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LETTER TO THE EDITOR

A note on acid rain in an Amazon rainforest

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A recent short communication in this journal by Haines et al. (1983) reported that 70 storms collected in an Amazon rainforest in southern Venezuela had a volume weighted average pH of 4.7. The authors speculated that this acidity may have resulted from the volatilization of P and S from the forest into the atmosphere, where these elements were oxidized to PO_4^{-3} and SO_4^{-2} and returned to the forest as H_3PO_4 and H_2SO_4 in rainwater.

In support of their speculation concerning acidity from H_3PO_4, the authors referenced the precipitation chemistry data of Jordan et al. (1980). Unfortunately, these data corresponded to bulk samples which were collected on a weekly basis and therefore contained a large but unknown amount of dry deposition. The authors presented no precipitation chemistry data in support of their speculation concerning acidity from H_2SO_4.

Between September 1980 and March 1981, we, in cooperation with the authors and the Instituto Venezolano de Investigaciones Cientificas, collected and analyzed 19 precipitation events at the same study site in southern Venezuela. This research was carried out under the auspices of the Global Precipitation Chemistry Project (GPCP). The first 14 events we analyzed had a volume weighted average pH of 4.81 (Galloway et al., 1982). In their paper, the authors correctly stated that the GPCP data corroborated their measurements of pH. However, the authors failed to mention that our measurements of PO_4^{-3} and SO_4^{-2} did not support their speculations concerning the source of free acidity in the samples. Based on ratios of $H_2PO_4^-/H^+$ and SO_4^{-2}/H^+, we calculated that, on a volume weighted basis, H_3PO_4 contributed a maximum of 4% of the free acidity and that H_2SO_4 contributed a maximum of 18% of the free acidity (Galloway et al., 1982). Unmeasured proton donors accounted for a minimum of 65% of the free acidity in the 14 samples analyzed. Preliminary analyses for formic and acetic acids indicated that they were present in the samples at concentrations high enough to support the free H^+ concentrations (Galloway et al., 1982).

Using techniques developed by Keene et al. 1983a), organic acidity was accurately measured in the last two events we received from the Venezuela site. Formic and acetic acids contributed 4.9 μeq/l or 55% of the free acidity in one sample and 1.5 μeq/l or 25% of the free acidity in the second sample.

Keene et al. (1983b) also developed a technique for estimating organic acidity in samples for which only inorganic data were available. In the 11 samples for which sufficient data existed, we estimated that, on a volume weighted basis, formic and acetic acids contributed 7.3 μeq/l or 49% of the free acidity.

In closing, we feel that the authors' very hypothetical speculations concerning the source of free acidity in precipitation at the site were based on inappropriate or non-existent precipitation chemistry data. The GPCP data set for San Carlos is admittedly small and therefore precludes a definitive statement. However, it is the only data set, generated from samples collected on an event basis at the site, which includes chemical data other than pH. Based on actual measurements and on calculations using inorganic data, we have estimated that, on a volume weighted basis, organic acids contributed between 49% and 65% of the free acidity in precipitation at the site.

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