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ACID RAIN AND MAJOR SEASONAL VARIATION OF HYDROGEN ION LOADING IN A TROPICAL WATERSHED

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ABSTRACT

The hydrogen ion loading rate associated with bulk precipitation increases by four orders of magnitude from the begining to the end of the dry season in the Aragua Valley, Venezuela. Widespread seasonal burning of the vegetation appears to be responsible for the release of nitrogen oxides that are converted to nitric acid in sufficient quantities to decrease the pH of rainfall to values as low as 3.4.

PRECIPITACION ACIDA Y VARIACIONES ESTACIONALES DE LA CARGA DE IONES HIDROGENO EN UNA CUENCA HIDROGRAFICA TROPICAL

RESUMEN

La tasa de carga de iones hidrógeno, asociada a la precipitación total, incrementa en cuatro órdenes de magnitud desde el principio hasta el final de la época de sequía en el Valle de Aragua, Venezuela. Las frecuentes quemas estacionales de vegetación aparentan ser responsables de la liberación de óxidos de nitrógeno que son convertidos en ácido nítrico, en suficientes cantidades para bajar el pH de la lluvia a valores tan bajos como 3.4.

INTRODUCTION

Precipitation chemistry has received as rapidly increasing share of scientific attention over the past decade, and the trend promises to continue. This interest reflects a growing appreciation of the fundamental biological and geochemical significance of chemical transport through the atmosphere, as identified by a handful of pioneering investigators about 25 years ago.[1-4] In addition, major changes in the chemical characteristics of precipitation have come forcefully to the attention of industrialized nations because of the possibility of widespread environmental damage.[5] The most intensive recent focus for investigation has been the acidity of precipitation. It has become conventional, on the basis of the computed pH of water under the influence of atmospheric CO_2, to define precipitation events with a pH below 5.6 as "acid precipitation".[6] Acid precipitation implies the presence of strong mineral acids, which are in turn usually linked with fossil fuel combustion. Numerous other sources of such acids are known, however. A major difficulty in evaluating the significance and extent of acid precipitation is the paucity of information about the hydrogen ion content and general chemistry of precipitation under a representative variety of conditions over the globe.

Our investigation of precipitation chemistry in northern Venezuela has unexpectedly documented highly acidic precipitation and very large seasonal changes in the hydrogen ion loading rate, both of which we believe are connected with an extended tropical dry season and with sources of nitrogen oxids other than fossil fuels. Our precipitation chemistry studies have been conducted in the watershed of Lake Valencia, which occupies a large graben in the Aragua Valley of Venezuela near the coastal mountain (10°10′ N, 6°25′ E). The natural vegetation of the watershed is tropical deciduous forest at lower elevations (450 m) and rain or cloud forest at the highest elevations (1800 m). About 85% of the watershed has been cleared of forest. The lowland areas are used extensively for cultivation of sugar cane, and the hillsides are used some for pasture.

SITE DESCRIPTION AND METHODS

The amount of rainfall in the Lake Valencia watershed varies with elevation. The lake surface in 404 m asl, and the collections were made at 430 m asl, 100 m distant from the edge of the lake. At this elevation the total annual rainfall is 750-800 mm yr^{-1}. Rainfall is extremely seasonal. Beginning about December of each year, the Aragua Valley experiences the effects of a regional dry season lasting approximately 100 days during which the rainfall is negligible (Fig. 1). Starting in 1976, we collected bulk precipitation (composite of all wet and dry materials) reaching a large collector (0.23 m^2) mounted on a tower 3 m above the ground. The collections were made in a vegetated area isolated from traffic, agricultural activity, and vegetation burning. Perching birds did not constitute a problem at the collection site during the collection period reported here. Contents of the collector were analyzed comprehensively for chemical constituents by standard methods.[7] The amounts of precipitation constituents from the collector were then converted to weekly loading rates (mg m^{-2} wk^{-1}). Loading rates for a chemical constituent can of course be significant whether or not there is any wet precipitation in a particular week. We focus here almost entirely on loading rates, as concentrations are of less basic significance due to their intimate dependence on precipitation volume.

RESULTS

Fig. 1 shows the hydrogen ion loading rate over a two year period beginning 1977. Some of the pH values corresponding

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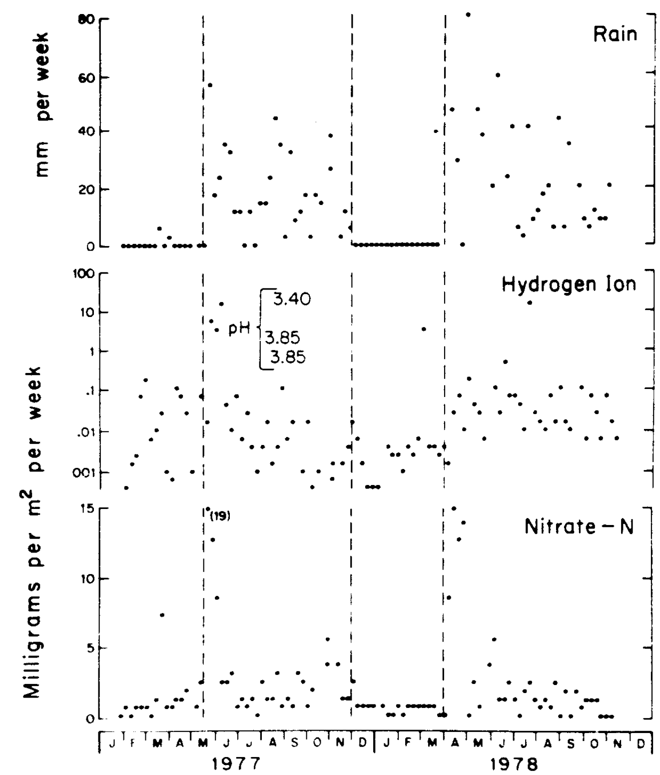

Fig. 1. Rain, hydrogen ion loading, and nitrate loading in the Lake Valencia watershed, 1977 and 1978.

to the highest hydrogen ion loading rates are also indicated. The hydrogen ion loading rate tends to be low at the beginning of the dry season, but increases as the dry season progresses. A jump in hydrogen ion loading rate occurs just as the dry season has ended. Close examination of the data shows that this jump actually occurs in conjunction with the first few rains following the dry season. The balance of the rainy season is characterized by declining hydrogen ion loading rates. The total annual range of weekly hydrogen ion loading rates is extremely large (5 orders of magnitude). At the highest hydrogen ion loading, the pH of precipitation is remarkably low (ca 3.5), suggesting extreme acidification of the rainfall by mineral acids. In contrast, the pH of precipitation over much of the year is quite high (ca 6-7). Although the trends show some variation from one year to the next, the data leave little doubt of true seasonal changes in hydrogen ion loading.

DISCUSSION

Anion composition of the precipitation implicates nitric and sulfuric acids as major mineral acids. Sulfate loading (338 eq ha^{-1} yr^{-1}) is higher than nitrate loading (91 eq ha^{-1} yr^{-1}), but the nitrate ion accounts for a greater amount of variance in the hydrogen ion than any other variable. Multiple regression analysis on log-transformed data shows that R for weekly nitrate loading predicting weekly hydrogen ion loading is 0.44, R for nitrate and bicarbonate is 0.68, and R for nitrate, bicarbonate, and sulfate is 0.72 ($P < 0.01$ for all variables). The supply of bases may of course change independently of the acidic materials and will thus affect the hydrogen ion loading; this explains why bicarbonate has significance as a predictor in addition to nitrate and sulfate. Although changes in the availability of bases can explain some of the total variance in hydrogen ion loading, bases cannot explain the major seasonal changes in hydrogen ion loading, as terrestrial particulates, which are the source of bases, vastly increase during the dry season but are overwhelmed by the large amounts of acidic materials toward the beginning of the rainy season.

The marked seasonality in nitric acid and its effects on hydrogen ion loading rate raise questions about the sources of nitrogen oxides in the watershed. Although the Aragua Valley is moderately industrialidez, fossil fuel combustion for power production is low by comparison with an area of comparable population density (ca 400 individuals km^{-2}) in the United States or Europe. Moreover, power consumption shows no marked seasonal pulses that might account for the seasonality in nitric acid. Automobile traffic is heavy around the cities of Maracay and Valencia, but is not seasonal.

Several factors may contribute to an explanation of the major seasonal changes in nitrate content and acidity of precipitation. The proximate explanation of the nitrate flush in the first few rains is the effectiveness of rain in removing accumulated nitrogen oxides from the atmosphere, causing low pH values. Our own data and data from Caracas[8] show that both nitrate and sulfate are associated in measurable amount with particles. However it is clear from the Lake Valencia data that nitrate in particular is transported much more efficiently by moisture. The nitrogen oxides apparently build up in the atmosphere during the dry season. The sudden onset of seasonal rains, or any small amount of dry season rain (Fig. 1), brings an impressive flush of nitrate to the ground. This accounts for the major change in precipitation chemistry just at the transition between the wet and the dry season. As the wet season pregresses, the atmosphere is brought once again into equilibrium with wet season sources of nitrogen oxides, and the total loading rates for nitrate and the hydrogen ion consequently decrease.

Although the transition from low to very high nitrate loading is caused by rain, this is not a complete explanation. Very large dry season sources of fixed nitrogen must be found to account for the large oxide buildup. It would appear from Fig. 1 that the dry season sources must exceed normal wet season sources. The pronounced biological changes of the dry season could affect nitrogen cycling mechanisms in the watershed in such a way as to increase the source of atmospheric fixed nitrogen toward the end of the dry season. However, in those few instances where changes in the loss rate of volatile fixed nitrogen compounds from terrestrial systems have been documented,[9] increased losses to the atmosphere have been associated with increases in moisture, yet especially rapid nitrogen oxide buldup near Lake Valencia seems to occur in the dry season. Another explanation might be a seasonal variation in efficiency of nitrogen oxide transport from distant pollution sources. The city of Caracas (population ca. 3×10^6) is an obvious source,[10] but the prevailing wind trajectories would not suggest efficent transport. A third possible explanation has to do with widespread regional combustion of organic material during the dry season. Beginning about December of each year, the Aragua Valley and other parts of Venezuela experience widespread vegetation fires, which become more numerous as the dry season progresses. Fires in the Aragua valley burn about 5-15% of the land surface each year, depending on the severity of the preceding drought. During the dry season of 1976-77 government records show that 7500 ha of cane and 2800 ha of grassland, scrub, and forest were burned. The composite of these is 4% of the watershed area. Since the combustion of natural organic matter is known to release significant amounts of nitrogen oxides,[11,12] the major accumulation of nitrogen oxides during the dry season and the high amounts of nitric acid in rainfall at the beginning of the wet season may be attributable at least partly to seasonal burning. It is possible to show by rough computation that the vegetation combustion is in fact a significant N source. For 1976-77, the early wet season nitrate loading totalled about 40 mg m^{-2}. Our field approximations indicate combustion of about 4 kg m^{-2}, and N content of about 1%. Conversion of dry plant organic N to NO_x has an efficiency of at least 1.5%.[12] Together with the estimate of 4% watershed combustion by area, these figures indicate a source of NO_x from vegetation burning of at least 12 mg m^{-2} for the watershed as a whole, which is the same order of magnitude as the observed loading pulse.

High precipitation acidity ("acid rain") may not be new to the industrial era, but may have occurred extensively on a seasonal basis wherever widespread burning of the vegetation was customary before fossil fuels came into use. If natural vegetation is a major potential source of atmospheric fixed nitrogen, significant swings in the acidity of precipitation and in the transport of nitrogen by rainfall may in fact be typical of tropical areas which experience a pronounced dry season.

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