

Free Acid in British Soils

UNDER the humid climate of northern and western Britain organic materials often accumulate as *mor*¹ humus layers on well-drained woodland soils or as bog peats in wetter locations. Both types of humus are characteristically very acid, and this communication examines the possibility that sulphuric acid is mainly responsible for their low pH values.

To study this question in the wetter habitats, water samples were collected from pools on seven areas of bog, listed in order of increasing hydrogen ion concentration in their waters: Cooran Lane, Galloway; Drumbasbie and Strathy, Sutherland; Rannoch Moor; Tregaron, Cardiganshire; Dergoals and Kilkahockadale, Galloway; Moor House, Cumberland; Coom Rigg, Northumberland. All exhibit a good cover of *Sphagnum* moss, a sign that the peats are very wet and in a more or less natural condition. Moreover, they are so deep and extensive that the bog surfaces probably depend for their ion supply almost wholly upon the atmosphere.

Hydrogen ion concentration in the seven areas ranges from 0.03 to 0.13 m.equiv./l., averaging 0.066 m.equiv./l.; while sulphate ranges from 0.06 to 0.24 m.equiv./l., and averages 0.133 m.equiv./l. The coefficient of correlation (r) between free hydrogen ions and sulphate is 0.964, a highly significant value which may be increased by taking into account the appreciable amount of sulphate reaching the bogs in blown sea spray. This fraction may be estimated by assuming all chlorides in these waters to be derived from sea spray^{2,3}, and dividing the chloride values by 9.7—the ratio of chloride to sulphate in sea water. On subtracting the sea spray contribution from total sulphate, the correlation coefficient between hydrogen ions and the remaining sulphate becomes 0.985. Such a high coefficient strongly suggests that the low pH values of these bog waters are indeed due to sulphuric acid. A similar correlation has been observed for individual pools within the Moor House bog⁴. The regression of hydrogen ions upon corrected sulphate in the seven bog areas follows the formula $y = 0.556x + 0.006$.

The highest acidities are recorded from bogs near industrial areas, while the lowest come from sites remote from industry. Since fuel combustion produces large amounts of sulphur dioxide, which oxidizes to sulphuric acid, bog acidities are directly increased by industrial development nearby. Ringinglow Bog outside Sheffield provides an extreme example, with water analyses from this bog—now in a far from natural state—yielding hydrogen ion and sulphate concentrations of 0.57 and 0.96 m.equiv./l. respectively. In this connexion also, the influence of air pollution on rain acidity is clearly evident in the English Lake District, where the pH of precipitation averages less than 4.5 and may occasionally^{2,3} go below 4.0.

It may be noted that in these bog waters hydrogen ions are only equivalent to 61 per cent of sulphate (exclusive of that from sea spray). In the Lake District rain the proportion is rather similar.

The free acid in *mor* humus layers was investigated by expressing the soil solution, with the aid of a hydraulic press, from sixteen samples collected in Lake District oakwoods on Silurian substrata. These *mors* overlie heavily leached mineral soils transitional between brown earths and podzols, and exhibiting strong profile development¹.

Hydrogen ion concentration in the *mor* waters ranges from 0.02 to 0.36 m.equiv./l., averaging

0.109 m.equiv./l.; while sulphate ranges from 0.26 to 1.01 m.equiv./l. and averages 0.508 m.equiv./l. The correlation between free hydrogen ions and sulphate (after subtraction of sulphate from sea spray) is again highly significant, with $r = 0.872$. Once more, sulphuric acid seems likely to be the main factor responsible for low soil pH values, and must greatly enhance leaching. The regression of hydrogen ions upon corrected sulphate follows the formula $y = 0.307x - 0.033$.

The association between hydrogen ions and sulphate is stronger for the bog waters than for the *mor* soil solutions ($r = 0.985$ as against 0.872). Moreover, the proportion of sulphate balanced by hydrogen ions is much greater in the bog waters than in the *mor* solutions (61 as against 24 per cent). It seems likely that an appreciable part of the *mor* acid is neutralized by bases from mineral soil particles embedded in the humus, in which case a lower correlation between hydrogen ions and sulphate is not surprising. It may also be remarked that the average corrected sulphate level in the *mors* (0.46 m.equiv./l.) is considerably above the highest bog value (0.24 m.equiv./l.), owing probably to concentration of the interstitial water in these well-drained soils by evaporation.

As in the case of the bog waters, air pollution can account for much of the free acid in Lake District *mors*³. However, even in areas without much industry, sulphuric acid will probably be produced from decomposing organic sulphur compounds⁵. Support for this view may be found in the inter-correlations between free hydrogen ions, sulphate and dissolved organic carbon in waters of Nova Scotian lakes, draining acid peaty soils on substrata low in lime⁶.

In conclusion, it must be pointed out that the pH values of both bog waters and *mor* soil solutions are a good deal higher than those obtained by direct insertion of a durable glass electrode into fresh soil. For example, at Moor House the pH range of 3.7–4.1 for six surface pools may be compared with a range of 3.3–3.9 for eight fresh peats from the same area; while the pH range of ten Lake District *mor* solutions, 3.8–4.6, may be compared with a range of 3.2–3.5 for the fresh soil. The much lower pH values of the fresh soils are presumably due to a 'suspension effect' on the glass electrode by hydrogen ions adsorbed on soil colloids. Exchangeable hydrogen ions are abundant in both woodland *mors* and bog peats^{1,7}, and must be, like the sulphuric acid free in solution, of great importance for soil development.

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Influence of Water-Content of Sand on Rate of Uptake of Rubidium-86

THE relationship between nutrient absorption and the moisture content of the soil has been the object of numerous investigations. Complications arise, however, if an attempt is made to disentangle the separate processes involved. The growth of the plant itself is strongly influenced by the moisture content of the soil and the ionic equilibria between