THE EVALUATION OF PLANT-AVAILABLE SULPHUR IN SOILS

I. THE CHEMICAL NATURE OF SULPHATE IN SOME AUSTRALIAN SOILS

by C. H. WILLIAMS and A. STEINBERGS

Division of Plant Industry, C.S.I.R.O., Canberra, A.C.T.

Except under anaerobic conditions when reduced forms of sulphur, particularly sulphides, may predominate, most of the inorganic sulphur in soils usually occurs as sulphates. Under normal aerobic conditions the amounts of reduced sulphur compounds are generally small.

In the surface horizons of most well-drained acid soils nearly all of the sulphur is present in organic forms and only small amounts (usually only a few parts per million) of sulphate are present. In subsoil horizons, however, appreciable amounts of sulphate may accumulate and inorganic sulphur compounds may make up a major proportion of the total sulphur.

The occurrence of sulphates as soluble salts of sodium, magnesium, and calcium in soils is well known, but, except under arid or poorly drained conditions the presence of appreciable amounts of soluble sulphates is likely only in subsoil horizons. Insoluble sulphates may also occur, although precise knowledge of their true chemical nature is somewhat limited. Barium sulphate is a possible form of insoluble sulphate in some soils but, if present, the small amounts likely make positive identification difficult. Beattie and Haldane, however, have identified barytes occurring as small concretions in certain New South Wales soils. Williams, Williams, and Scott have recently reported the occurrence of insoluble sulphate associated with calcium carbonate in calcareous soils in Scotland. This too could be a common form of insoluble sulphate in soils.

Sulphate may also be retained in soils by adsorption on clay.
colloids. Ensminger 2 found that most surface horizons and light textured soils had only low capacity to adsorb sulphate but that appreciable adsorption was possible in B- and C-horizons. Kamp-rath, Nelson and Fitts 6 showed that the amount of sulphate adsorbed by soils was influenced by the type of clay mineral present and by pH. Steinbergs (unpublished) has shown that sulphate adsorption by soils and clays reaches a maximum in the pH range 2 to 4.

It is apparent that insoluble sulphates and adsorbed sulphate probably account for most of the inorganic sulphur retained by soils under leaching conditions. An examination has been made of a number of Australian soils with the object of assessing the nature and relative importance of sulphates as components of the total soil sulphur. Acid, alkaline, and calcareous soils representing both surface and subsoil horizons have been examined, together with a number of naturally occurring and artificially prepared samples of calcium carbonate.

**METHODS**

Total sulphur in soils was determined by the method of Steinbergs 10 and soluble sulphate by extraction with 0.15% calcium chloride as described by Williams and Steinbergs 15. Total sulphur in calcium carbonate was determined by direct digestion of the sample by the method of Johnson and Nishita 4. Adsorbed sulphate was extracted by the method of Ensminger 2 using potassium dihydrogen phosphate solution containing 500 ppm of phosphorus. Adsorbed sulphate was also determined by “calcium carbonate extraction”. For this extraction 0.5 g of sulphur-free calcium carbonate was added to 5 g of soil and shaken overnight with 20 ml of water. Sulphate was determined in these and all other extracts by the method of Johnson and Nishita 4.

Sulphate adsorption was measured by shaking 5 g of soil with 20 ml of water or acid containing 250 µg of sulphur (added as potassium sulphate) for 18 h at 20°C. Sulphate remaining in solution was then determined.

Calcium carbonate in soils was determined by the method of Hutchinson and MacLennan as described by Piper 7, soil pH using a glass electrode and a 1 : 5 suspension of soil in water, free iron oxides by the method of Williams 12 and free alumina by extraction of the soil with Tamm’s 11 acid oxalate reagent. Nitrogen was determined by a Kjeldahl method using selenium as a catalyst and calcium was determined using an E.E.L. flame-photometer and lanthanum to suppress possible interferences 13.