Sulfur

Sulfur (S) is an essential plant nutrient distributed heterogeneously throughout the earth's crust and soils. The element and its compounds exhibit five different oxidation states, including four in geological environments and as S⁶ in gases and sulfates (Ure and Berrow 1982). Total S concentrations range widely from 3 to over 10 000 mg S/kg, with a mean around 430 mg S/kg. Pyrite (FeS₂) and pyrrhotite (Fe_nS_{n+1}) are common sulfide minerals, and many of the metals of economic importance occur as sulfides (Ure and Berrow 1982).

Many different forms of organic and inorganic fractions of S occur in soils and in soil OM (Williams 1975). In general, organic S fractions are highly correlated with TOC and TSN. The C/N/organic-S ratio of soils is commonly around 140:10:1.3 (Probert and Samosir 1983). Long-term studies on cultivated soils, however, have shown a decline in organic S levels of 50% in 20–30 years (Kamprath and Till 1983).

In aerobic soils of humid regions, most S is in the organic fraction. As with N, this organically bound S must be mineralised before it becomes available to plants, predominantly as sulfate (SO_4^{2-}). There are important exceptions, however. For example, sulfides (S^{2-}) predominate in acid-sulfate soils (see Chapter 20), in recent marine deposits, and in many miningwaste dumps, while elemental S can exist in and around areas of recent volcanic activity and associated soils. Inorganic, solid-phase S (notably gypsum; $CaSO_4.2H_2O$) is very common at the wetting front of soil profiles in semi-arid and arid regions of inland northern Australia (Rayment *et al.* 1983).

The reactive surfaces of highly weathered clays and the surfaces of Fe and Al oxides and hydroxides can adsorb relatively large amounts of SO_4^{2-} , but this propensity decreases as phosphate concentrations increase and as soils become less acidic (Kamprath and Till 1983). Sulfate ions can displace NO_3^{-} and Cl⁻ from anion exchange surfaces when present at similar soil solution activities. The chemical activity of SO_4^{2-} in soil solutions allows the formation of ionic species such as CaSO₄⁰ and AlSO₄¹⁺ (Adams 1974).

The focus of this chapter is on the chemical measurement of soil S, particularly as a plant nutrient. For interpretative information, refer to Lewis (1999).

Total S

Measurements of total S are undertaken to assess the size of the soil S pool. Concentrations >0.5% S and certainly >1.0% S also warn of the likely presence of potential or actual ASS (see Chapter 20). In general, total S is poorly correlated with plant response to applied S fertiliser, except when soil S reserves are very low. Total S is also a poor indicator of a soil's tendency to corrode concrete, except at concentrations of $\geq 1\%$ S, particularly under oxidising conditions.

Two methods for total soil S are included. The first is based on X-ray fluorescence with dry-powder pellets. The second is a combustion furnace method, similar to equivalent