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CHEMICAL COMPOSITION OF RAINFALL AT SELECTED SITES IN PUERTO RICO

Open-File Report 75-364

Prepared in cooperation with the
Commonwealth of Puerto Rico

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By Ferdinand Quiñones-Márquez

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ABSTRACT

Chemical analyses of rainfall were made for major constituents in samples collected at about monthly intervals from 1963 to 1967 from four locations in Puerto Rico. Mean values and other statistics were computed for chloride, bicarbonate, and calcium, which are the major ions in the rainfall. Mean values for chloride, bicarbonate, and calcium range from 2.8 to 5.0 milligrams per litre, 4.3 to 11 milligrams per litre, and 1.0 to 1.8 milligrams per litre, respectively. There is a higher concentration of dissolved solids during the dry season than during the wet season. Poor correlation ($r = 0.20$) was found between the amount of rainfall and its specific conductance. The data show that there is a general decrease in the dissolved-solids concentration in rainfall from east to west across the island.

The ions present in rainfall contribute significantly to the quality of surface waters. Computations in two basins show that virtually all the chlorides in streamflow may be supplied from rainfall. Contributions from rainfall range from 7 to 15 percent for calcium, and from 16 to 63 percent for magnesium. Sulfate contributions from rainfall range from 54 to 62 percent of the streamflow outputs.

INTRODUCTION

The presence and importance of dissolved solids in rainfall have been demonstrated by Egner and others (1949), Gorham (1955), and Gambell and Fisher (1966) among other investigators. Most of the investigations have covered continental areas where the influence of oceanic salts have been minimal. This report presents data on the chemical composition of rainfall and its contribution to the quality of surface waters in Puerto Rico.

For use of those readers who may prefer to use metric units rather than English units, the conversion factors for the terms used in this report are listed on the following page:

Multiply English unit	By	To obtain metric unit
inches (in)	25.40	millimetres (mm)
feet (ft)	0.3048	metres (m)
miles (mi)	1.609	kilometres (km)
cubic feet per second (ft^3/s) . . .	0.02832	cubic metres per second (m^3/s)
tons(short, 2,000 lbs) .	0.9072	tonnes (t)

Study Area and Rainfall-Sampling Network

A project for the collection and quantitative determination of some constituents in rainfall was started in 1963 by the U.S. Geological Survey with the establishment of four rainfall collection sites in Puerto Rico (fig. 1). No attempt was made to obtain island-wide coverage. The collection sites were determined largely by the availability of collaborating unpaid observers near established National Weather Service rain gages. Two sites were near the coast but far enough inland so as not to be affected by direct sea spray, and two sites were on the north slope of the mountainous backbone of the island.

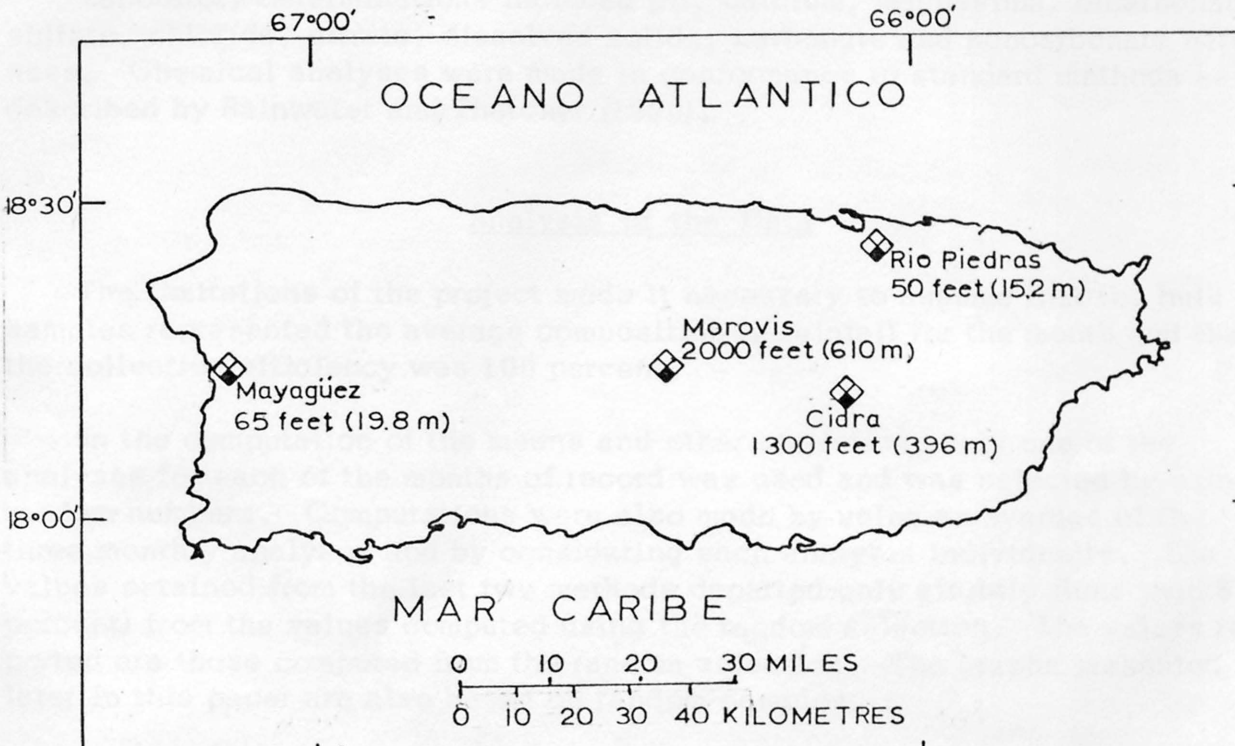

Figure 1.--Location and altitude of rainfall-collection stations.

Collection Apparatus and Sampling Methods

The rain collector used at each of the sampling sites consisted of three plastic funnels; each drained into a polyethylene bottle. The bottles were enclosed in a wooden box to minimize contamination and to reduce evaporation losses. A cotton swab in the stem of the funnel acted as a filter against foreign material.

The samples were collected at the end of each month. The rain collectors provided for a catch of three samples at each station. The purpose of three samples was to check reproducibility of results, by making analysis of the individual samples. Generally, good reproducibility was obtained; however, one or two samples only were obtained some months due to various operating difficulties. Monthly rainfall records were obtained from the National Weather Service rain gages located near the sampling stations.

Analytical Methods

Laboratory determinations included pH, calcium, magnesium, bicarbonate, sulfate, chloride, nitrate, dissolved solids, carbonate and noncarbonate hardness. Chemical analyses were made in conformance to standard methods as described by Rainwater and Thatcher (1960).

Analysis of the Data

The limitations of the project made it necessary to assume that the bulk samples represented the average composition of rainfall for the month and that the collection efficiency was 100 percent.

In the computation of the means and other statistics, only one of the analyses for each of the months of record was used and was selected by using random numbers. Computations were also made by using an average of the three monthly analyses and by considering each analysis individually. The values obtained from the last two methods departed only slightly (less than 5 percent) from the values computed using the random selection. The values reported are those computed from the random selection. The graphs presented later in this paper are also based on random samples.

CONCENTRATION OF DISSOLVED SOLIDS

Climatological Factors

The concentration of some of the dissolved solids in rainfall over Puerto Rico is affected by the prevailing winds. Colón (1958) described in detail the wind pattern along the North Coast of Puerto Rico. At an elevation of about 5,000 ft (1,520 m), winds from the northeast to southeast quadrants predominate from 70 to 95 percent of the time. Winds at this elevation are representative of the low level circulation, resulting in an easterly wind most of the time. Thermal differences between the land and the sea generate a wind component that fluctuates diurnally. During the day, when the land is warmer, the air over it rises, generating a surface wind from the ocean. The opposite occurs during the night, when the land cools at a faster rate than the ocean. The combination of both air currents results in a northeast-wind pattern, about 80 percent of the time (Colón, 1970). The action of the wind on the surface of the ocean transports minute droplets of sea water. These remain suspended in the air, permeating dusts and other particles and moving inland, carried by the wind. The solids contained in the droplets and particles are eventually washed from the atmosphere by rainfall (Clarke, 1959). The concentration of the dissolved solids in the catch may be affected by the amount of rainfall (as suggested in fig. 2) and the distance along the pathway of the prevailing winds.

The relationship of specific conductance to the amount of rainfall at Río Piedras is shown in figure 2. Considerable scatter is shown and the correlation was found to be poor ($r = 0.20$). It is probable that a more detailed sampling program, designed to collect individual samples for storms of different intensity and duration, would produce a better correlation.

Mean Values and Other Statistics

Mean values, standard deviations, and extremes for the parameters determined in the samples are shown in table 1. High variance and nonnormality of the data are indicated.

The concentrations of calcium, magnesium, and dissolved solids in the samples collected at Río Piedras generally are higher than those at the other stations. Mean concentrations of chloride are lower at Mayaguez than at any of the other stations. Pearson and Fisher (1971) have suggested that wind-borne dusts are the source of bicarbonates in rainfall samples.

Except for the samples collected at Río Piedras, the mean pH of the samples collected at the other stations are similar. The variations in pH could be a result of the length of time the samples were stored before analysis.

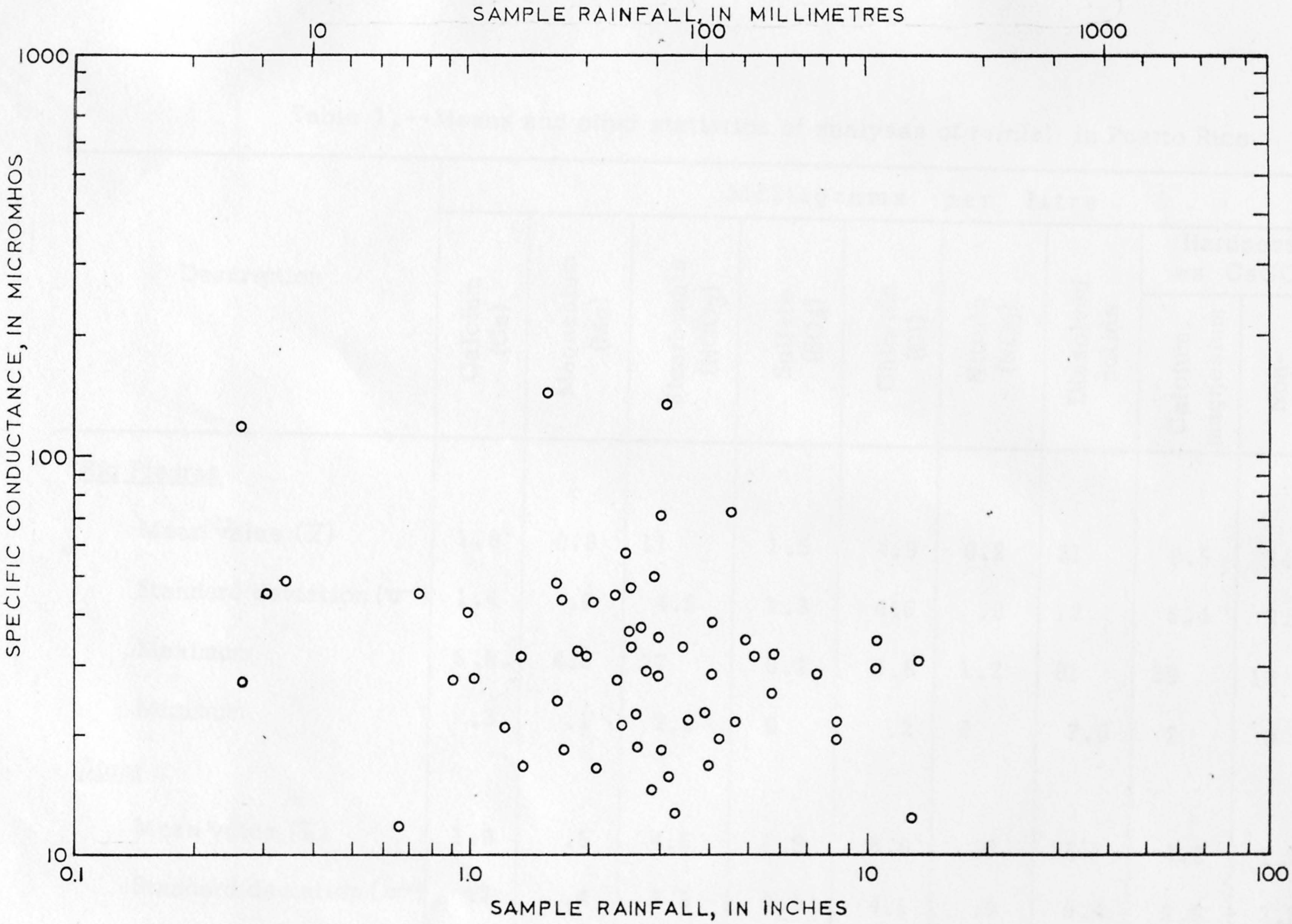

Figure 2.--Specific conductance versus rainfall at Río Piedras.

Table 1.--Means and other statistics of analyses of rainfall in Puerto Rico

Description	Milligrams per litre									pH
	Calcium (Ca)	Magnesium (Mg)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Nitrate (NO_3)	Dissolved solids	Hardness as $CaCO_3$		
								Calcium, magnesium	Non-carbonate	
Río Piedras										
Mean value ($\overline{x}$)	1.8	0.8	11	1.5	4.9	0.2	21	8.5	1.0	6.8
Standard deviation (σ)	1.4	.6	4.5	1.3	4.6	.8	12	5.4	2.2	.4
Maximum	6.5	4.6	27	5.2	9.8	1.2	81	29	13	7.6
Minimum	.3	.1	2.0	0	.2	0	7.0	2	0	5.7
Cidra										
Mean value ($\overline{x}$)	1.0	.5	4.5	1.8	5.0	.6	15	4.2	1.3	6.0
Standard deviation (σ)	.7	.4	2.5	2.0	4.1	.9	9.4	2.6	2.5	.6
Maximum	3.2	2.2	15	5.6	10	3.4	37	14	7.2	7.3
Minimum	.2	0	2.0	0	1.0	0	6.0	1.0	0	5.4

Table 1.--Means and other statistics of analyses of rainfall in Puerto Rico--Continued

Description	Milligrams per litre									pH
	Calcium (Ca)	Magnesium (Mg)	Bicarbonate (HCO_3)	Sulfate (SO_4)	Chloride (Cl)	Nitrate (NO_3)	Dissolved solids	Hardness as $CaCO_3$: Calcium, magnesium	Hardness as $CaCO_3$: Non-carbonate	
Morovis										
Mean value ($\overline{x}$)	1.2	0.6	4.7	1.8	4.5	0.5	18	5.4	1.8	6.1
Standard deviation (σ)	.7	.5	2.1	1.7	3.1	.9	10	2.9	2.3	.6
Maximum	3.2	1.9	11	8.4	12	5.8	45	16	7.7	7.1
Minimum	0	0	2.0	0	1.0	0	5.0	2.0	0	4.8
Mayagüez										
Mean value ($\overline{x}$)	1.5	.5	4.3	2.5	2.8	.6	12	5.7	2.4	6.1
Standard deviation (σ)	.9	.4	1.6	1.9	1.6	.7	9.0	3.0	2.4	.6
Maximum	3.6	1.4	8.0	8.0	7.4	3.2	39	11	8.7	7.5
Minimum	0	0	2.0	0	.2	0	4.0	2.0	0	5.2

Variability of Dissolved Solids

The variability of the concentration of dissolved solids is shown in figure 3. The concentration-duration curves, in addition to indicating the range of values obtained, define a grouping of the components. The values for Río Piedras in general are higher than those for the other stations. The lower values for the other sites could be due to the distance and time involved in the movement of clouds away from the contributing ocean surface. By the time the clouds are carried across the island, the variability has been smoothed out either by previous scrubbing action or by mixing of droplets containing different concentrations of solids.

The concentration of dissolved solids in rainfall varies seasonally. During the dry months, usually December through March, the concentration of solids in the atmosphere increases. Light showers dissolve relatively large amounts of these solids. As the amount of rainfall increases during the wet months, the available solids in the atmosphere decrease and a lower concentration is observed. Figures 4a, b, c, and d illustrate seasonal change in the dissolved-solids concentration at the four stations.

CONTRIBUTIONS OF IONS IN RAINFALL TO THE QUALITY OF SURFACE WATERS

The ions present in rainfall contribute significantly to the quality of the surface water. To assess the magnitude of the contribution, a computation was made of the average annual-rainfall input and streamflow output of calcium, magnesium, chloride and sulfate for the upper Río Grande de Manatí and the Río Lajas basins (fig. 5). The computations were based on the mean concentration of the ions in rainfall and in streamflow (fig. 6). A long-term mean annual rainfall of 80 in (2,030 mm) was used for both basins (Colón, 1970). Average annual runoff of 126 ft^3/s (3.57 m^3/s) and 14.9 ft^3/s (0.42 m^3/s) were used for the Río Grande de Manatí and the Río Lajas basins, respectively. Because the upper basins of the streams are close to one another, the assumption was made that a similar concentration of the ions in rainfall was present over both basins and that the rainfall-sampling site at Cidra was representative of both. The Cidra site was chosen as representative because it is intermediate in elevation, as compared to the Río Piedras and Morovis sites. Unlike the Río Piedras station, it is free of the influence of urban emissions. Except for calcium, mean values at the Cidra site are close to those at the Morovis station.

The data in figure 6 reflect several important features relative to both basins. A significant percentage of the streamflow discharges of the major ions may be supplied from rainfall. For the Río Grande de Manatí basin (above

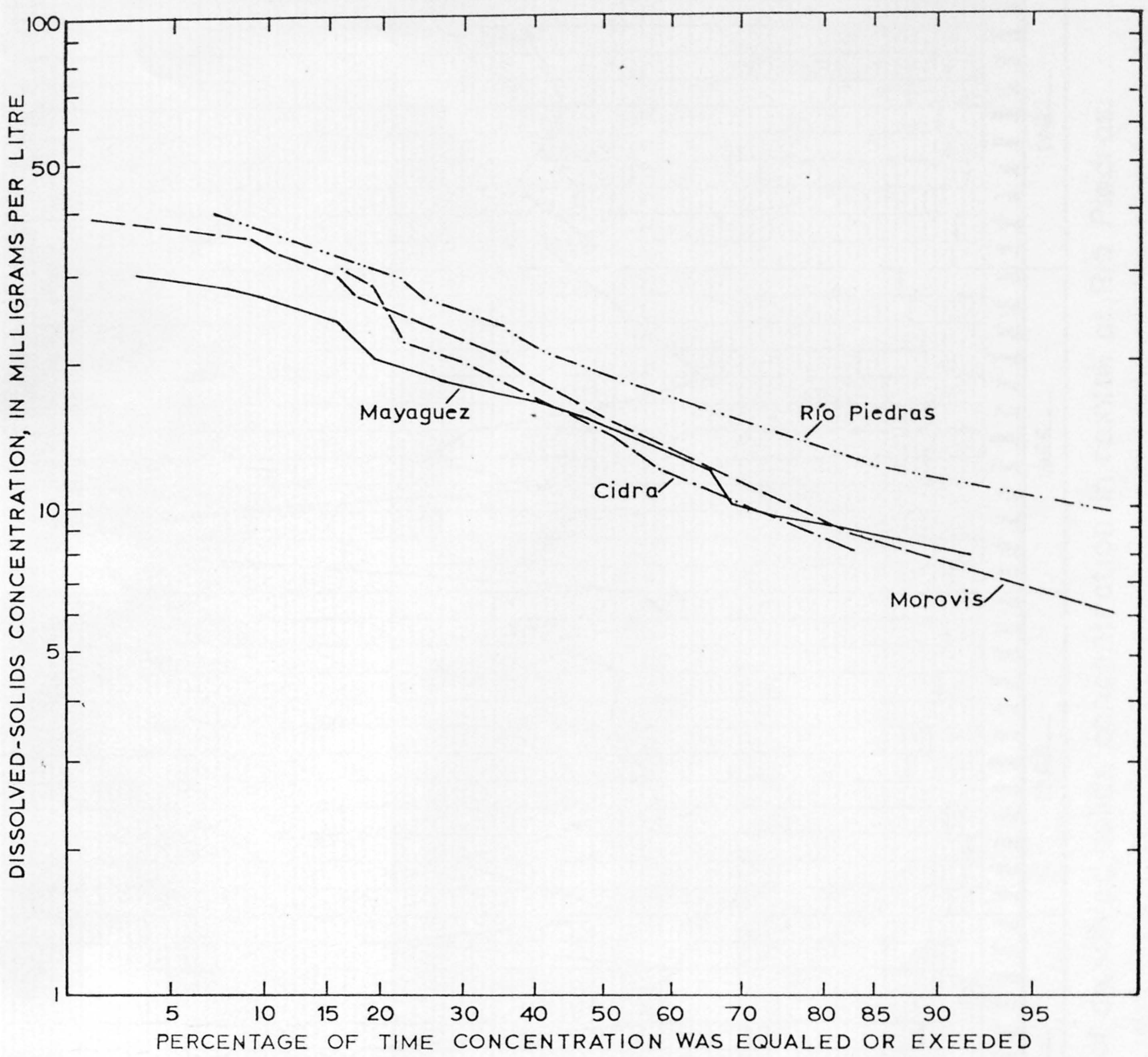

Figure 3.--Duration curves of dissolved-solids concentration in rainfall.

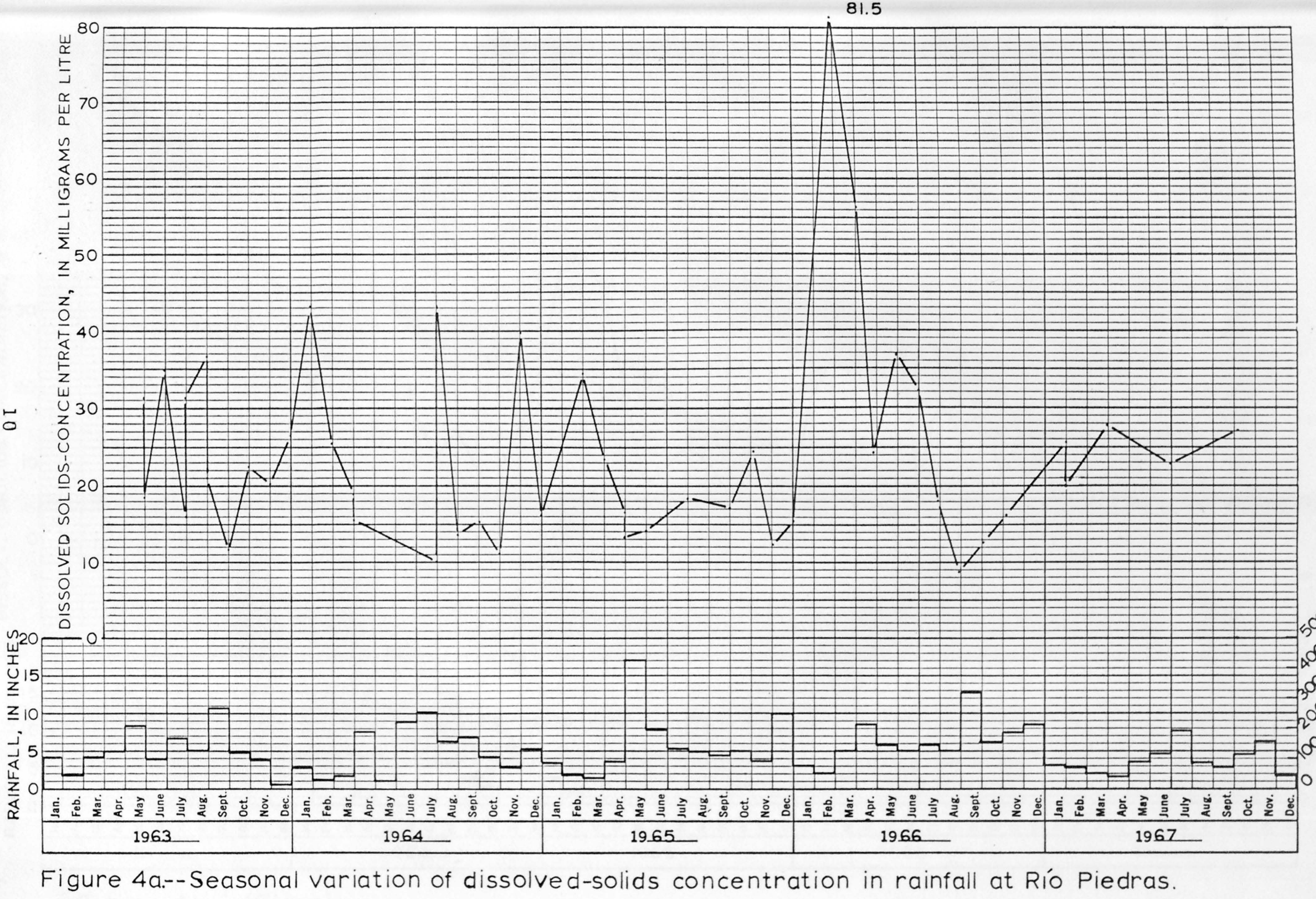

Figure 4a.--Seasonal variation of dissolved-solids concentration in rainfall at Río Piedras.

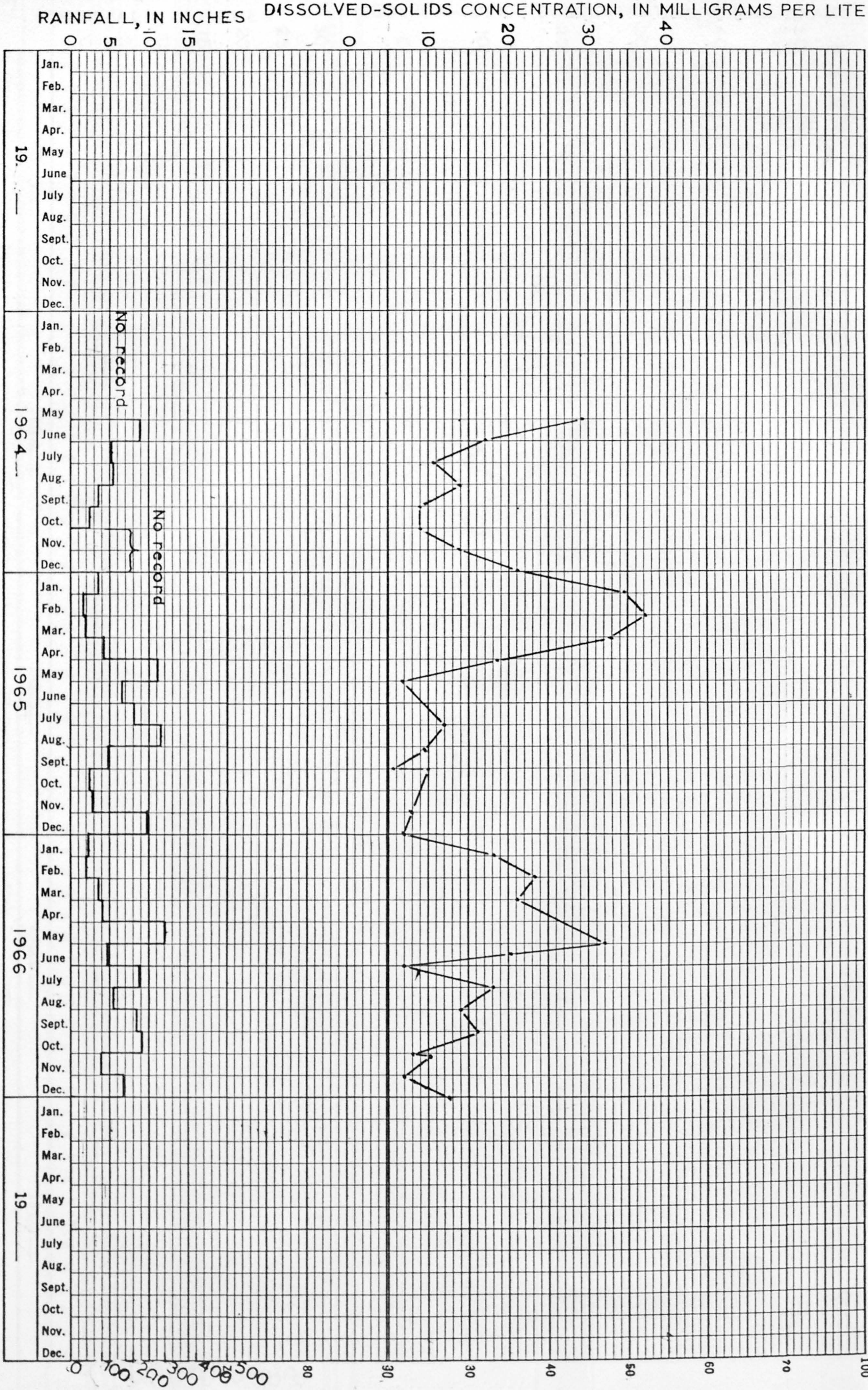

Figure 4b.--(Cidra)

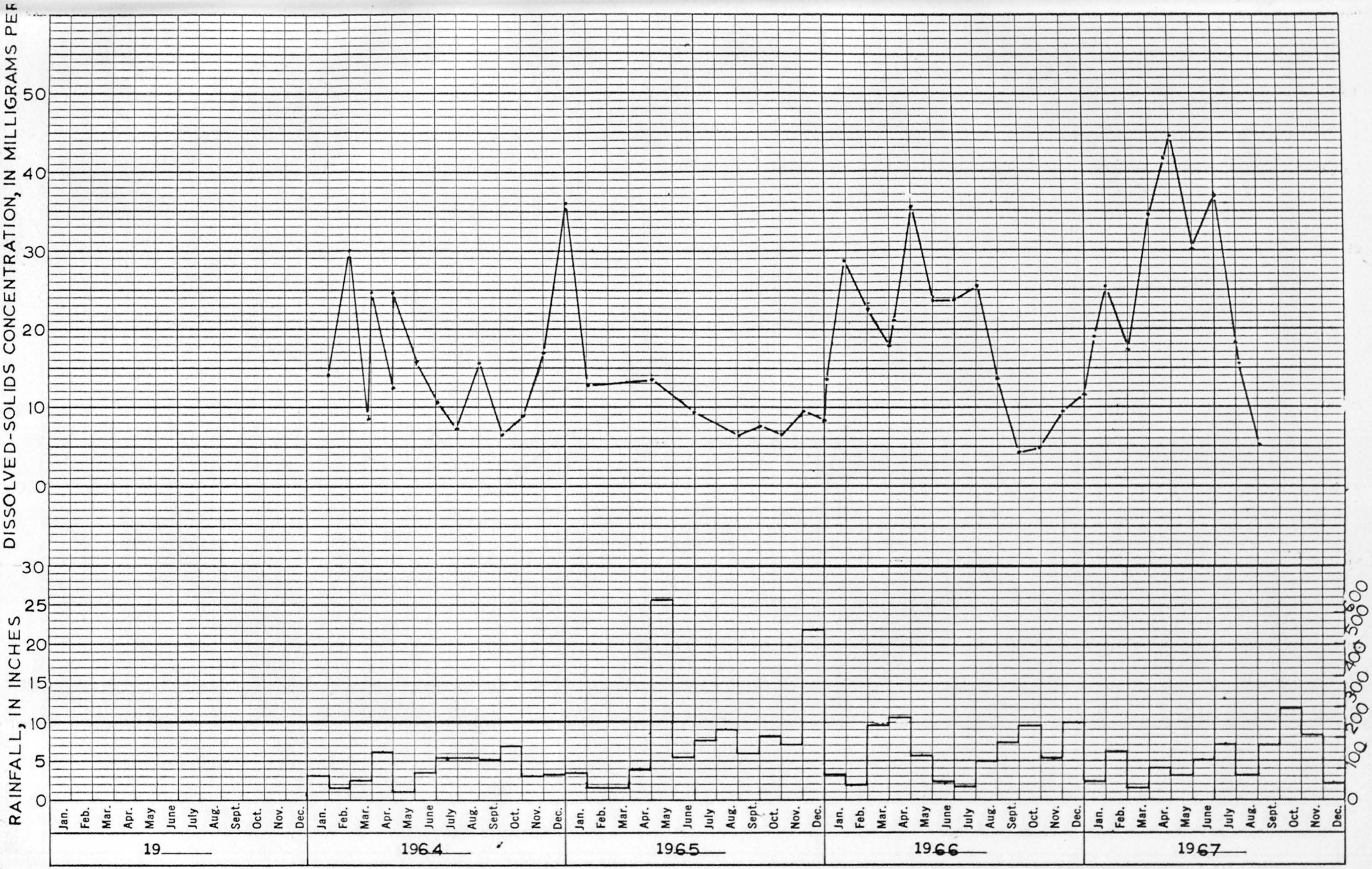

Figure 4c.--(Morovis)

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Figure 4d.--(Mayaguez)

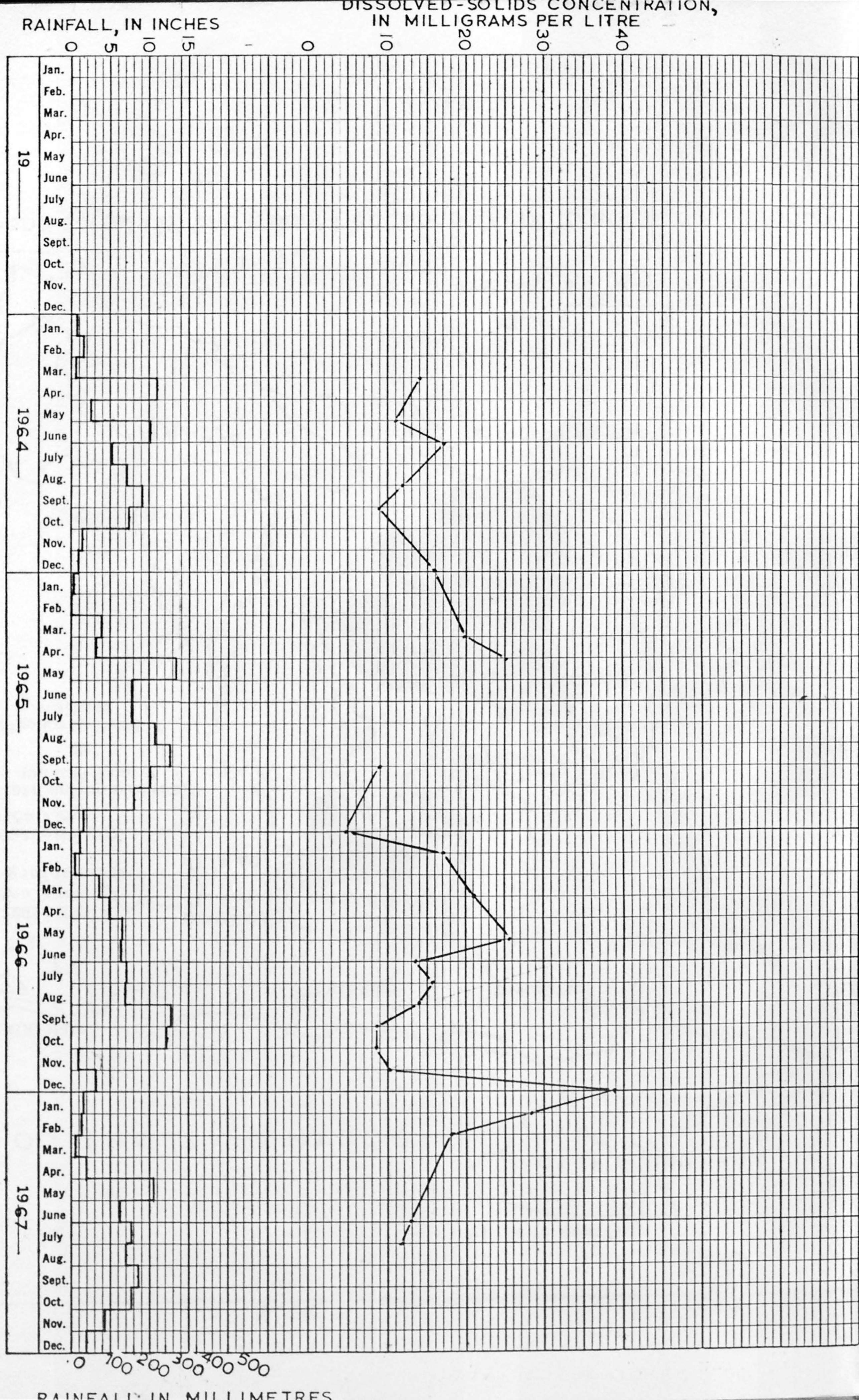

Figure 5.--Location of Río Grande de Manatí and Río Lajas basins.

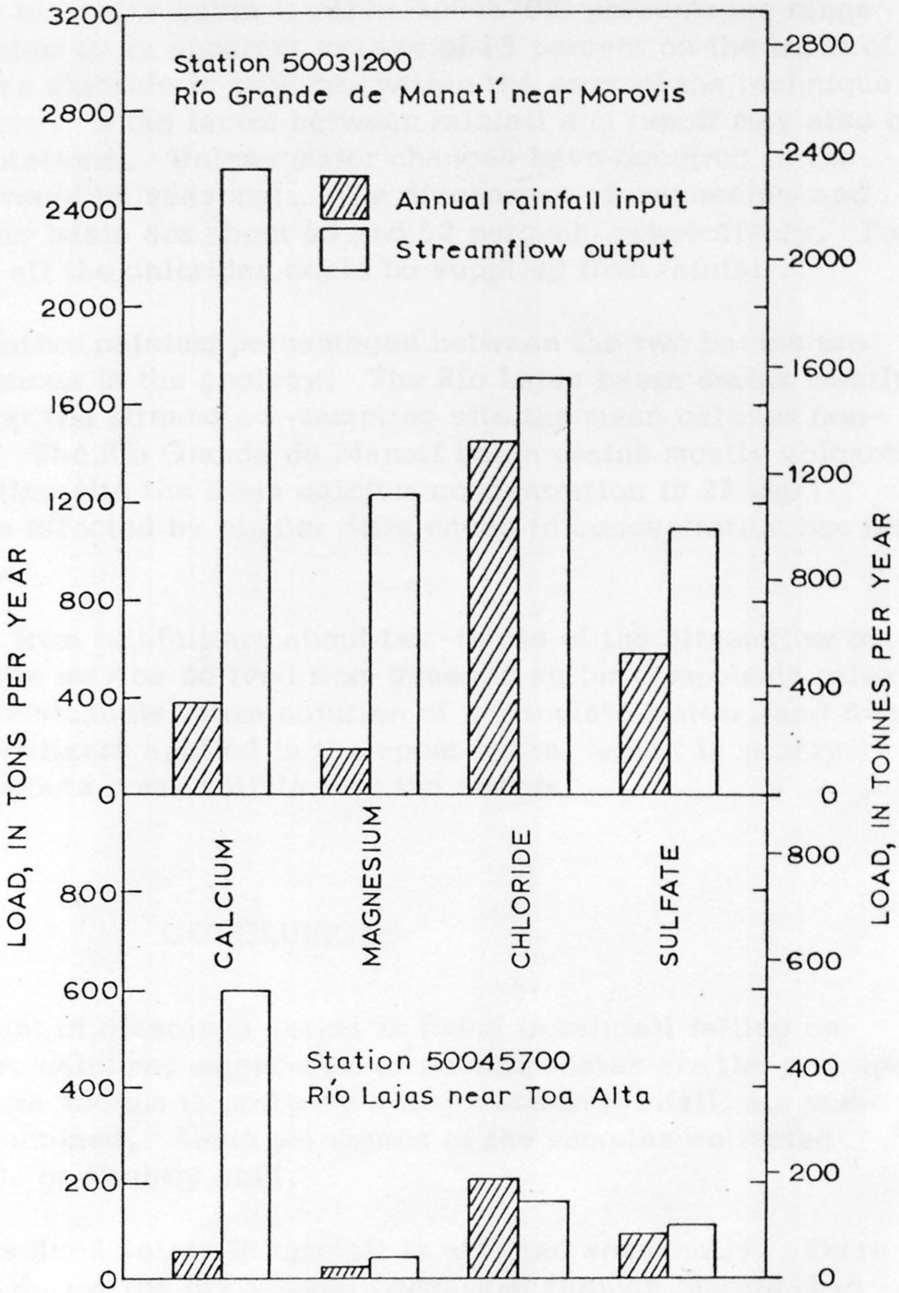

Figure 6.--Annual rainfall input and streamflow output of ions at stream-gaging stations 50031200 and 50045700.

station 50031200) percentages range from 15 percent for calcium to 85 percent for chloride. Magnesium and sulfate discharges are about 16 and 54 percent, respectively. For the Río Lajas basin (station 50045700) percentages range from 7 percent for calcium to an apparent excess of 19 percent on the input of chlorides. This excess chloride is probably within the error of the technique used in the computations. A lag factor between rainfall and runoff may also be reflected by the computations. Unless major changes have occurred in the basin, the lag factor would be seasonal. The discharges of magnesium and sulfate for the Río Lajas basin are about 63 and 62 percent, respectively. For both basins, virtually all the chlorides could be supplied from rainfall.

Differences in relative calcium percentages between the two basins are probably due to differences in the geology. The Río Lajas basin drains mostly limestone terrane and at the streamflow-sampling site the mean calcium concentration is 78 mg/l. The Río Grande de Manatí basin drains mostly volcanic rocks and at the sampling site the mean calcium concentration is 21 mg/l. Magnesium outputs are affected by similar differences in concentration because of geological features.

Sulfate ions input from rainfall are about two-thirds of the streamflow output. In rainfall, sulfate may be derived from gaseous sulfur compounds released in the combustion of fossil fuels, from solution of particulate matter, and from oceanic aerosols. Fertilizers applied in the upper basin, which is mainly agricultural, may contribute some sulfate into the stream.

CONCLUSIONS

A significant amount of dissolved solids is found in rainfall falling on Puerto Rico. Chloride, calcium, magnesium and bicarbonates are the principal ions detected. Although sodium is probably a major ion in rainfall, its concentration was not determined. Mean pH values of the samples collected ranged from 6.0 to 6.8, or slightly acid.

The amount of dissolved solids in rainfall is affected seasonally. There is a higher concentration during the dry season (December through March) than during the wet season (August through November).

The samples collected at the four sites suggest that the dissolved-solids concentration generally decreases with distance from the eastern end of the island in the direction of the prevailing winds.

The contribution of ions in rainfall to the quality of surface waters is significant. Computations from two separate basins show that virtually all the chloride discharged in streamflow could be supplied from precipitation. Calcium and magnesium inputs, as compared to streamflow discharges, range from 7 to 15 percent for calcium to 16 to 63 percent for magnesium. Sulfate discharges, in rainfall, range from 54 to 62 percent of the discharge in streamflow.

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