Acidity in Rainwater: Has an Explanation Been Presented?

The recent report by Likens and Bormann (1) certainly points out the manifold ecological problems, both present and potential, that are associated with the possibility of acid rain. It cannot be disputed that the tall smokestacks introduced in recent years disperse the emitted SO2 over a broader area. That is precisely the philosophy behind tall stacks. Whether there has been a concomitant increase in acidity in the rainwater of rural areas in the northeastern United States has not been documented in the data of Likens and Bormann since, as shown in their figure 1, the pH remained relatively constant over an 8-year period.

The authors, however, do show in their figure 2 a striking 70 percent decrease in SO2 since 1950 in rainwater at Ithaca, New York. This change is probably correctly attributed to the shift in use from coal (high in sulfur) to natural gas (low in sulfur). The statement is made (correctly) that the drop in the sulfur concentration is difficult to reconcile with the proposed (not substantiated) recent increase in acidity. The contention is then made that high particulate loadings from the combustion of coal in the past could have caused neutralization of the acid sulfate. Likens and Bormann further conclude that the installation of particle-removing devices in tall smokestacks eliminates these alkaline substances, consequently permitting appreciable quantities of SO2 to be converted to acid.

This argument cannot be correct. As an example, coal could contain 3 percent sulfur (6 percent as SO2) and 15 percent ash (composed of 50 percent SiO2, 30 percent Al2O3, 15 percent Fe2O3, and 3 percent CaO). The alumina and silica are quite inert, and there is just not enough material left to neutralize the SO2. The only component of any possible significance is Fe2O3. Even if we consider the highly unlikely overall reaction

$$3\text{SO}_2 + \text{Fe}_2\text{O}_3 + \frac{3}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{(SO}_4\text{)}_3$$

it would require essentially all of the Fe2O3 to consume an appreciable amount of the SO2. Since there are so many competing processes, it is most unreasonable to assume that a reaction could appreciably proceed when the reactants are present in a near stoichiometric relationship. Furthermore, 25 years ago particulate-removal devices in operation in the northeast, if they were mechanical, removed > 50 percent of the ash or, if electrostatic (in common usage), > 75 percent. Modern electrostatic
precipitators remove ~99 percent of the ash. This increase in particulate removal made possible by the use of modern electrostatic precipitators is hardly enough to be significant for the enormous difference in neutralization proposed by the authors. Finally, there is no evidence that Fe₂(SO₄)₃ was ever a major component of rainwater SO₄²⁻.

Certainly, the introduction of tall smokestacks and particulate-removal devices has reduced the local "soot problem." Whether these procedures have altered (positively or negatively) the regional "acid problem" is an unanswered question.

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References

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Both Newman and the news media have chosen to emphasize a speculative conclusion from our report (1) rather than the critical points that acid precipitation is a by-product of the combustion of fossil fuels, is falling over most of the eastern United States, and may have potentially serious ecological effects.

It seems clear that this regional "problem" is a recent phenomenon in the eastern United States, since (i) bulk precipitation samples collected during the first half of this century in the eastern United States contained significant amounts of HCO₃⁻ and were not as acid as samples collected since 1950 (2, 3); (ii) acid precipitation has been falling on most of the northeastern United States since at least 1955–1956, yet both the intensity and particularly the area of acid deposition (pH < 5.6) have increased markedly since then (3); (iii) records from the Hubbard Brook Experimental Forest in New Hampshire show that, although the concentration was variable (figure 1 in (1)), the annual H⁺ input in precipitation increased by 36 percent during the 10-year period from 1964–1965 through 1973–1974 (4); (iv) based on a stoichiometric formation process, the neutralizing component (5) in precipitation samples from central New York State was much lower after 1950 than before, and at Hubbard Brook the neutralizing component decreased from 40 μeq/liter in 1955–1956 to 25 μeq/liter in 1965–1966 and to 18 μeq/liter by 1973–1974, even though in the 1955–1956 and 1965–1966 samples dry fallout was excluded and in the 1973–1974 samples dry fallout was not excluded (3); and (v) although the SO₄²⁻ concentrations in precipitation samples from central New York State dropped during the mid-1950's, the NO₃⁻ concentrations have increased since then (2), and the contribution of SO₄²⁻ to precipitation acidity (based on a stoichiometric balance) dropped from 78 to 65 percent between 1955 and 1973, whereas the contribution of NO₃⁻ increased from 22 to 30 percent during the same period (3).

Whether particle removal from combustion gases has contributed significantly to the increased regional acidity of precipitation remains an unanswered question. However, the following points should be noted: (i) no other explanation has been put forth by Newman or others to explain the results of Gorham (6) and particularly Overrein (7), as cited in our report (1), which apparently show that particles in smoke are very effective in neutralizing acidity in local precipitation; (ii) likewise, no alternate explanation has been offered for the "substantiated" recent drop in SO₄²⁻ concentrations in central New York precipitation, coexisting with low pH values, whereas earlier high concentrations of SO₄²⁻ in precipitation samples coexisted with higher pH values [also substantiated (2, 3)]; and (iii) fly ash may be highly alkaline and produce high pH values in water suspensions (8). In view of the importance of aerosols and larger particles in neutralizing H⁺ in bulk precipitation samples, we would like to see some field or experimental data to support Newman's claim that particle removal may not permit "appreciable quantities of SO₂ to be converted to acid" (emphasis ours).

Important points that should not be overlooked are that the acid precipitation problem in the northeastern United States is due to increased amounts of strong acids (H₂SO₄ and HNO₃) in precipitation coincident with increased combustion of fossil fuels and to the regional dispersal of combustion gases from taller smokestacks.

Although we cannot say with certainty when precipitation in the northeast generally became acid (pH < 5.6), that is, whether it was 20 or 35 years ago, it seems that the major change may have been associated with the other dramatic changes in the precipitation chemistry of the mid-1950's (1). Although the precise date is elusive, it is clear that the pattern and intensity of acid deposition are recent and increasing, that the root cause is most likely the combustion of fossil fuels, and that this problem may be further exacerbated by "careless rush to solve the energy crisis."

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References and Notes
4. Based on a regression equation, Y = 0.033 X² + 0.83, where Y is the H⁺ input in kilograms per hectare and X is the year. The correlation coefficient was .74 and the probability of a large value was .01.
5. By "neutralizing component" we mean all cations except H⁺; in excess of that contributed by sea salt (3).

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