
Abstract. Hydrogen ions in precipitation are correlated much more closely with sulfate than with nitrate, whereas ammonium ions are correlated more closely with nitrate than with sulfate. Target loadings of 14 to 16 kilograms of wet sulfate deposition per hectare per year, instead of 20 as suggested hitherto, are probably necessary to produce average pH values of 4.6 to 4.7, the approximate boundary levels for damage to aquatic ecosystems. Cluster analysis reveals that there are three linked groups of ions related to air pollution, agriculture, and sea spray.

Statistical examination of the correlations between volume-weighted, mean annual ionic concentrations in wet deposition at stations operated by the U.S. National Atmospheric Deposition Program east of 95°W indicates that concentrations of H⁺ are predicted better by concentrations of SO₄²⁻ than by NO₃⁻ or the sum (SO₄²⁻ + NO₃⁻). In assessing sources of acidity in precipitation, however, H⁺ is usually assigned stoichiometrically to SO₄²⁻ and NO₃⁻ except in maritime areas where SO₄²⁻ from sea spray may be subtracted (1). The assumption is that oxides of sulfur and nitrogen are equally likely to produce acids, although these may be partially neutralized in the atmosphere by NH₃ from coal combustion and agriculture or by calcareous particulates from fly ash or soil (2). Nevertheless, it is conceivable that emissions higher in one of the two gaseous oxides may also be enriched in alkaline neutralizing materials, so that the other oxide has a greater potential to cause acid precipitation. Alternatively, alkaline materials may react more effectively with one of the two oxides or may more closely follow its transport, transformation, and rainout-washout behavior, leaving the other as the more important acid precursor. These possibilities have not been addressed in relation to acid deposition, although differential behavior of gaseous HCl and SO₂ in northern British cities has been suggested (3).

Let us assume that acid deposition is caused by the conversion of SO₂ and oxides of nitrogen (NOₓ) to acids, and that the resultant H⁺ is partially neutralized by atmospheric NH₃ and calcium carbonate from various sources (4). Other ions contributing to the charge balance are statistically insignificant. Then the sum (H⁺ + NH₄⁺ + Ca²⁺) should equal the sum (SO₄²⁻ + NO₃⁻). Statistics for 33 stations in 1980 and 49 in 1981 are consistent with this hypothesis. The structural regression, used instead of normal regression because neither variable is dependent (5), is (in microequivalents per liter)

\[ (\text{H}^+ + \text{NH}_4^+ + \text{Ca}^{2+}) = 0.982(\text{SO}_4^{2-} + \text{NO}_3^-) - 6.02 \]

\[ r^2 = 0.98 \]

The chief individual correlation (Fig. 1) is between H⁺ and SO₄²⁻ (r² = 0.85). The next highest correlation is between NO₃⁻ and SO₄²⁻ (r² = 0.73), followed by that between H⁺ and NO₃⁻ (r² = 0.63). Corrections for the influence of maritime sea spray are negligible.

If SO₂ and NOₓ, after reaction with substances in the atmosphere, are equally prone to produce H⁺, one would expect H⁺ to correlate most strongly with (SO₄²⁻ + NO₃⁻), provided that the variances are comparable, as in this case. In fact, and contrary to McNaughton’s analysis of a much smaller number of sites (6), the correlation is slightly less (r² = 0.83) than that between H⁺ and SO₄²⁻ alone.

At eight sites in Pennsylvania, New York, and New Hampshire H⁺ exceeds SO₄²⁻ (by 1 to 10 μeq liter⁻¹); at these sites some H⁺ must be related to NO₃⁻. Moreover, in dilute Minnesota precipitation (pH range, 3.9 to 6.4; median, 5.1) H⁺ is weakly correlated with NO₃⁻ but not with SO₄²⁻ (7). From 1964 to 1979, NO₃⁻ also increased at Hubbard Brook, New Hampshire, while SO₄²⁻ decreased and H⁺ showed no change (8). Despite these individual cases, much of the correlation between H⁺ and NO₃⁻ over the broad geographic range examined here is probably due to their strong mutual correlation with SO₄²⁻.

There is a better correlation between NH₄⁺ and NO₃⁻ than between NH₄⁺ and SO₄²⁻ (r² = 0.47 and 0.30, respectively); the same is true of Ca²⁺, to a much lesser degree (r² = 0.30 and 0.23). The sum of the base cations (NH₄⁺ + Ca²⁺) exceeds NO₃⁻ on average by 2 μeq liter⁻¹ (Fig. 1).

It appears from these correlations that H⁺, which averages 82 percent of SO₄²⁻, is more closely correlated to that anion than to NO₃⁻, which it exceeds almost twofold. Residuals (Studentized) from a variety of pairwise chemical regressions provide further evidence. Those from plots of H⁺ and NO₃⁻ on SO₄²⁻ are not significantly correlated, contrary to ex-

**Fig. 1.** The relations between various ions and SO₄²⁻ in precipitation in the eastern half of the United States, shown as structural regressions (5) with neither variable dependent. Data from 1981 and 1982 are similar; scatter plots indicate linearity of regression. The mean annual precipitation for the region, 88.7 cm, is used to convert SO₄²⁻ concentrations to deposition, the correlation between precipitation and SO₄²⁻ concentration being negligible (r² = 0.035).
pectations if NO$_3^-$ are just as likely as SO$_2$ to produce acidity. By contrast, residuals from plots of NH$_4^+$ and Ca$^{2+}$ versus SO$_2^-$ are strongly correlated, as expected if SO$_2$ is a major source of H$^+$. Nevertheless, the recent and projected increases of NO$_x$ emissions (8) are a cause for concern if they lead to an excess of NO$_3^-$ over base cations in precipitation.

The relation of H$^+$ concentration and precipitation pH to wet SO$_2^-$ deposition is of great interest in connection with the atmospheric loading of SO$_2^-$ that is likely to be the target of any emission-control strategy. Precipitation below the pH range 4.6 to 4.7 is regarded as damaging to sensitive aquatic ecosystems (11). Figure 1 shows that 20 kg of wet SO$_2^-$ per hectare per year, suggested recently as an appropriate target (12), produces an average pH in precipitation of 4.44, well below the damage threshold. According to Fig. 1, much lower loadings of SO$_2^-$, 14 to 16 kg ha$^{-1}$ year$^{-1}$, produce precipitation acidities at the damage threshold of pH 4.6 to 4.7.

The minimum volume-weighted, mean annual pH of precipitation in remote areas scarcely influenced by air pollution is believed to be about 5.0 (13). Figure 1 indicates that in the eastern United States this pH is produced by a wet SO$_2^-$ loading just above 10 kg ha$^{-1}$ year$^{-1}$.

Figure 1 provides only an approximate estimate of the pH that will actually result from specific reductions of wet SO$_2^-$ loadings to 14 to 16 kg ha$^{-1}$ year$^{-1}$, because it shows the pH response to simultaneous changes in loadings of all ions. Each control technique will have a different effect upon the concentrations and interactions of SO$_2$, NO$_x$, and base cations, so that the precise reduction in precipitation pH will require separate investigation.

The mean SO$_2^-$ deposition for all sites in the eastern United States is 23.1 kg ha$^{-1}$ year$^{-1}$. (The relatively small number of sites in the less polluted western and southern regions may be counterbalanced by the choice of only rural sites in the more heavily polluted north and east.) The suggested target loadings of 14 and 16 kg ha$^{-1}$ year$^{-1}$ are 61 and 69 percent, respectively, of the mean SO$_2^-$ deposition, and only 31 and 35 percent, respectively, of the maximum deposition observed.

As shown for North America as a whole (14), the three environmental factors important in determining precipitation chemistry in the eastern United States are air pollution, agriculture, and sea spray. A cluster analysis (BMDP, PL1M, distance-measure ABSCORR, average-linkage method) of the ten ions in Fig. 2 supports this conclusion. Air pollution is clearly the major source of ions; SO$_2^-$ plus NO$_3^-$—largely anthropogenic (15)—make up 91 percent of the total ions, and H$^+$ alone accounts for 54 percent of the cations. These air pollution variables form a tight group and are less closely linked to a second group, NH$_4^+$ and Ca$^{2+}$. It is known that NH$_3$ is present in emissions from fossil-fuel combustion; Ca$^{2+}$ is a component of fly ash.

The linkage between NH$_4^+$ and Ca$^{2+}$ can also be partly agricultural; NH$_4^+$ is a fertilizer and a product of animal wastes, whereas Ca$^{2+}$ is a component of carbonate and silicate soil minerals blown into the atmosphere after cultivation (as well as dust roads and construction sites). Two predominantly agricultural variables are only loosely connected. Both K$^+$ and PO$_4^{3-}$ are major fertilizers and are also present in windblown soil.

Another group of variables, Cl$^-$, Na$^+$, and Mg$^{2+}$, reflects the influence of sea spray. There is a close correlation between Na$^+$ and Cl$^-$ ($r^2 = 0.81$), and the average Na$^+$ exceeds the amount pre-
dicted from the Na/Cl ratio of seawater by only 1 µeq liter⁻¹. However, Mg²⁺ is much less closely linked to Na⁺ and Cl⁻, probably because it is also related significantly to the agricultural components of Ca²⁺ and NH₄⁺. Like Ca²⁺, Mg²⁺ is a component of windblown soil.

A three-cluster analysis (BMDP, K-means, no standardization) of the 49 sites studied in 1981 reveals a geographical pattern of concentric rings related to concentrations of the major pollutant ions, SO₄²⁻, H⁺, and NO₃⁻. All three are high at 15 sites subject to severe air pollution in northern Illinois and Indiana through Ohio, West Virginia, Virginia, and Pennsylvania to New York. The same ions are of intermediate concentration at 16 surrounding sites in Michigan, southern Illinois, Tennessee, the Carolinas, New York, New Hampshire, and southern Maine. A third group, low in these ions, forms an outer ring of 18 sites in Minnesota, Wisconsin, Upper Michigan, Arkansas, Mississippi, Florida, Georgia, Tennessee, North Carolina, and northern Maine. In the most polluted group of sites, H⁺ averages 61.7 µeq liter⁻¹ (pH 4.21) and about equals the sum of the two base cations. Wet deposition of the most polluted group is approximately twice as great (31 kg ha⁻¹ year⁻¹) as in the least polluted group (15 kg ha⁻¹ year⁻¹).

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References and Notes
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12. Recommended by Canadian members of work group on impact assessment, final report under the United States-Canada Memorandum of Intent on Transboundary Air Pollution, 1983.
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