season, producing an increase in the loading rate of nitrogen oxides, which in solution become nitric acid, a major source of hydrogen ions (Montes et al., unpublished data). This was also reported by Lewis and Weibezahn (1981) and Lewis (1981), for the Lake Valencia basin. Other possible sources are weak organic acids (Galloway et al., 1982; Keene et al., 1983; Keene and Galloway, 1984); locally

recycling biological processes (Alexander, 1977) and atmospheric pollution (Prospero, 1979).

Finally, long-term studies of this nature should be carried out in the Trachypogon savannas with the purpose of detecting changes in acidity and chemical composition of rainwater before and after petroleum exploration begins in the "bituminous oil belt" of the Orinoco River. This becomes a priority when we consider the fact that this ecosystem develops on oligotrophic acid soils.

4. Acknowledgements

We are grateful to Dr. L. Labouriau for his challenging ideas and to Dr. Omar Arenas for his suggestions on the statistical test. The work was carried out during the tenure of a "Consejo Nacional de Investigaciones Científicas y Tecnológicas Grant" (CONICT-Venezuela-SIDF.DC. FORT-1-EBLL).

REFERENCES

- Alexander, M. 1977. *Introduction of soil microbiology*, 2nd edition. Wiley & Sons, New York.
- Blydenstein, J. 1962. The Trachypogon savannas at the high Llanos. *Bol. Soc. Venez. Cienc. Nat.* 23, 139–206 (in Spanish).
- Conover, W. J. 1980. *Practical nonparametric statistics*, 2nd edition. Wiley & Sons, New York.
- Esso Resources Canada Ltd, 1979. Cold Lake Project. Final environmental impact assessment. Vol. II. *Biophys. Res. Impact Assessment*, Canada, 416 pp.
- Galloway, J. N., Likens, G. E., Keene, W. C. and Miller, J. M. 1982. The composition of precipitation in remote areas of the world. *J. Geophys. Res.* 87, 8771–8786.
- Haines, B., Jordan, C., Clark, H. and Clark, K. E. 1983. Acid rain in an Amazon rain forest. *Tellus* 35B, 77–80.
- Keene, W. C., Galloway, J. N. and Holden Jr. J. D. 1983. Measurement of weak organic acidity in precipitation from remote areas of the world. *J. Geophys. Res.* 98, 5122–5130.
- Keene, W. C. and Galloway, J. N. 1984. Organic acidity in precipitation of North America. *Atmos. Environ.* 18, 2491–2497.
- Lewis, W. M. Jr. 1981. Precipitation chemistry and nutrient loading by precipitation in a tropical watershed. *Water Resour. Res.* 17, 169–181.
- Lewis, W. M. Jr. and Weibezahn, F. H. 1981. Acid rain and major seasonal variation of hydrogen ion loading in a tropical watershed. *Acta. Cient. Venez.* 32, 236–238.
- Noether, G. E. 1956. Two sequential tests against trends. *Amer. Stat. Assoc. J.* 51, 440–450.
- Prospero, J. M. 1979. Mineral and sea salt aerosol concentrations in various ocean regions. *J. Geophys. Res.* 84, 725–731.
- San Jose, J. J. and Garcia-Miragaya, J. 1981. Operational factors on the organic matter production of the Trachypogon savannas. *Bol. Soc. Venez. Cienc. Nat.* 139, 347–374 (in Spanish).
- San Jose, J. J., Montes, R., Garcia-Miragaya, J. and Orihuela, B. 1985. Bio-production of Trachypogon savannas in a latitudinal cross-section of the Orinoco Llanos, Venezuela. *Oecol. Gener.* 6, 25–43.
- Steinhardt, U. and Fassbender, H. W. 1979. Chemical composition of the precipitation at the Venezuelan Western Andes. *Turrialba* 29, 175–182 (in Spanish).
- Whitehead, H. G. and Feth, J. H. 1964. Chemical composition of rain, dry fallout and bulk precipitation at Menlo Park, California, 1957–1959. *J. Geophys. Res.* 69, 3319–3333.