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SHORT CONTRIBUTION

pH of rainwater in Coimbra, Portugal: the seasonal variation

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ABSTRACT

Daily measurements of pH and conductivity of rainwater at Coimbra, Portugal in the period between autumn 1978 to autumn 1980 are reported. The average conductivity is 26 $\mu\Omega^{-1}$ cm^{-1} and the average pH is 4.75. Neutral salt contribution to conductivity is significant and is highest in autumn/winter. Correlations between neutral salt conductivity and wind direction were found. pH values have a large dispersion and more than 30% of the samples had a pH <5.0. A seasonal variation of 1.2 pH units was found for the acidity with the highest average pH in autumn and the lowest in summer. A bimodal pH frequency distribution was found for the winter and spring seasons with a minimum frequency ranging from 5.7 to 5.3 pH units.

1. Introduction

Acidic rainwater is a matter of great concern to many countries, because of its association with atmospheric pollution and with drastic changes that it has brought about in many water systems and in their respective ecosystems. Rainwater is a weakly buffered system with respect to hydrogen ion concentration, and consequently its pH value can be affected by many different water contaminants (Granat, 1972). In polluted areas, the acidity of rain is attributed mainly to anthropogenic emissions of SO_2 and NO_x, although some natural sources of biological action for H_2S and also for NO and NO_2 can contribute to the overall acidity. This paper contains the first results of study of acidity and conductivity of rainwaters in Portugal, based on daily measurements undertaken over a period of 2 years (November 1978 to December 1980). The station was situated in a Geophysical Institute in the central part of Coimbra. Coimbra is situated in the middle of the country, at a distance of 25 km from the coast; as far as the amount of precipitation is concerned, the station is representative of the average situation in Portugal with an annual average value of 944 mm (s.d. 190 mm) (de Morais and Pereira, 1954).

2. Experimental procedure

The daily samples were collected (9 a.m.) through cylindrical Jena glass bottles with funnels of 19·5 cm diameter with the tip 1·5 m from the ground. The site of collection was at the top of a small hill with open access to rains from any direction. The funnels and collectors were cleaned every day. The volume of the collected rainfall was measured at the site and the pH and conductivity were determined within an hour after collection, in the laboratory; however, no significant effect was found for the pH and conductivity values measured several days after the collection, after the water had been kept in polyethylene bottles in the dark.

The pH values were measured with a digital Sargent Welch pH-meter (model NX) and a glass electrode; the pH-meter was calibrated every week. Conductivities were measured with a "YSI" conductivity bridge model 31 and a YSI 3402 conductivity cell with a cell constant of 0.1. Owing to the volume requirements for these measurements, only collections of rainfalls >1 mm were analysed, although we used a funnel diameter larger than usual. Data were analysed statistically using the usual procedures for arithmetic means and standard deviations (σ); the Student t-test was applied as a test of significance, and the χ^2-test was employed to analyse the Gaussian behaviour of the observed distributions. Correlations between bivariate normal data were measured by the linear correlation coefficient r.

3. Results

Over a period of 25 months, we analysed 195 samples. The average amount of precipitation per sample was 11 mm and the average total amount of rain per year was 990 mm. The rains are concentrated in two dominant local wind directions NW–NNW (40%) and S–SSE (36%). The conductivity had an average value of $\bar{K} = 26.0$ $\mu\Omega^{-1}$ cm^{-1} ($\sigma = 28.0$ $\mu\Omega^{-1}$ cm^{-1}). No correlation was found between conductivity and the local wind directions, the amount of precipitation or the corresponding pH values (90% confidence). Neither was a seasonal variation found for the conductivity.

The average pH calculated as an average of H^+ concentration is 4.75 with extremes at 3.5 (spring 1979) and 7.7 (autumn 1979). More relevant for assessing rainfall with respect to acid characteristics is the frequency of the several types of rain: pH >7.0, 2%; $7.0 \geqslant$ pH >6.0, 11%; $6.0 \geqslant$ pH $\geqslant 5.0$, 54%; $5.0 >$ pH $\geqslant 4.0$, 31%; $4.1 >$ pH, 2%. The average pH values for each season reveal a large variation with the season. Such a variation is statistically significant (99% confidence) between all the seasons. The seasonal variation of pH was not only observed on an average basis, but was also observed for each year, as Fig. 1 reveals. An annual pH cycle is present, whereas pH is higher in autumn–winter and lowest in summer.

The autumn and summer data have a Gaussian distribution (95% confidence level). However, the spring and winter data seem to have a bimodal distribution with relatively more rains of pH >5.5, relatively few rains with pH values around 5.5 and again relatively more rains with pH >5.5 (Fig. 2). A search for correlations of pH with some meteorological data was carried out, but no correlations were found with the amount of precipitation, the number of days of rain or with the local wind directions (90% confidence).

Since conductivity is not correlated with pH, there must be a significant amount of neutral salts in the rainwaters. The conductivity due to such salts can be estimated approximately by considering that acid conductivity is mainly due to H^+ and $SO_4^=$. This "neutral salt conductivity", K_{ns}, is much

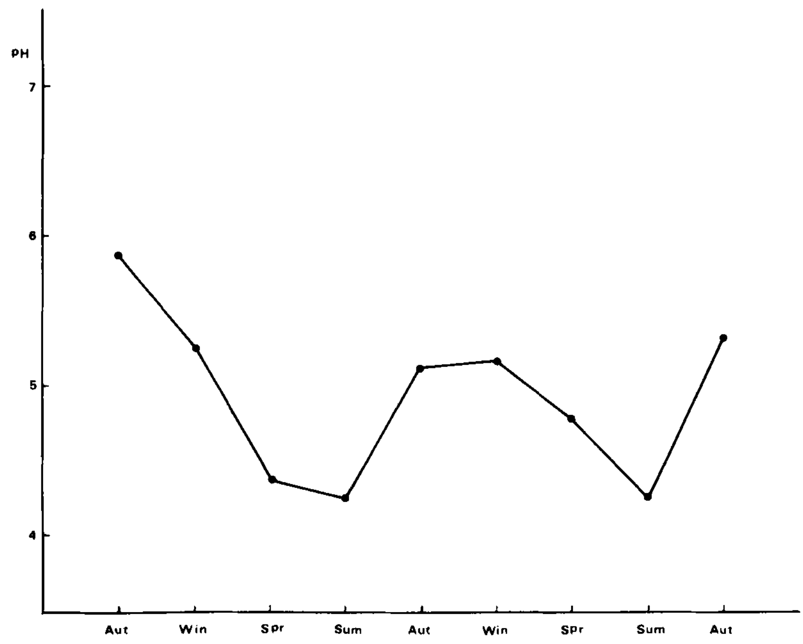

Fig. 1. Seasonal pH variation of rainwater in Coimbra from autumn 1978 to autumn 1980.

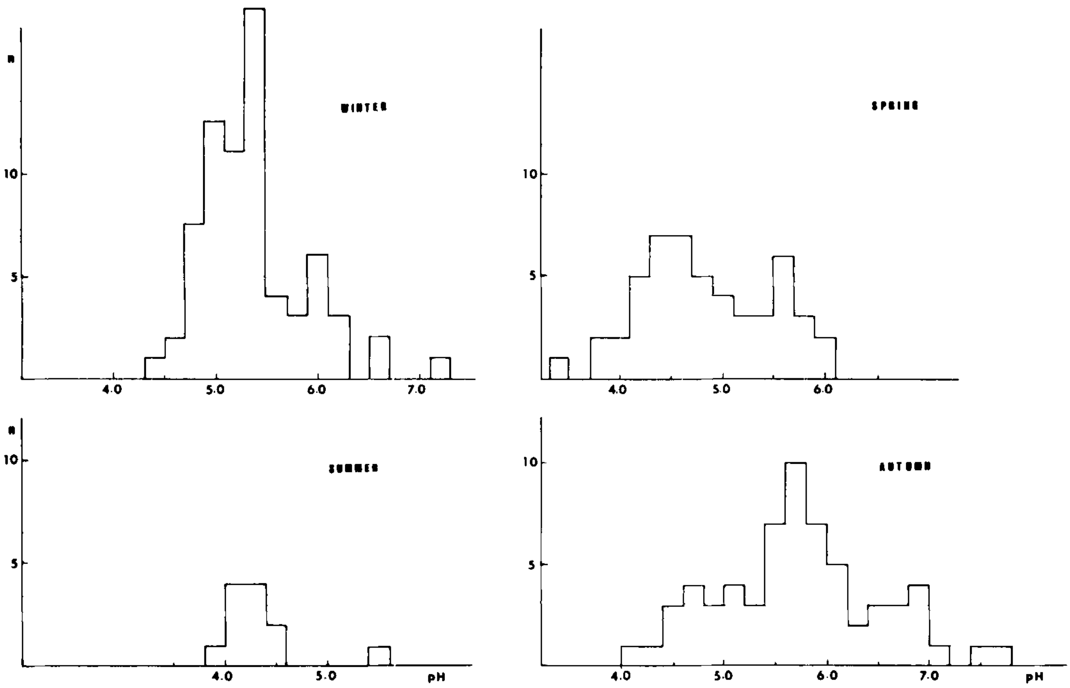

Fig. 2. Frequency of rain events as a function of pH.

lower in spring/summer ($\bar{K}_{ns} = 4.9\ \mu\Omega^{-1}\ cm^{-1}$; $\sigma = 18.4$) than in autumn/winter ($\bar{K}_{ns} = 25{\cdot}7\ \mu\Omega^{-1}\ cm^{-1}$; $\sigma = 37.3$). A significant difference (90% confidence) was found between the two dominant wind directions NW–NNW ($\bar{K}_{ns} = 19.2$, $\sigma = 26$) and S–SSE ($\bar{K}_{ns} = 13.7$, $\sigma = 20.5$). However, conductivity does not lead to an explanation of the annual cycle and although SO_2 emissions in Portugal and Spain (Semb, 1978) may be significant for the reported observations, more detailed chemical analyses are required for a satisfactory explanation of the pH data.

4. Acknowledgements

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