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SHORT CONTRIBUTION

Acid rain in an Amazon rainforest

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ABSTRACT

Acid rain is reported from the Amazon territory of Venezuela. The volume weighted average pH was 4.7 for 70 storms sampled from January 1979 through February 1980. At this location, remote from point sources of industrial pollution, acid rain might result from natural biogeochemical processes in the rainforest, from global atmospheric pollution, or from some combination of natural and pollution processes.

1. Introduction

During a preliminary survey of rainfall pH at San Carlos de Rio Negro, Venezuela (about 20 km S of the confluence of the Rio Negro and Rio Casiquiare, Lat 1°56′N, Long, 67°03′W., alt. 119 m), pH values less than 5.6 were frequently recorded. Because this site is distant from point sources of industrial pollutants, a more detailed study was initiated. Earlier we reported a volume weighted average pH of 4.65 for 23 storms from January through March 1979 (Clark *et al.*, 1980). Here we present additional data for a total of 70 storms sampled over one year.

Rain having a pH value less than 5.65, the value resulting from the equilibrium between atmospheric CO_2 and water at 25 °C (Stumm and Morgan, 1970), can be termed acid rain. Acid rain might result from natural biological processes, from industrial pollution or from some combination of these processes. Acid rain is the subject of growing environmental concern in northern Europe (Barret and Brodin, 1955; Brosset, 1973; Hutchinson and Havas, 1980), in northeastern United States (Cogbill and Likens, 1974; Likens and Bormann, 1974; Likens and Butler, 1981), and in western United States (Lewis and Grant, 1979), where it is thought to result from the scavenging of oxides of nitrogen and sulfur from the atmosphere by rain. These oxides are thought to come from the burning of fossil fuels (MacCracken, 1978; Likens, 1976). Because H^+ ions can displace elements out of plant leaves (Kratky *et al.*, 1974; Wood and Bormann, 1975; Fairfax and Lepp, 1975) and out of soils (Wiklander, 1973/74), and inhibit element acquisition by plant roots (Black, 1968), acid rain has the potential to disrupt mineral element cycling upon which farm and forest production are partly dependent.

2. Methods and results

At San Carlos, four polypropylene bottles were supported on 2 m high posts in an open field to sample individual rainstorms for pH. The pH was measured with an Orion 4047A portable meter using an Ag–AgCl glass electrode standardized with pH 4.01 and pH 7.0 reference buffers before and after each set of pH determinations. The pH values were converted to μ eq·l^{-1}. A volume weighted average was computed as $\sum[(\mu$ eq·l^{-1} of H^+ in rain event) (volume of rain event)]/(total volume of all rain events), then reconverted to pH units. Seventy storms were sampled for pH from 24 January, 1979, through 17 February, 1980. The pH values ranged from 4.0 to 6.7. The volume weighted average H^+ concentration was 20.2 μ eq·l^{-1} which corresponds to pH 4.69.

3. Discussion

The finding of acid rain in this study is consistent with the earlier report of acid rain at Manaus,

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Brazil (Anonymous, 1972; Ungemach, 1970) some 920 km to the southeast of San Carlos de Rio Negro. At Manaus, analyses of 100 storms from 1966 to 1968 showed rainfall pH values as low as 3.6 and monthly means ranging from pH 4.2 to 5.3 with a median value of 4.6. Rainfall pH averaging 4.66 (range 4.4–4.9) has been reported from the rainforest at La Selva, Costa Rica, Central America (Johnson *et al.*, 1979). Hence, acid rain may be widely distributed in the American Tropics.

Possible causes of acid rain at San Carlos are A) long distance transport of industrial pollutants and/or B) local element recycling. The closest sources of industrial pollutants are Caracas, Venezuela, 930 km to the north and Puerto Ordaz, Venezuela, 860 km to the northeast of San Carlos. The industrial centers of Sao Paulo and Rio de Janeiro, Brazil, lie about 3600 km to the southeast. The global dispersion of radioisotopes following release into the atmosphere (Jacobs, 1968) and the transport of sulfur for distances greater than 1000 km is known from Europe (Rodhe, 1972). Winter arctic aerosols at Barrow, Alaska, had high concentrations of V, SO_4^{-2}, and ^{210}Pb that were "... quantitatively consistent with polluted European air masses as the source followed by transport over European Russia and then to the north ..." a distance of 13,000 km (Rahn and McCaffrey, 1980).

While long distance transport of pollutants cannot be excluded, some hydrologic processes and some characteristics of the rain chemistry itself suggest alternative explanations for acid rain at San Carlos. Salati *et al.* (1978) calculated that about 50% of the water falling in rain is evaporated from within the Amazon basin while the other half comes from the Atlantic Ocean. This suggests to us that air masses could be washed free of pollutants by passage through numerous convective storm cells before reaching San Carlos de Rio Negro.

The unusually low pH of the rain may result from the volatilization of P compounds into the atmosphere, their oxidation to PO_4^{-3}, and their return in rain. Herrera (1979) demonstrated the release of volatile P from waterlogged soils by placing pairs of polypropylene vessels containing 5-*N*-HNO_3 beneath inverted polypropylene boxes on the forest floor. One vessel of each pair was sealed from the atmosphere (blank) while the other (experimental) was covered with a nylon mesh to exclude insects. The pairs of vessels were maintained on the forest floor for periods ranging from 1 to 30 days. The P concentrations were determined and the differences between experimental and blank vessels were plotted against exposure time. The slope was 0.14 μg P m^{-2} day^{-1} ($r = 0.92$). While the recovery efficiency of this method is unknown and the emission rate could account for only 53 μg m^{-2} yr^{-1}, qualitatively at least, it demonstrates the loss of volatile P compounds from the forest floor. A volume weighted average annual concentration of 0.617 mg P/l or 59.7 μ eq P/l can be calculated from the P flux and the amount of rainfall at San Carlos given by Jordan *et al.* (1980). If all of the P in the rain had been volatilized out of the forest floor into the atmosphere, oxidized to PO_4^{-3}, and returned in rain having pH values between 4 and 6, the equilibrium between one atom of P and H_2O would contribute one $H_2PO_4^-$ and one H^+ (Lindsay, 1979, p. 168). Thus, the concentration of H^+ would be 19.9 μ eq/l and result in a solution pH of 4.7. The concentration 0.617 mg P/l in rain at San Carlos is at least 200 times greater than the volume weighted mean concentration in rain at, for example, Hubbard Brook, New Hampshire, USA (Likens *et al.*, 1977).

The volatilization of S from the forest, its oxidation to SO_4^{-2}, and its return to the forest as H_2SO_4 in rain is also possible. In the Ivory Coast, Delmas *et al.* (1980) quantified emissions of H_2S from humid forests from between 0.009 and 2.5 g S m^{-2} yr^{-1}. If 2.5 g S m^{-2} yr^{-1} were volatilized out of the forest at San Carlos, oxidized to SO_4^{-2} returned in the 3.4 m annual rainfall, the resulting pH would be about 4.3

Evidence for the volatilization of both P and S from the Amazon rainforest near Manaus, Brazil, has been presented by Lawson and Winchester (1979). Volatilization of H_2S from Amazon floodplain lakes near Manaus was reported by Brinkman and Santos (1974). They argue that the emitted H_2S is recycled on a local or regional scale by convective rainstorms.

Chemistry and pH at San Carlos are now being monitored as part of a global precipitation network headed by Galloway and Keene, University of Virginia and by Likens, Cornell University. The

pH data for the first few months from the network collector corroborate our finding of acid rain at San Carlos (J. Galloway, personal communication).

If natural processes are producing acid rain in the Amazon basin, similar processes may be contributing to acid rain in other regions of the earth where their effects may be added to those of industrially derived pollutants. Alternatively, the existence of acid rain in the Amazon may indicate that acid forming industrial pollutants now completely blanket the globe.

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