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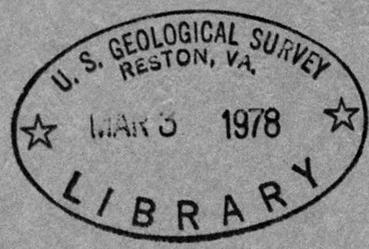
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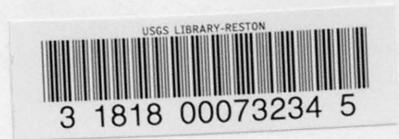
SELECTED CHEMICAL PROPERTIES OF RAINFALL
IN THE RIO PIEDRAS BASIN, PUERTO RICO

Open-File Report 78-159

Prepared in cooperation with the
Commonwealth of Puerto Rico



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SELECTED CHEMICAL PROPERTIES OF RAINFALL
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By Ferdinand Quiñones-Márquez

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Prepared in cooperation with the
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San Juan, Puerto Rico

1978

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SELECTED CHEMICAL PROPERTIES OF RAINFALL

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ABSTRACT

Determinations were made of some of the principal ions, pH, and specific conductance in rainfall samples collected in the Río Piedras urbanization area, Puerto Rico, during 1972-73. Calcium and chloride were two of the principal ions in the samples. Mean calcium concentrations ranged from 2.0 to 9.6 milligrams per liter, while mean chloride concentrations ranged from 2.6 to 6.6 milligrams per liter. Most of the samples were slightly acidic ranging in pH from a median of 6.5 to 7.0. A correlation ($r = -0.52$) was found between the specific conductance and the amount of rainfall (5 percent level of significance). The chloride concentration decreases with increasing distance from the ocean in the direction of the prevailing winds, as shown from a significant correlation ($r = -0.90$). About 240 metric tons of calcium, 200 metric tons of chloride, and 128 metric tons of sodium were contributed from rainfall over the basin during 1972. These loads would contribute a maximum of 6.9 milligrams per liter of calcium, 5.8 milligrams per liter of chloride, and 3.7 milligrams per liter of sodium to the average runoff of the lower basin, assuming no retention of these ions in the soil.

INTRODUCTION

The contribution of ions in rainfall to the quality of surface water can be important. Investigations by Junge (1958), Fisher (1968), Pearson and Fisher (1971), among others, have shown that a large percentage of certain ions in surface runoff may be contributed from rainfall.

In 1970, the U. S. Geological Survey in cooperation with the Commonwealth of Puerto Rico, started a detailed study of the hydrology and water quality of the Río Piedras basin. The water quality part of the study, initiated in 1972, included the collection and analyses of samples of rainfall. The purpose of this aspect of the study was to determine the principal chemical and physical characteristics of rainfall over the basin and the chemical loads contributed from certain ions.

Rainfall samples were collected from June 1972 to January 1973 and chemical analyses were made of calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^+), chloride (Cl^-), and potassium (K^+). Determinations were also made of the pH and specific conductance in all the samples.

DESCRIPTION OF THE AREA AND SAMPLING NETWORK

The Río Piedras basin (fig. 1) is a highly urbanized district of metropolitan San Juan. The basin, which has an area of about 63.1 km^2 consists of a gently sloping plain near the coast with a moderately hilly area in the southern part. The basin is densely populated. Most of the population live in single dwelling units, which together with the roads and other structures, cover a large portion of the surface area. Intense storms develop in the upper hills, and as a result of the large impervious area, extensive flooding occurs in the lower basin (Haire and others, 1972).

Rainfall sampling sites were located as shown in figure 1. Automatic digital recorders were used to record the amount of rainfall. The rainfall collector was located on top of the shelter that housed the recorders. The collector drained through plastic tubing into a plastic pipe. A float system connected to the recorder was used to measure the amount of rainfall in the pipe. The samples were collected from the pipe through a drainage port or by use of a small hand pump. There were no adjustments for dry fallout, although the samples were filtered through a cotton plug to remove large size particles of debris. The chemical analyses were performed within 2 weeks after collection of the sample, although most of the pH and specific conductance determinations were made immediately upon arrival of the sample to the laboratory. All analyses were performed in accordance with methods described by Brown and others (1970).

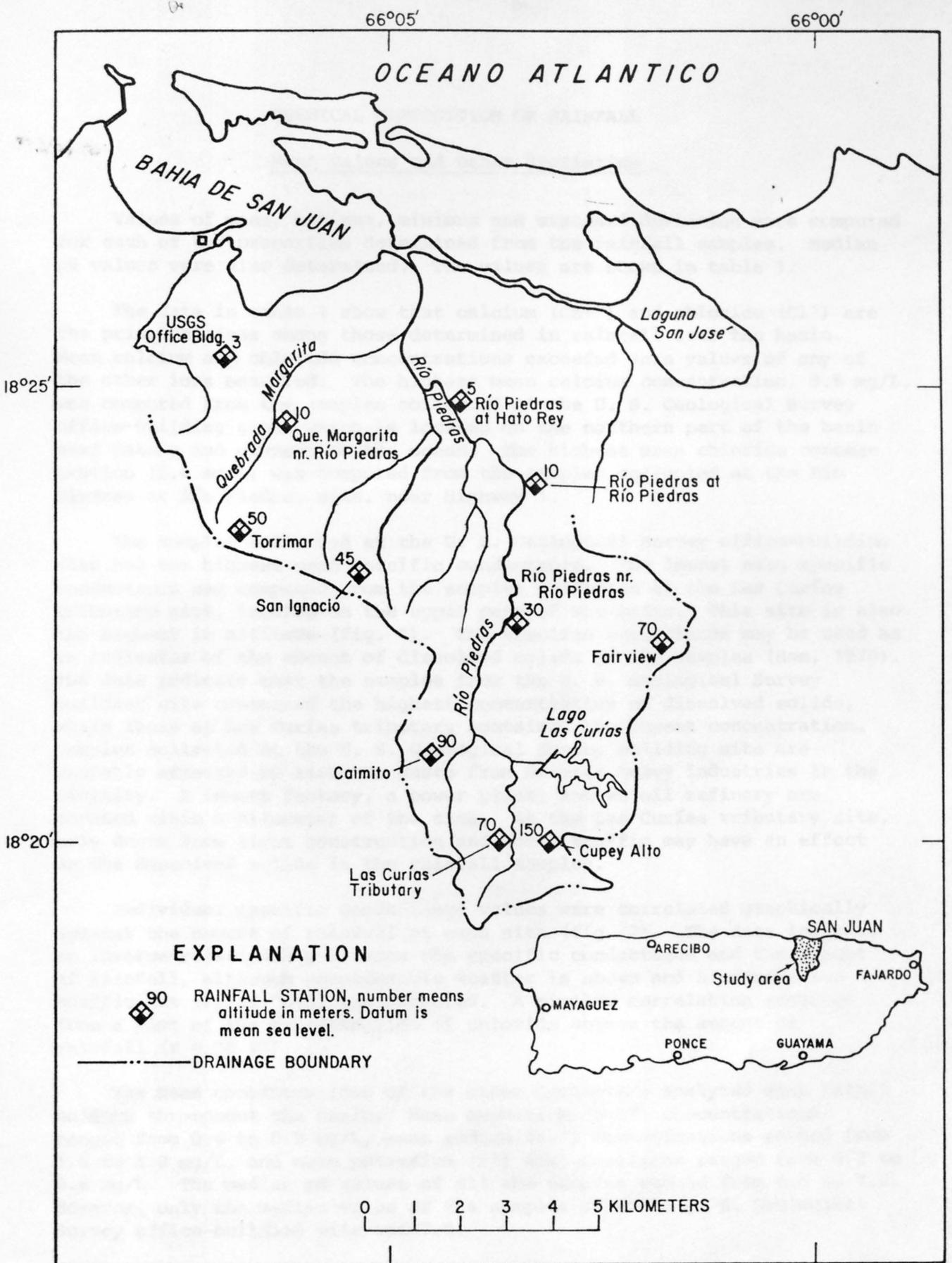


Figure 1.--Study area and sampling network.

CHEMICAL COMPOSITION OF RAINFALL

Mean Values and Other Statistics

Values of mean, maximum, minimum and standard deviation were computed for each of the properties determined from the rainfall samples. Median pH values were also determined. The values are shown in table 1.

The data in table 1 show that calcium (Ca^{++}) and chloride (Cl^-) are the principal ions among those determined in rainfall over the basin. Mean calcium and chloride concentrations exceeded mean values of any of the other ions measured. The highest mean calcium concentration, 9.6 mg/L, was computed from the samples collected at the U. S. Geological Survey office-building site, which is located on the northern part of the basin near Cataño and closest to the ocean. The highest mean chloride concentration (6.6 mg/L) was computed from the samples collected at the Río Piedras at Río Piedras site, near Highway 1.

The samples collected at the U. S. Geological Survey office-building site had the highest mean specific conductance. The lowest mean specific conductance was computed from the samples collected at the Las Curías tributary site, located on the upper part of the basin. This site is also the highest in altitude (fig. 1). The specific conductance may be used as an indicator of the amount of dissolved solids in the samples (Hem, 1970). The data indicate that the samples from the U. S. Geological Survey building site contained the highest concentration of dissolved solids, while those at Las Curías tributary contained the lowest concentration. Samples collected at the U. S. Geological Survey building site are probably affected by airborne dusts from several heavy industries in the vicinity. A cement factory, a power plant, and an oil refinery are located within a kilometer of the site. At the Las Curías tributary site, only dusts from light construction and local traffic may have an effect on the dissolved solids in the rainfall samples.

Individual specific conductance values were correlated graphically against the amount of rainfall at each site (fig. 2). The data indicate an inverse relationship between the specific conductance and the amount of rainfall, although considerable scatter is shown and a correlation coefficient (r) of -0.52 was computed. A similar correlation resulted from a plot of the concentration of chloride versus the amount of rainfall ($r = -0.42$).

The mean concentrations of the other parameters analyzed were fairly uniform throughout the basin. Mean magnesium (Mg^{++}) concentrations ranged from 0.4 to 0.9 mg/L, mean sodium (Na^+) concentrations ranged from 1.6 to 3.0 mg/L, and mean potassium (K^+) concentrations ranged from 0.2 to 0.8 mg/L. The median pH values of all the samples ranged from 6.5 to 7.0. However, only the median value of the samples from the U. S. Geological Survey office-building site was 7.0.

Table 1.--Mean values (median value for pH) and other statistics from analyses of rainfall samples in the Río Piedras basin, Puerto Rico.

All analyses in milligrams per liter, except for pH (units) and specific conductance (micromhos per centimeter at 25°C). Samples collected from June 1972 to January 1973.

| Site | Statistics | Calcium (Ca ⁺⁺) | Magnesium (Mg ⁺⁺) | Sodium (Na ⁺) | Chloride (Cl ⁻) | Potassium (K ⁺) | Specific conduct- ance | Median pH |
|------------------------------------|---------------|--------------------------------|----------------------------------|------------------------------|--------------------------------|--------------------------------|------------------------------|--------------|
| U.S.G.S. Bldg., Ft. Buchanan | Mean | 9.6 | 0.8 | 2.4 | 4.5 | 0.3 | 90 | 7.0 |
| | Standard dev. | 4.2 | 1.0 | 1.6 | 3.1 | .3 | 37 | |
| | Maximum | 20 | 1.6 | 8.5 | 16 | 1.8 | 147 | |
| | Minimum | 2.2 | .2 | .9 | 1.2 | .01 | 7 | |
| Caimito | Mean | 3.2 | .5 | 2.5 | 3.5 | .8 | 42 | 6.5 |
| | Standard dev. | .9 | .2 | 1.2 | 1.8 | .9 | 12 | |
| | Maximum | 4.4 | .9 | 5.1 | 7.6 | 3.3 | 59 | |
| | Minimum | 1.6 | .2 | 1.2 | 1.4 | .2 | 22 | |
| Torrimar | Mean | 3.3 | .5 | 2.0 | 4.3 | .2 | 34 | 6.7 |
| | Standard dev. | 1.5 | .1 | .6 | 2.1 | .07 | 12 | |
| | Maximum | 6.9 | .7 | 3.0 | 8.5 | .4 | 53 | |
| | Minimum | 1.5 | .3 | 1.0 | 1.0 | .2 | 16 | |
| San Ignacio | Mean | 2.3 | .4 | 1.7 | 3.4 | .5 | 33 | 6.5 |
| | Standard dev. | 1.3 | .2 | .5 | 1.4 | .2 | 16 | |
| | Maximum | 5.5 | 1.1 | 2.4 | 5.9 | 1.9 | 79 | |
| | Minimum | .4 | .1 | 1.0 | 1.0 | .2 | 12 | |
| Fairview | Mean | 4.6 | .6 | 2.6 | 4.0 | .3 | 68 | 6.8 |
| | Standard dev. | 2.4 | .3 | 1.7 | 2.0 | .2 | 48 | |
| | Maximum | 11 | 1.1 | 5.9 | 7.4 | .6 | 195 | |
| | Minimum | 1.6 | .4 | .9 | 1.2 | .2 | 27 | |

Table 1.--Mean values (median value for pH) and other statistics from analyses of rainfall samples in the Río Piedras basin, Puerto Rico.--Continued

| Site | Statistics | Calcium (Ca ⁺⁺) | Magnesium (Mg ⁺⁺) | Sodium (Na ⁺) | Chloride (Cl ⁻) | Potassium (K ⁺) | Specific conduct- ance | Median pH |
|--|---------------|--------------------------------|----------------------------------|------------------------------|--------------------------------|--------------------------------|------------------------------|--------------|
| Cupey Alto | Mean | 2.0 | 0.4 | 1.9 | 3.2 | 0.2 | 30 | 6.8 |
| | Standard dev. | .9 | .2 | 1.0 | 1.8 | .1 | 9.5 | |
| | Maximum | 4.2 | .7 | 4.2 | 7.6 | .6 | 42 | |
| | Minimum | 1.3 | .2 | .8 | 1.3 | .1 | 16 | |
| Las Curías tribu- tary | Mean | 2.4 | .6 | 1.6 | 2.6 | .3 | 27 | 6.9 |
| | Standard dev. | .8 | .3 | 1.0 | 1.5 | .2 | 12 | |
| | Maximum | 3.6 | 1.1 | 3.4 | 5.1 | .5 | 47 | |
| | Minimum | .9 | .2 | .6 | 1.1 | .1 | 11 | |
| Río Piedras nr Río Piedras | Mean | 3.8 | .9 | 1.8 | 3.3 | .4 | 61 | 6.9 |
| | Standard dev. | 2.0 | .2 | .8 | 1.7 | .4 | 18 | |
| | Maximum | 10 | 1.2 | 2.9 | 6.4 | 1.3 | 98 | |
| | Minimum | 3.7 | .6 | 1.0 | 1.2 | .2 | 40 | |
| Río Piedras at Río Piedras | Mean | 7.8 | .8 | 2.1 | 6.6 | .2 | 83 | 6.9 |
| | Standard dev. | 1.8 | .2 | 1.0 | 2.0 | .2 | 16 | |
| | Maximum | 11 | 1.3 | 3.8 | 10 | .4 | 109 | |
| | Minimum | 6.0 | .6 | 1.1 | 4.2 | .1 | 66 | |
| Río Piedras at Hato Rey | Mean | 3.6 | .6 | 3.0 | 6.1 | .3 | 49 | 6.6 |
| | Standard dev. | 1.0 | .1 | 2.0 | 3.3 | .1 | 17 | |
| | Maximum | 4.8 | 1.1 | 7.7 | 12 | .5 | 74 | |
| | Minimum | 1.1 | .3 | 1.0 | 2.1 | .1 | 24 | |
| Quebrada Margarita nr Río Piedras | Mean | 7.4 | .6 | 1.9 | 5.0 | .3 | 72 | 6.9 |
| | Standard dev. | 1.6 | .2 | .6 | 3.1 | .1 | 12 | |
| | Maximum | 9.3 | 1.0 | 2.6 | 9.1 | .5 | 89 | |
| | Minimum | 5.2 | .4 | .9 | 1.7 | .2 | 52 | |

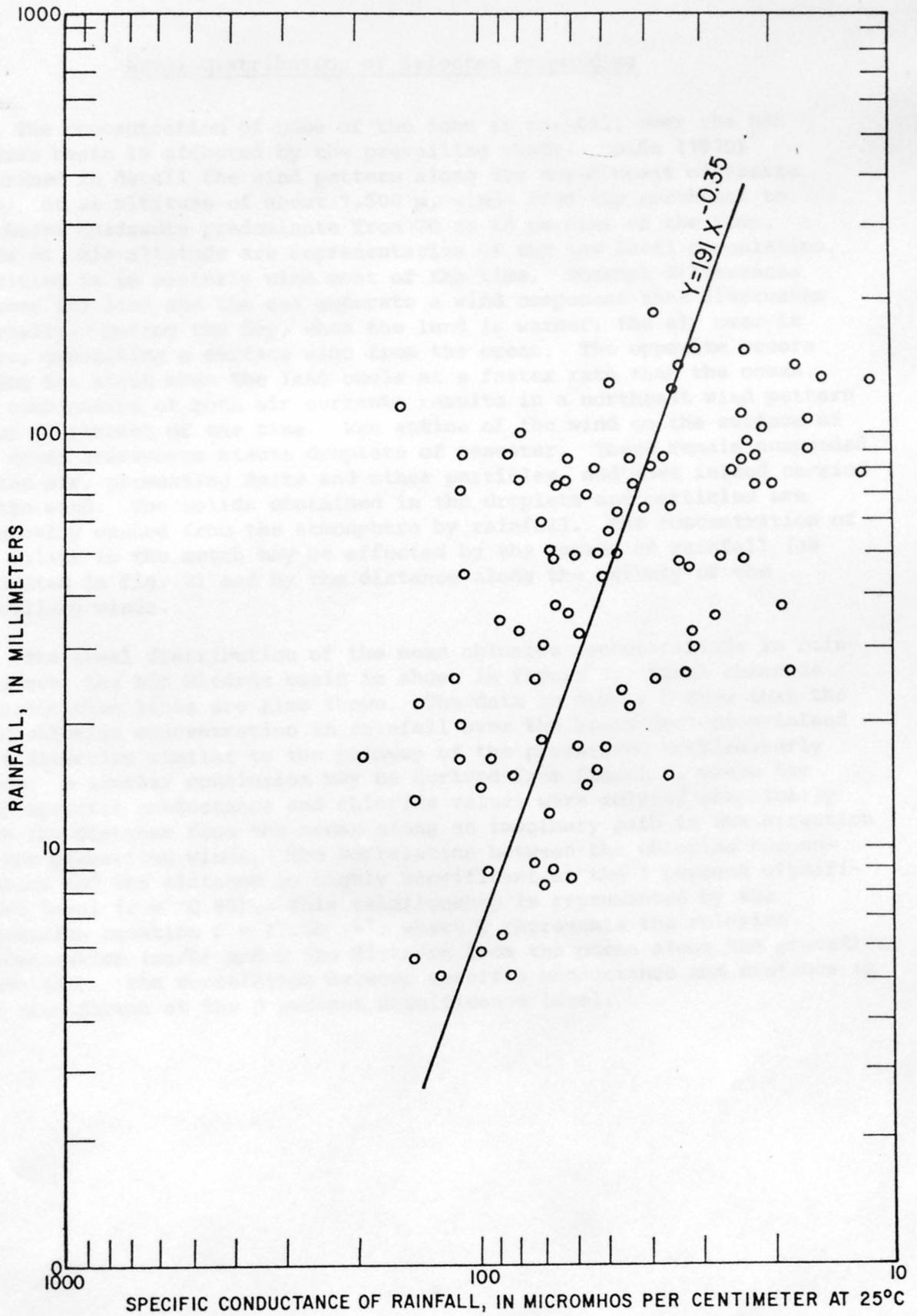


Figure 2.--Specific conductance of rainfall versus amount of rainfall in the Río Piedras basin.

Areal Distribution of Selected Properties

The concentration of some of the ions in rainfall over the Río Piedras basin is affected by the prevailing winds. Colón (1970) described in detail the wind pattern along the north coast of Puerto Rico. At an altitude of about 1,500 m, winds from the northeast to southeast quadrants predominate from 70 to 95 percent of the time. Winds at this altitude 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. The action of the wind on the surface of the ocean transports minute droplets of seawater. These remain suspended in the air, permeating dusts and other particles, and move inland carried by the wind. The solids contained in the droplets and particles are eventually washed from the atmosphere by rainfall. The concentration of the solids in the catch may be affected by the amount of rainfall (as indicated in fig. 2) and by the distance along the pathway of the prevailing winds.

The areal distribution of the mean chloride concentrations in rainfall over the Río Piedras basin is shown in figure 3. Equal chloride concentration lines are also shown. The data in figure 3 show that the mean chloride concentration in rainfall over the basin decreases inland in a direction similar to the pathway of the prevailing northeasterly winds. A similar conclusion may be derived from figure 4, where the mean specific conductance and chloride values were related graphically with the distance from the ocean along an imaginary path in the direction of the prevailing winds. The correlation between the chloride concentration and the distance is highly significant at the 1 percent significance level ($r = -0.90$). This relationship is represented by the regression equation $C = 17.5D^{-.61}$, where C represents the chloride concentration (mg/L) and D the distance from the ocean along the prevailing winds (km). The correlation between specific conductance and distance is not significant at the 5 percent significance level.

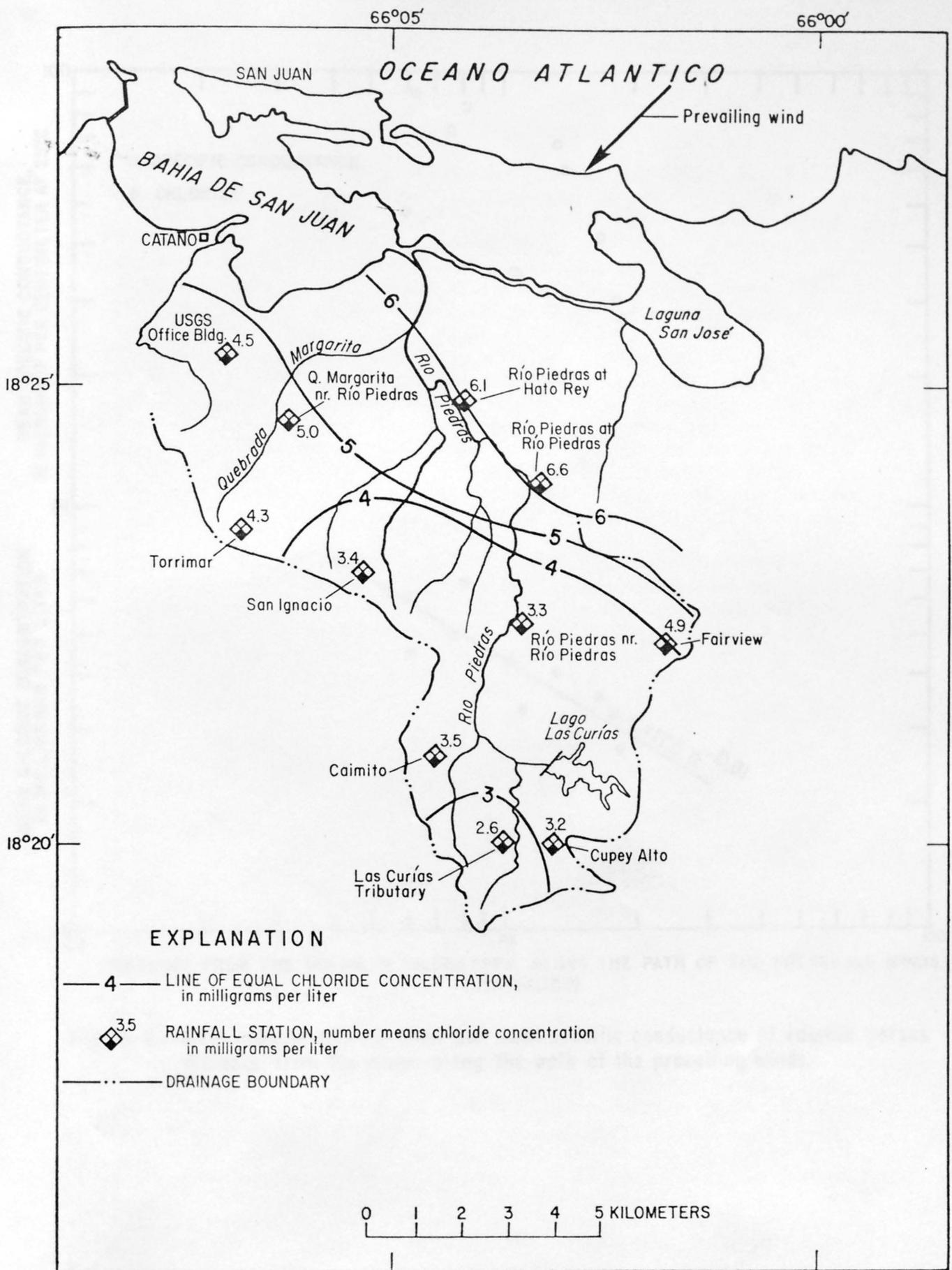


Figure 3.--Areal distribution of mean chloride concentration in rainfall over the Rio Piedras basin from June 1972 to January 1973.

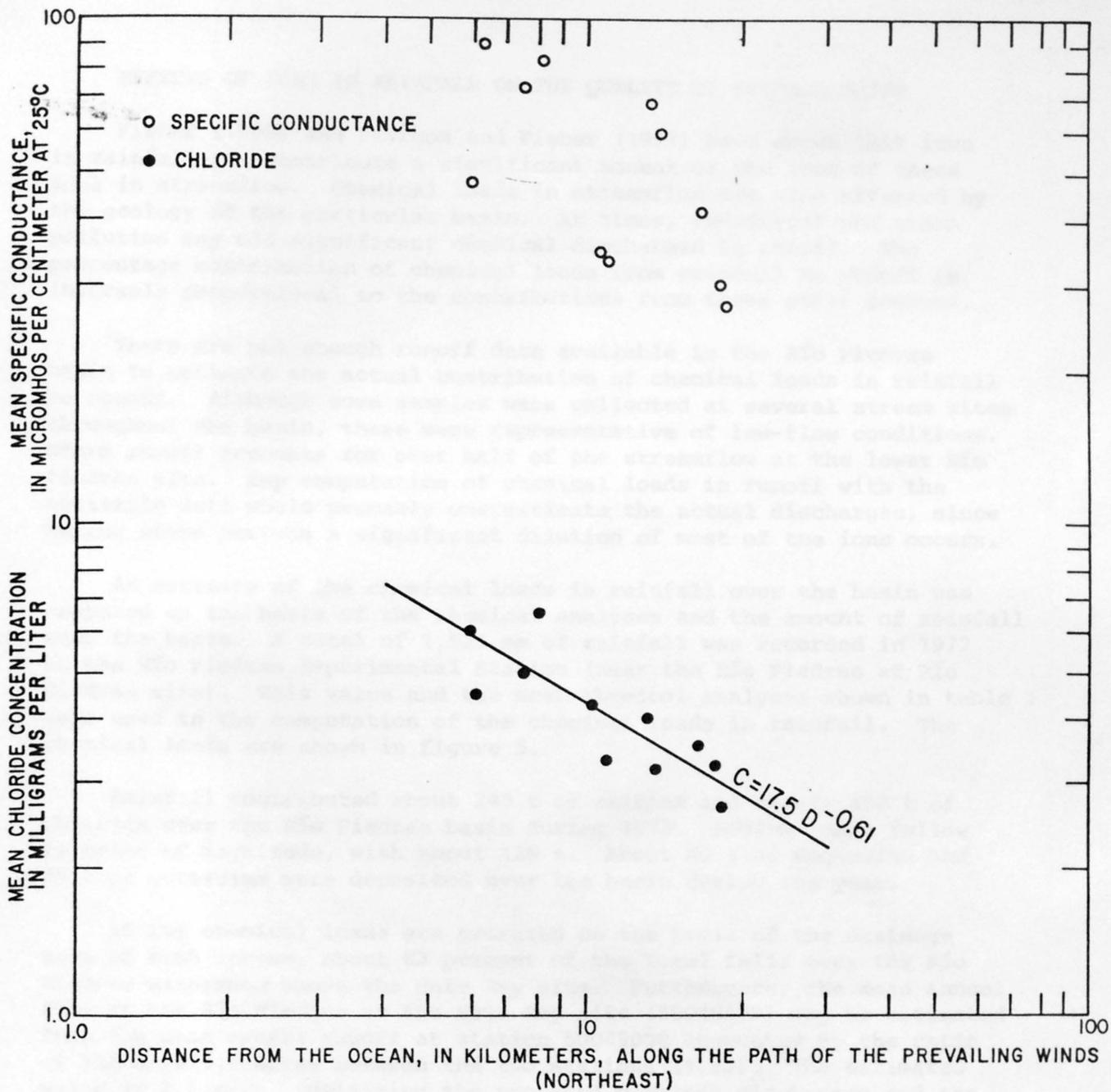


Figure 4.--Mean chloride concentration and mean specific conductance of rainfall versus distance from the ocean along the path of the prevailing winds.

EFFECTS OF IONS IN RAINFALL ON THE QUALITY OF SURFACE WATER

Fisher (1968) and Pearson and Fisher (1971) have shown that ions in rainfall can contribute a significant amount of the load of these ions in streamflow. Chemical loads in streamflow are also affected by the geology of the particular basin. At times, industrial and urban pollution may add significant chemical discharges to runoff. The percentage contribution of chemical loads from rainfall to runoff is inversely proportional to the contributions from these other sources.

There are not enough runoff data available in the Río Piedras basin to estimate the actual contribution of chemical loads in rainfall to runoff. Although some samples were collected at several stream sites throughout the basin, these were representative of low-flow conditions. Storm runoff accounts for over half of the streamflow at the lower Río Piedras site. Any computation of chemical loads in runoff with the available data would probably overestimate the actual discharges, since during storm periods a significant dilution of most of the ions occurs.

An estimate of the chemical loads in rainfall over the basin was computed on the basis of the chemical analyses and the amount of rainfall over the basin. A total of 1,525 mm of rainfall was recorded in 1972 at the Río Piedras Experimental Station (near the Río Piedras at Río Piedras site). This value and the mean chemical analyses shown in table 1 were used in the computation of the chemical loads in rainfall. The chemical loads are shown in figure 5.

Rainfall contributed about 240 t of calcium and nearly 200 t of chloride over the Río Piedras basin during 1972. Sodium loads follow in order of magnitude, with about 128 t. About 40 t of magnesium and 25 t of potassium were deposited over the basin during the year.

If the chemical loads are prorated on the basis of the drainage area of each stream, about 63 percent of the total falls over the Río Piedras watershed above the Hato Rey site. Furthermore, the mean annual flow at the Río Piedras at the Hato Rey site (50049100) may be estimated from the mean annual runoff at station 50049000 augmented by the ratio of the drainage areas between the two stations (1.23). The estimated value is $1.1 \text{ m}^3/\text{s}$. Utilizing the prorated chemical discharges and the estimated mean annual runoff, the maximum mean potential contribution from rainfall to runoff may be computed. The estimates indicate that rainfall could contribute an average of 6.9 mg/L of calcium, 5.8 mg/L of chloride, and 3.7 mg/L of sodium to the runoff at Río Piedras near Hato Rey. Although these estimates are mean maximum potential contributions, they are probably representative of the actual conditions. The possibility of retention of some of the ions from rainfall by the soils is reduced owing to the large amount of soil covered by impermeable material. However, some of the impermeable materials may be dissolved by the acidic rain, contributing to the load of solids. The contribution of chemical ions from rainfall may be a significant part of the ions in runoff.

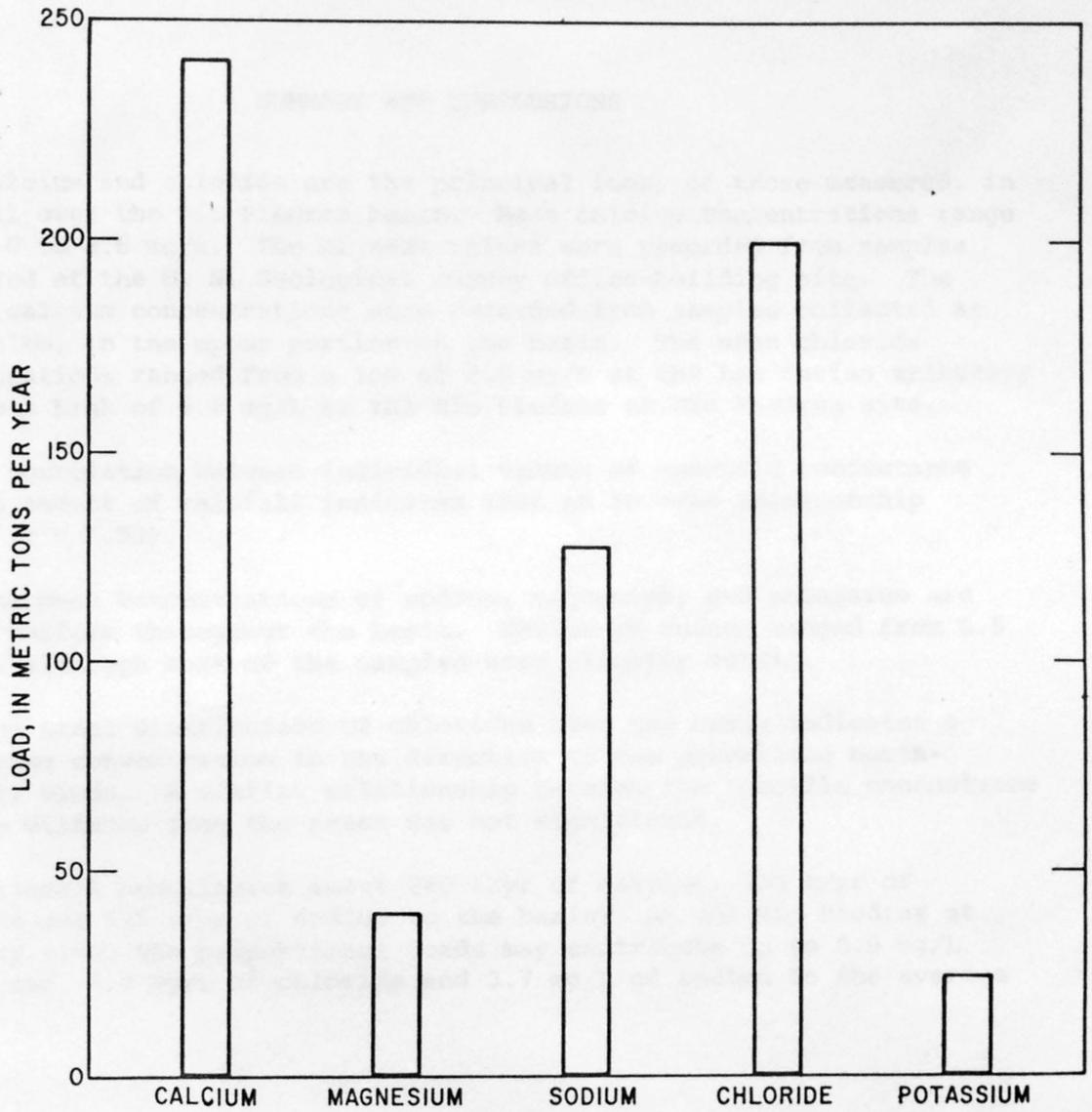


Figure 5.--Average annual loads of selected ions in rainfall over the Río Piedras basin.

SUMMARY AND CONCLUSIONS

Calcium and chloride are the principal ions, of those measured, in rainfall over the Río Piedras basin. Mean calcium concentrations range from 2.0 to 9.6 mg/L. The highest values were recorded from samples collected at the U. S. Geological Survey office-building site. The lowest calcium concentrations were recorded from samples collected at Cupey Alto, in the upper portion of the basin. The mean chloride concentrations ranged from a low of 2.6 mg/L at the Las Curías tributary site to a high of 6.6 mg/L at the Río Piedras at Río Piedras site.

A correlation between individual values of specific conductance against amount of rainfall indicates that an inverse relationship exists ($r = -.52$).

The mean concentrations of sodium, magnesium, and potassium are nearly uniform throughout the basin. Median pH values ranged from 6.5 to 7.0, although most of the samples were slightly acidic.

The areal distribution of chlorides over the basin indicates a decreasing concentration in the direction of the prevailing north-easterly winds. A similar relationship between the specific conductance and the distance from the ocean was not significant.

Rainfall contributes about 240 t/yr of calcium, 200 t/yr of chloride and 128 t/yr of sodium to the basin. At the Río Piedras at Hato Rey site, the proportional loads may contribute up to 6.9 mg/L of calcium, 5.8 mg/L of chloride and 3.7 mg/L of sodium to the average runoff.

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