Reports

Acid Rain: Ionic Correlations in the Eastern United States, 1980–1981

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 SO_4^{2-} than by NO_3^- or the sum ($SO_4^{2-} + NO_3^-$). In assessing sources of acidity in precipitation, however, H^+ is usually assigned stoichiometrically to SO_4^{2-} and NO_3^- except in maritime areas where SO_4^{2-} 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 NH_3 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 SO_2 in northern British cities has been suggested (*3*).

Let us assume that acid deposition is caused by the conversion of SO_2 and oxides of nitrogen (NO_x) to acids, and that the resultant H^+ is partially neutralized by atmospheric NH_3 and calcium carbonate from various sources (*4*). Other ions contributing to the charge balance are statistically insignificant. Then the sum ($H^+ + NH_4^+ + Ca^{2+}$) should equal the sum ($SO_4^{2-} + NO_3^-$). 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)

$$(H^+ + NH_4^+ + Ca^{2+}) = 0.982(SO_4^{2-} + NO_3^-) - 6.02$$

$$r^2 = 0.98$$

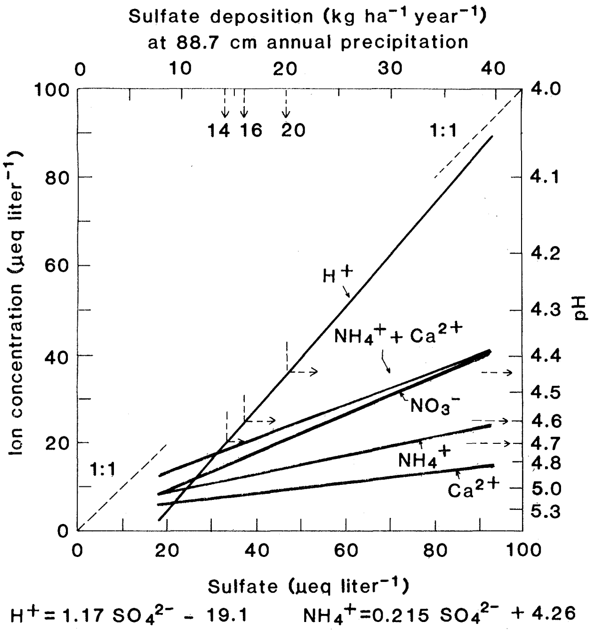
The chief individual correlation (Fig. 1) is between H^+ and SO_4^{2-} ($r^2 = 0.85$). The next highest correlation is between NO_3^- and SO_4^{2-} ($r^2 = 0.73$), followed by that between H^+ and NO_3^- ($r^2 = 0.63$). Corrections for the influence of maritime sea spray are negligible.

If SO_2 and NO_x, after reaction with substances in the atmosphere, are equally prone to produce H^+, one would expect H^+ to correlate most strongly with ($SO_4^{2-} + NO_3^-$), 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 ($r^2 = 0.83$) than that between H^+ and SO_4^{2-} alone.

At eight sites in Pennsylvania, New York, and New Hampshire H^+ exceeds SO_4^{2-} (by 1 to 10 μeq liter^{-1}); at these sites some H^+ must be related to NO_3^-. Moreover, in dilute Minnesota precipitation (*p*H range, 3.9 to 6.4; median, 5.1) H^+ is weakly correlated with NO_3^- but not with SO_4^{2-} (*7*). From 1964 to 1979, NO_3^- also increased at Hubbard Brook, New Hampshire, while SO_4^{2-} decreased and H^+ showed no change (*8*). Despite these individual cases, much of the correlation between H^+ and NO_3^- over the broad geographic range examined here is probably due to their strong mutual correlation with SO_4^{2-}.

There is a better correlation between NH_4^+ and NO_3^- than between NH_4^+ and SO_4^{2-} ($r^2 = 0.47$ and 0.30, respectively); the same is true of Ca^{2+}, to a much lesser degree ($r^2 = 0.30$ and 0.23). The sum of the base cations ($NH_4^+ + Ca^{2+}$) exceeds NO_3^- on average by 2 μeq liter^{-1} (Fig. 1).

It appears from these correlations that H^+, which averages 82 percent of SO_4^{2-}, is more closely correlated to that anion than to NO_3^-, which it exceeds almost twofold. Residuals (Studentized) from a variety of pairwise chemical regressions provide further evidence. Those from plots of H^+ and NO_3^- on SO_4^{2-} are not significantly correlated, contrary to ex-



$H^+ = 1.17\ SO_4^{2-} - 19.1$ $NH_4^+ = 0.215\ SO_4^{2-} + 4.26$

$NO_3^- = 0.431\ SO_4^{2-} + 0.416$ $Ca^{2+} = 0.117\ SO_4^{2-} + 3.85$

Fig. 1. The relations between various ions and SO_4^{2-} 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 SO_4^{2-} concentrations to deposition, the correlation beween precipitation and SO_4^{2-} concentration being negligible ($r^2 = 0.035$).

pectations if NO_x are just as likely as SO_2 to produce acidity. By contrast, residuals from plots of H^+ and SO_4^{2-} on NO_3^- are strongly correlated, as expected if SO_2 is a major source of H^+. Furthermore, residuals from plots of NH_4^+ and Ca^{2+} versus SO_4^{2-} correlate significantly with residual NO_3^-, whereas, after plots versus NO_3^-, residuals of these cations do not correlate with residual SO_4^{2-}. Residuals of both NH_4^+ and Ca^{2+} plotted on SO_4^{2-} and on NO_3^- exhibit negative correlations with residual H^+ plotted on the same two anions, but much more strongly in the case of SO_4^{2-}.

This analysis suggests that we need to take a much closer look at the abundance of NH_4^+ and Ca^{2+} in relation to the proportions of SO_2 and NO_x in urban-industrial emissions, and at how these cations from various sources interact with SO_2, SO_4^{2-}, NO_x, and NO_3^- during long-range transport, rainout, and washout. For example, Harriss has pointed out (*9*) that NO_x, NH_3, and Ca^{2+} have major sources—automobiles, agriculture, and windblown soils—with low-altitude emissions into the planetary boundary layer, whereas SO_2, primarily from smokestacks, is more prone to enter the free troposphere where contact with base cations is less likely.

This analysis also supports the focus of emission control upon SO_2, both because SO_4^{2-} is more abundant and more strongly correlated with H^+ than NO_3^- and because the sum of base cations (NH_4^+ + Ca^{2+}) is on average sufficient to counterbalance the NO_3^- resulting from NO_x emissions. Moreover, when NH_4^+ is balanced by NO_3^-, it is not an acidifying agent in the soil as it is when balanced by SO_4^{2-} (*10*). 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 *p*H to wet SO_4^{2-} deposition is of great interest in connection with the atmospheric loading of SO_4^{2-} that is likely to be the target of any emission-control strategy. Precipitation below the *p*H range 4.6 to 4.7 is regarded as damaging to sensitive aquatic ecosystems (*11*). Figure 1 shows that 20 kg of wet SO_4^{2-} per hectare per year, suggested recently as an appropriate target (*12*), produces an average *p*H in precipitation of 4.44, well below the damage threshold. According to Fig. 1, much lower loadings of SO_4^{2-}, 14 to 16 kg ha^{-1} $year^{-1}$, produce precipitation acidities at the damage threshold of *p*H 4.6 to 4.7.

The minimum volume-weighted, mean annual *p*H 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 *p*H is produced by a wet SO_4^{2-} loading just above 10 kg ha^{-1} $year^{-1}$.

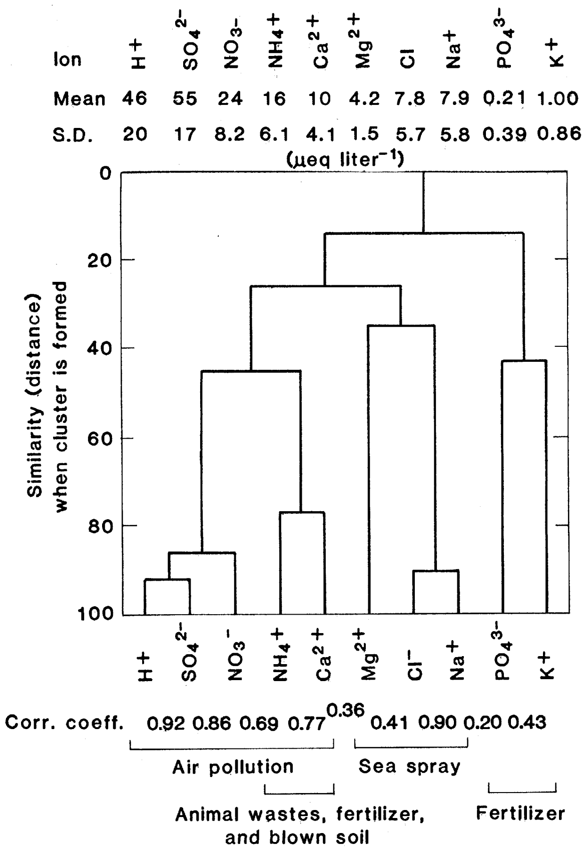


Fig. 2. A cluster analysis by average linkage of correlations among ten ions in wet deposition in the eastern United States (the lower the junction, the closer the linkage of clustered ions). Groups have been rotated successively upward to maximize end-member linkages between them.

Figure 1 provides only an approximate estimate of the *p*H that will actually result from specific reductions of wet SO_4^{2-} loadings to 14 to 16 kg ha^{-1} $year^{-1}$, because it shows the *p*H 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 *p*H will require separate investigation.

The mean SO_4^{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_4^{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, P1M, 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_4^{2-} plus NO_3^-—largely anthropogenic (*15*)—make up 91 percent of the total anions, 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 from dirt 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 predicted from the Na/Cl ratio of seawater by only 1 μeq $liter^{-1}$. However, Mg^{2+} is much less closely linked to Na^+ and Cl^-, probably because it is also related significantly to the agricultural components of Ca^{2+} and NH_4^+. Like Ca^{2+}, Mg^{2+} 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, SO_4^{2-}, H^+, and NO_3^-. 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 $liter^{-1}$ (*p*H 4.21) and is almost twice the concentration of the summed base cations ($NH_4^+ + Ca^{2+}$), whereas in the least polluted group it averages 21.4 μeq $liter^{-1}$ (*p*H 4.67) and about equals the sum of the two base cations. Wet SO_4^{2-} deposition in 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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Thermogenic Gas Hydrates in the Gulf of Mexico

Abstract. *Thermogenic gas hydrates were recovered from the upper few meters of bottom sediments in the northwestern Gulf of Mexico. The hydrates were associated with oil-stained cores at a water depth of 530 meters. The hydrates apparently occur sporadically in seismic "wipeout" zones of sediments in a region of the Gulf continental slope at least several hundred square kilometers in area.*

We report here the occurrence of thermogenic gas hydrates in ocean sediments. The hydrates were discovered fortuitously during geochemical surveys involving piston coring operations at 27°47′N and 91°30′W in 530 to 560 m of water in the northwestern Gulf of Mexico. Hydrates were observed dispersed in carbonate rubble in three cores and ranged in size from minute crystals to objects several centimeters in diameter. Although the cores were severely disrupted by gas expansion during the 10- to 15-minute interval between coring and retrieval on deck, the gas hydrates appeared to be distributed from the top of the core to a sediment depth of at least several meters. Samples of the hydrates were preserved in liquid nitrogen for laboratory analysis.

Gas hydrates are solid icelike clathrate structures in which gases are occluded in a crystalline water lattice under appropriate conditions of high pressure and low temperature. Hydrates can exist in two forms. Structure I gas hydrates have a symmetrical shape and exclude molecules larger than ethane. Structure II hydrates are slightly larger and can accommodate not only methane and ethane but also propane and isobutane. Molecules as large or larger than *n*-butane cannot be accommodated in either lattice structure (*1*). The stability zone of gas hydrates in marine sediments is generally found in continental slope areas where water depths are greater than 500 m and water temperatures at the bottom are near 0°C. Although a wide range of molecules (methane, ethane, propane, isobutane, CO_2, N_2, O_2, and H_2S) can form hydrates, methane and possibly CO_2 are the only gases found in sufficient quantities in deep-sea sediments to form gas hydrates. Under conditions of temperature and pressure appropriate for hydrate stability, gas concentrations must exceed solubility levels before hydrates can form. Therefore, methane hydrates can be found only in regions where there is significant biogenic methane production or where there is migration of thermogenic gases from deeper horizons. Thermogenic gases do not form hydrates at their site of production because the ambient temperatures are outside the stability zone of hydrates.

The presence of gas hydrates in marine sediments has long been suspected on the basis of laboratory stability studies and the existence, in some sediments, of a bottom-simulating reflector (BSR)—an anomalous acoustic reflector that approximately parallels the bottom topography, cutting across bedding planes and deepening with increasing water depth (*2*). The BSR is thought to represent the lower boundary of gas hydrate stability, below which gas hydrates decompose because of increased temperatures. The existence of hydrates has been inferred in many ocean areas on the basis of seismic records (*3*). Gas hydrates appear to be common in the continental margins of all the oceans. However, to our knowledge the only direct observations of gas hydrates in marine sediments have been in shallow cores from the Black Sea (*4*); at a subbottom depth of 238 m on leg 76 of the Deep Sea Drilling Project/International Phase of Ocean Drilling (DSDP/IPOD) in the Blake Outer Ridge of the Atlantic Ocean (*5*); and on DSDP/IPOD legs 66, 67, and 84 in the Middle America Trench off Mexico and Guatemala (*6*). Because hydrates are not stable at atmo-