Sulfur

Fig. 15.1 Sulfur response in wheat in Arsi, Ethiopian Highlands. Nutrients added are indicated; CK = control plot. Courtesy of Assefa Mena, Sokoine University and Ray Weil, University of Maryland

In the first edition I wrote: "Rapidly accumulating evidence indicates that sulfur deficiencies may be more widespread in the tropics than potassium deficiencies. Sulfur deficiencies have been unconsciously corrected by the use of sulfur-bearing fertilizers such as ammonium sulfate and single superphosphate. With the use of high-analysis sources that contain no sulfur, such as urea and triple superphosphate, reports of severe sulfur deficiencies have become widespread." That was an understatement.

The sulfur-bearing fertilizers actually contain more sulfur (S) than nitrogen (N) or phosphorus (P) (ammonium sulfate contains 21 percent N and 24 percent S; single superphosphate contains 9 percent P and 12 percent S), thereby preventing sulfur deficiencies (Weil and Mughogho 2000). On the positive side, atmospheric deposition of sulfur nowadays plays a major role, but higher-yielding crop cultivars require more nutrients because of their higher biomass. Weil and Mughogho also suspected that mineralization of soil organic sulfur, and manure applications that provide sufficient sulfur to produce 1 t/ha of grain crop yield, are unable to do so with higher-yielding cultivars (Fig. 15.1).

Widespread sulfur deficiencies and crop yield responses to sulfur have been reported throughout the tropics for over half a century, with Greenwood's (1951) work in the savannas of northern Nigeria being among the first. This contrasts with the history of field research on sulfur deficiency in the temperate region (Haneklaus *et al.* 2008), where major efforts started in the 1980s – with noteworthy exceptions, such as earlier research on Ultisols of the southeastern United States (Ensminger 1954, Kamprath *et al.* 1957).

One of the first tropical reports was from the Cerrado of Brazil, where McClung *et al.* (1959) observed crop responses to sulfur. In Central America, sulfur deficiencies are also widespread, particularly in Andisols, where their volcanic origin would lead one to assume that such soils would be high in available sulfur (Muller 1965, Bornemisza and Llanos 1967, Fitts 1970). Volcanic ash soils are often high in sulfates but sulfur is rapidly leached in humid climates (Hasan *et al.* 1970). In Africa, sulfur is limiting in Alfisols and Oxisols with annual rainfall greater than 600 mm (Bolle-Jones 1964). Sulfur deficiencies are known to occur in Asia, particularly the Indo-Gangetic Plain of southern Asia and in Malaysia (Olson and Englestad 1972). They also have been reported in Australia (Williams 1972), Hawaii (Fox *et al.* 1971) and Zambia (Vogt 1966).

Since the 1980s, reports of sulfur deficiencies from all over the tropics have continued (Kanwar and Mudahar 1986, Buri *et al.* 2000, Itanna 2005, Lilienfein *et al.* 2000, Weil and Mughogho 2000, Ribeiro *et al.* 2001, Yamada *et al.* 2007, Khurana *et al.* 2008, Weil 2011 and many others). From the temperate region, a book was published by the American Society of Agronomy with the noteworthy title, *Sulfur: A Missing Link between Soils, Crops and Nutrition*, edited by Joseph Jez (Jez 2008). However, generally little attention continues to be given to sulfur deficiency in spite of the fact that it not only decreases crop yields but decreases the formation of two amino acids in plants, methionine and cysteine, and hence of protein, with the direct detriment to human and animal nutrition.

Sulfur deficiency to plant growth occurs in a wide variety of soils. These are often sandy, well-drained and subject to leaching, with variable- or permanent-charge mineralogy, and low in soil organic matter (SOM). Soils subject to repeated annual burning are often sulfur-deficient because most of the plant s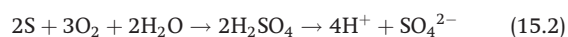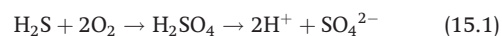ulfur is volatilized by fire. Sulfur-deficient soils generally occur in unpolluted inland areas where the atmosphere is low in sulfur.

Unlike nitrogen deficiency, which starts as chlorosis (yellowing) of the older leaves, sulfur deficiency starts as chlorosis of the younger leaves (shown Fig. 12.1). Chlorophyll meters or other spectrally based instruments can establish the degree of deficiency of nitrogen when aimed at the older leaves and for sulfur when aimed at the younger leaves. Iron deficiencies show similar symptoms, but since they occur only on calcareous soils, chlorosis of the youngest leaves in soils below pH 7.2 is likely to indicate sulfur deficiency.

15.1 The Sulfur Cycle

The sulfur cycle contains elements of both the nitrogen and phosphorus cycle. It resembles the nitrogen cycle in that the atmosphere plays an important role, although its sulfur content is very small. It also resembles the nitrogen cycle, in that most of the topsoil's sulfur is in the organic form and that sulfur undergoes similar mineralization–immobilization processes; and also as sulfate anions, like nitrate, can both be retained in subsoils by anion exchange and can be leached. The sulfur cycle resembles the phosphorus cycle in that the original sources of sulfur are primary minerals and that sulfur retention is important in soils high in iron and aluminum oxides. It differs from both cycles in that microbial oxidation–reduction (redox) reactions play a central role. Figure 15.2 shows the main stocks and flows.

Redox reactions are central to the sulfur cycle, and most are carried out by bacteria. Oxidation of elemental sulfur, sulfides and thiosulfates to sulfate are carried by the autotrophic genus *Thiobacillus* and the heterotrophic genera *Pseudomonas, Arthrobacter* and *Bacillus*. Autotrophic bacteria of the genera *Desulfovibrio* and *Desulfotomacalum* are responsible for the reduction of sulfates into sulfides and elemental sulfur (Brady and Weil 2008, Schoenau and Malhi 2008). The main oxidation reactions are the oxidation of hydrogen sulfide (H_2S) and elemental sulfur (S) to sulfate (SO_4^{2-}):

$$H_2S + 2O_2 \rightarrow H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \qquad (15.1)$$

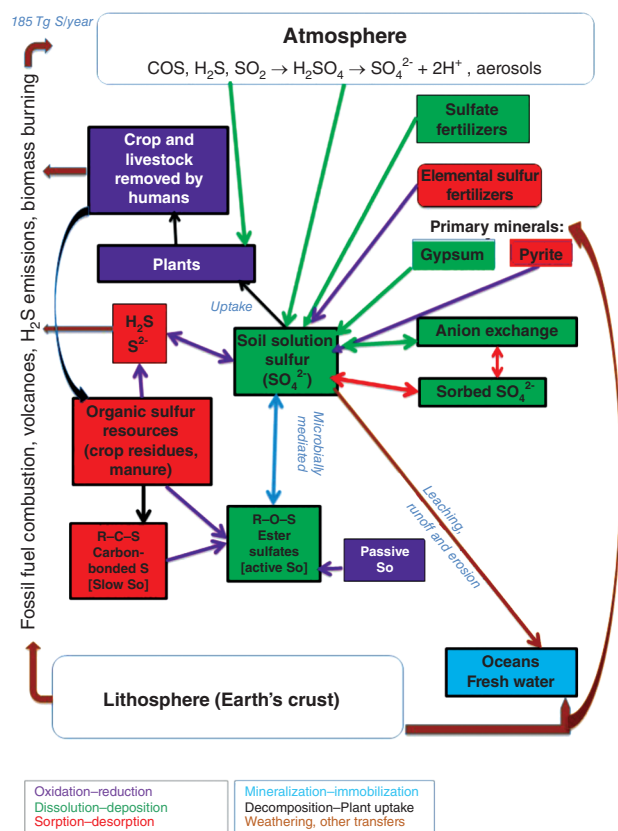$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \rightarrow 4H^+ + SO_4^{2-} \qquad (15.2)$$

Equation 15.2 is relevant when applying elemental sulfur as fertilizer, which is in the reduced state. This equation also partly explains the acidifying effect of ammonium sulfate fertilizers.

The main reduction reaction is the reduction of sulfate to sulfide using an electron acceptor, in this case an alcohol (RCH_2OH):

$$2RCH_2OH + SO4^{2-} \rightarrow 2RCOOH + 2H_2O + S^{2-} \qquad (15.3)$$

Sulfide then hydrolyzes to hydrogen sulfide, which provides a rotten egg smell in reduced soils and swamps.

185 Tg S/year

Fossil fuel combustion, volcanoes, H₂S emissions, biomass burning

Atmosphere
COS, H₂S, SO₂ → H₂SO₄ → SO₄²⁻ + 2H⁺ , aerosols

Sulfate fertilizers

Elemental sulfur fertilizers

Primary minerals:
Gypsum   Pyrite

Crop and livestock removed by humans

Plants

Uptake

H₂S S²⁻

Soil solution sulfur (SO₄²⁻)

Anion exchange

Sorbed SO₄²⁻

Organic sulfur resources (crop residues, manure)

Microbially mediated

R–C–S Carbon-bonded S [Slow So]

R–O–S Ester sulfates [active So]

Passive So

Leaching, runoff and erosion

Oceans Fresh water

Lithosphere (Earth's crust)

Oxidation–reduction	Mineralization–immobilization
Dissolution–deposition	Decomposition–Plant uptake
Sorption–desorption	Weathering, other transfers

Fig. 15.2 The global soil sulfur cycle. Assembled from Stevenson (1986), Parton *et al.* (1989), Ribeiro *et al.* (2001), Aita and Giacomini (2007), Brady and Weil (2008), Dick *et al.* (2008), Schoenau and Malhi (2008) and my own ideas. Stocks in green are mainly in the oxidized state, those in red are in the reduced state and those in purple are in both. The legend for the flows is in different colors.

15.1.1 Sources of Soil Sulfur

The main sulfur inputs to soils are from primary minerals, organic inputs and atmospheric deposition of sulfur.

The primary soil minerals are gypsum ($CaSO_4 \cdot 2H_2O$) and pyrite (FeS_2) in igneous rocks, also known as fool's gold. Gypsum is highly soluble in acid soils, rapidly producing SO_4^{2-} ions. It can accumulate in Aridisols (suborder Gypsids), which cover 28 million hectares in tropical deserts. Such accumulation has been recorded in Aridisols of northern Kenya (Hesse 1957) and the Ethiopian Rift Valley (Itanna 2005). Pyrite requires microbial oxidation to transform S into SO_4^{2-} as indicated in Fig. 15.2. The SO_4^{2-} ions are readily taken up by roots. Sulfide ions (S^{2-}) and S are in the reduced state and are not available to plants.

Organic inputs of plant origin, including manures, generally contain about 0.3 percent S in dry mass, but low-quality cattle manures in Africa contain about 0.1 percent

(Chapter 11). The factors affecting their decomposition in soils are presumed to be similar to organic nitrogen inputs, described in Chapter 13.

The atmosphere contains various forms of sulfur gases, including sulfur dioxide (SO_2), carbonyl sulphide (COS), H_2S, plus solid aerosols. Their main sources are volcanic eruptions, biomass burning, H_2S emissions from soils and wetlands, sea spray, SO_2 from electricity generation (burning high-sulfur coal) and the combustion of high-sulfur diesel fuels. The decomposition of organic resources, particularly under anaerobic conditions, also produces H_2S emissions. These gases are eventually oxidized to sulfuric acid (H_2SO_4) in the atmosphere, which along with nitric acid causes acid rain. Rainfall contributes sulfur from sea spray near the oceans. Atmospheric deposition rates were as high as 200 kg S/ha per year, downwind from industrial areas with no pollution controls (Stevenson 1986). They are now 8–15 kg S/ha per year around industrial areas with effective clean-air controls in rich countries, but not around rapidly developing industrial areas in the tropics. Brady and Weil (2008) estimate the atmospheric deposition to be very small, 1–4 kg S/ha per year, in Africa.

Atmospheric sulfur gases such as SO_2 can also be taken up by the stomata of plant leaves and by the surfaces of fruits and then converted into SO_4^{2-}. Dick *et al.* (2008) consider that a concentration of at least 60 ppm S in the atmosphere can provide adequate sulfur nutrition to plants, absorbed both by soils and the plants themselves.

15.1.2 Total Sulfur

In the temperate region, total topsoil sulfur is positively correlated with SOM content and inversely correlated with the degree of weathering. Olson and Englestad (1972) provided the following average topsoil values for total sulfur in the temperate region: 500 mg/kg for Mollisols, 400 mg/kg for Alfisols and 200 mg/kg for Ultisols. Following this reasoning, they assumed that most tropical soils would average about 100 mg/kg. A summary of eastern Australian soils by Williams and Steinbergs (1958) shows an average content of 167 mg/kg S. Andisols that are high in organic matter and allophane, however, have large quantities of total sulfur. A Eutrudand from Hawaii contained 1280 mg/kg S in its topsoil (Fox *et al.* 1971), while a clayey Oxisol under native savanna contained 251 mg/kg S and a sandy Ultisol only 40 mg/kg S, the latter two from Brazil (McClung *et al.* 1959).

Unlike phosphorus, the subsoil often contains significant quantities of sulfur, which is very relevant to soil fertility management, especially in the tropics.

In neutral and alkaline soils, sulfate salts of calcium and magnesium can accumulate.

15.1.3 Organic Sulfur

Most (> 95 percent) of the sulfur in topsoils outside of arid climates is in the organic form. In subsoils with variable-charge clays, the relationship often flips over, with the vast majority being inorganic sulfur because of sulfate retention

processes (Fig. 15.2). Hesse (1957) was probably the first to report such a profile pattern, in forest soils of Kenya, Uganda and Tanzania. The C:N:S ratio of SOM is about 126:10:1 for soils of Nigeria and eastern Australia, according to surveys by Oke (1971) and Williams and Steinbergs (1958).

Soil organic sulfur stocks can be grouped into three fractions depending on their redox status and turnover rates: ester sulfates, carbon-bonded sulfur and inert organic sulfur (So) (Fig. 15.2). The oxidized forms are the ester sulfates (R–O–S) and thioglucosides and sulfamates (R–N–S) where carbon is not directly bonded to sulfur. They are easily hydrolyzed into sulfates, and in the case of the esters they are easily cleaved by extracellular enzymes, largely aryl sulfatase, as in the ester phosphates described in the previous chapter. Carbon-bonded sulfides (R–C–S) comprise complex reduced forms that include the amino acids methionine, cysteine and cystine. Many are chemically recalcitrant to mineralization (Schoenau and Malhi 2008). Inert organic sulfur can range from 3 percent to 59 percent of the organic sulfur and has very slow turnover (Aita and Giacomini 2007).

These three fractions resemble the active, slow and passive soil organic carbon (SOC) fractions in the Century model (Parton *et al.* 1989). They are eventually mineralized under aerobic conditions at different turnover rates into SO_4^{2-} ions, which are taken up by plants (Fig. 15.2).

15.1.4 Mineralization

Barrow (1961) found that organic sulfur mineralization occurs at C:S ratios lower than 200, while organic compounds with a C:S ratio > 400 or a sulfur concentration of less than 0.15 percent S are immobilized into microbial biomass, but eventually mineralized. The processes could go either way in ratios between 200 and 400 C:S (Dick *et al.* 2008). Andisols and other soils that are high in allophane are often high in organic sulfur, but plants growing on these soils are often deficient in sulfur because the mineralization rate of SOM is very slow when intimately associated with allophane (Munévar and Wollum 1977).

Flushes of sulfur mineralization upon wetting of previously dried soils have also been observed by Barrow (1961). It seems logical to assume that the processes involved are similar to those governing nitrogen flushes – the Birch effect. In fact, Cooper (1972) found increased aryl sulfatase activity at the start of the rainy season after a 6-month dry season in Alfisols of northern Nigeria. This ectoenzyme is responsible for the mineralization of sulfate esters. The fate of the mineralized sulfur, however, may be different from that of nitrates because of the sulfur sorption capacity of many soils of the tropics.

15.1.5 Inorganic Sulfur

Sulfates are the main inorganic form of sulfur in aerobic soils, and plants take it directly from the soil solution by mass flow pulled by the transpiration stream. Sulfates represent less than 5 percent of the total soil sulfur in the topsoil since most sulfur is present in the three organic pools shown in Fig. 15.2. Sulfate fertilizers like gypsum rapidly dissolve in acid soils and are immediately available to plants unless microorganisms immobilize them earlier to satisfy their needs, but then they are subsequently mineralized and made available to plants – just like nitrogen.

Reduced sulfur fertilizers like elemental sulfur have to be oxidized into sulfate before they can be taken up by plants. The same is the case with the primary mineral pyrite. In anaerobic soils, most of the oxidized forms of sulfate (gypsum [either as a primary mineral or fertilizer], some of the organic ester sulfates and soil solution SO_4^{2-}) are reduced to sulfites and H_2S. Some of the H_2S is volatilized and some reacts with reduced iron to form pyrite (not shown in Fig. 15.2). So, how do rice and other plants that thrive under anaerobic conditions take up sulfur? Oxidation occurs in the rhizosphere of such plants and oxygen is thus actually transported from the shoots to the roots and exuded to the rhizosphere – like a sort of snorkel effect, similar to that used by divers (Chapter 17).

15.1.6 Plant Uptake

Plant roots only take up sulfur in the oxidized sulfate form, which is reduced to sulfides (S^{2-}) after entering the plants and later converted to the amino acid cysteine (Malavolta and Moraes 2007). Cysteine is then converted into methionine and most other organic sulfur compounds (Kovar and Grant 2011). As mentioned before, stomata in plant leaves and some fruits also take up sulfur from the air.

Although we focus on the role of sulfur in amino acids and protein formation, Malavolta and Moraes (2007) remind us that "sulfur is present in all functions and processes that are part of the life of higher plants, from ion uptake to RNA and DNA."

15.1.7 Changes with Cultivation

As in the case with nitrogen, cultivation reduces the topsoil organic sulfur content because of the increased SOM decomposition rates. McClung *et al.* (1959) observed that the main decrease with cultivation was in the topsoil organic sulfur fraction, coupled by an increase in inorganic sulfur in the subsoil, suggesting organic sulfur mineralization and some leaching of sulfates into the subsoil (Table 15.1).

In volcanic soils of the Ethiopian highlands, Solomon *et al.* (2001) compared topsoils under natural forest, a tree plantation and cultivated areas with maize and sorghum without fertilization (Table 15.2). The plantations and cultivated areas were cleared from tropical mountain forests, 25–35 years before. Like the previous example, topsoil organic sulfur decreased under the two types of cultivation, with little change in inorganic sulfur. Solomon and co-workers also found that the carbon-bonded organic fraction also exhibited a significant decrease, while the sulfate ester fraction changed the least.

15.1.8 Acid Sulfate Soils

An extreme situation occurs in the 12.5 million hectares of the tropical soils classified as Sulfaquepts and Sulfaquents,

Table 15.1	Total, organic and inorganic topsoil sulfur in two Cerrado soils of São Paulo, Brazil, under native savanna vegetation, and after 20–30 years of cultivation. Adapted from McClung *et al.* (1959).						
Soil (location)	**Vegetation**	**Topsoil**			**Subsoil**		
		Total	**Organic**	**Inorganic**	**Total**	**Organic**	**Inorganic**
		(ppm S)					
Sandy Ultisol (Baurú)	Savanna	40	36	4	18	12	6
	Cultivated	27	24	3	22	10	12
Clayey Oxisol (Riberão Preto)	Savanna	251	247	4	14	11	3
	Cultivated	67	60	7	22	10	12

Table 15.2	Changes in topsoil sulfur fractions upon 25–35 years of land-use change at two volcanic sites in the Ethiopian highlands. Adapted from Solomon *et al.* (2001).							
Soil	**Land use**	**Clay**	**Bulk density**	**Total sulfur**	**Inorganic sulfur**	**Total organic sulfur**	**Carbon-bonded organic sulfur**	**Sulfate ester organic sulfur**
		(%)	**(g/cm³)**	**(mg/kg S)**				
Ultisol	Forest	57	0.69	1082	17	1065	891	174
	Tea plantation	57	0.87	719	14	705	544	161
	Crop cultivation	59	0.89	635	11	624	502	122
Oxisol	Forest	52	0.62	1041	16	1025	804	221
	Cypress plantation	44	0.77	903	11	892	712	180
	Crop cultivation	49	1.04	520	11	509	425	84

also known as cat clays or acid sulfate soils. They are defined by the sulfidic *c* attribute in the Soil Functional Classification (FCC) system. They occur in some coastal areas where sulfate from ocean waters reacts with large quantities of reduced iron, forming pyrite. They have pH values of about 7 then they remain anaerobic, but when drained, pyrite is oxidized to sulfate and even forms free sulfuric acid, with a pH of 1.5–3, which make them toxic to plants and harmful to life in drainage waters. There is more on how to manage these extreme soils in Chapter 17.

15.2 Sulfur Sorption

There are two mechanisms of sulfur retention in soils high in iron and aluminum oxides: anion exchange and sulfur sorption. The first process is similar to nitrate anions, and the second one, sorption, is similar to what happens to phosphate anions. Because SO_4^{2-} is subject to leaching like NO_3^-, but unlike $H_2PO_4^-$, many of these processes take place primarily in the subsoil. Figure 15.3 compares the organic and inorganic sulfur profiles in a Mollisol and an Oxisol (Brady and Weil 2008). The Mollisols do not have anion exchange capacity or sulfur sorption in the subsoil, but often have gypsum in the parent material, as in this example. Even in topsoils such relationships hold between Brazilian soils (mainly Oxisols) and Iowa soils (mainly Mollisols) (Neptune *et al.* 1975).

15.2.1 Anion Exchange

Anions are held by positive charges and sorption sites at different bonding strengths. Among the macronutrients, $H_2PO_4^-$ is held the tightest, followed by SO_4^{2-}, and last by NO_3^-.

Anion exchange occurs primarily when clay surfaces of iron and aluminum oxides (defined in Chapter 14 to include hydroxides and other species of iron and aluminum) have net positive charge because they are below the zero point of charge and have positive ΔpH values (Chapter 8). Most anion exchange capacity is located in the subsoil since topsoils usually have negative ΔpH even in oxidic mineralogies because SOM reacts with such minerals. $H_2PO_4^-$ anions seldom leach into the subsoil.
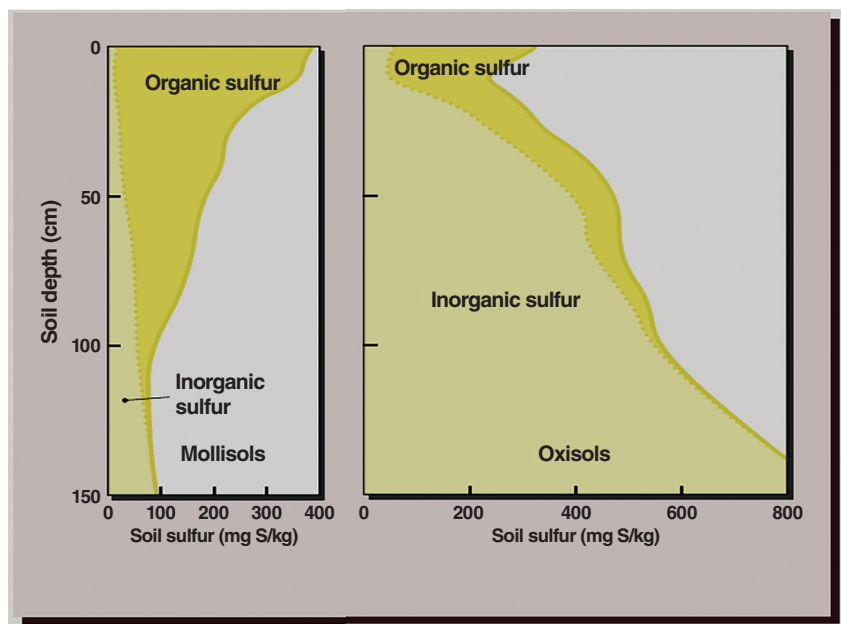
SO_4^{2-} can displace NO_3^- from these positive exchange sites. Anion exchange levels are generally low, 1–2 $cmol_c$/kg of soil, but such subsoil layers can be very deep, retaining large quantities of anions, as shown in Chapter 13 for NO_3^- and in Fig. 15.3 for SO_4^{2-}.

15.2.2 Sorption

The second mechanism is sorption. Sulfate ions are *ad*sorbed by ligand exchange between SO_4^{2-} and OH^-, in soils high in iron and aluminum oxides. This is shown in Eq. 15.4:

$$(15.4)$$
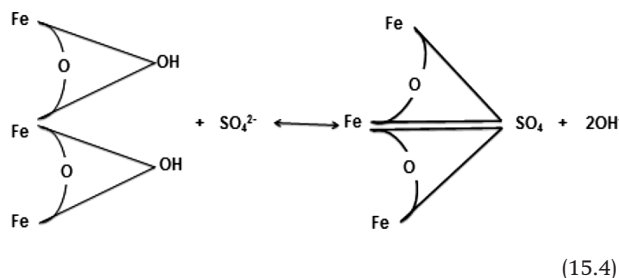
This reaction also occurs in exchange sites along the edges of kaolinite particles and positively charged organic radicals. In subsoils it may result in pH increases of 0.3 to 0.9 units.

Adsorbed sulfates are readily available to plant roots (Kovar and Grant 2011), in sharp contrast with adsorbed phosphates, which are not available to plant roots. Sulfate anions are retained more tightly by sorption than by anion exchange.

In addition, sulfates can also be *ab*sorbed when the SO_4^{2-} ions become part of an aluminum oxide matrix such as:

$$Al\,(OH)^{2+} + SO_4^{2-} \rightarrow Al(OH)_2SO_4 \qquad (15.5)$$

This happens in Andisols of Nicaragua (Delfosse *et al.* 2006), perhaps in a similar way as Barrow's (1974) slow reaction of phosphate absorption.

The sorption and desorption properties of sulfur can be characterized by "sorption isotherms," better termed sulfur retention curves, in a similar way to those used for phosphorus. Figure 15.4 shows examples of these relationships in some soils of the tropics. The smectic, permanent-charge Mollisol from the Cauca Valley of Colombia does not exhibit any sulfur sorption, a finding typical also of other soils with similar mineralogy from Hawaii and Australia, and of course the temperate region (Fox *et al.* 1971). Sandy and loamy Inceptisols and Entisols of the Indo-Gangetic Plain, which are derived from permanent-charge alluvium, also do not show sulfate sorption or anion exchange; most of them are deficient in sulfur (Khurana *et al.* 2008).

It is important to remember at this juncture that although this book focuses on variable-charge soils of the tropics, 10 percent of tropical soils have permanent charge, like the Mollisols, Entisols and Inceptisols indicated, and an additional 30 percent have a mixture of variable and permanent charge (Chapter 8). So, permanent-charge soils are important in the tropics, also because many of them are inherently fertile and are cultivated by high human populations, like in the Indo-Gangetic Plain of South Asia.

Several Oxisols show strong sulfur sorption, the Hawaiian Gibbsihumox showing stronger sorption capacity than the less oxidic Colombian Haplustox (Fig. 15.4). Figure 15.5 shows how much lower the sulfur sorption of the topsoil is than in the subsoil because of the higher SOM content of the topsoil that can block sorption sites.

How does sulfur retention compare with phosphorus retention? Figure 15.6 shows both retention curves with the same soils (Fox *et al.* 1971). The first observation is that the amounts of phosphorus sorbed are an order of magnitude higher than SO_4^{2-}-S sorbed. The second is that the curves give an indication of the mineralogy (the Gibbsihumox is oxidic, the Haplustox is kaolinitic and the Aqualf is probably siliceous).

Finally, the critical level of sulfur in soil solution obtained by Fox *et al.* (1971) for maximum yields of *Pennisetum*

clandestinum (kikuyu grass) was 5 mg/L SO_4^{2-}-S (1.6 mg/L S), an order of magnitude higher than the 0.2 mg/L P level commonly believed at that time to be the critical level, and two orders of magnitude higher than the 0.01 mg/L P proposed in the previous chapter. This shows that sorbed sulfur is held much less tightly than sorbed phosphorus by the same soils.

Sulfur retention is affected by the three core soil properties – texture, mineralogy and SOM, with mineralogy playing the predominant role. Since retention takes place in the clay fraction, the finer the texture the higher the potential to retain sulfur. Mineralogy is paramount, retaining sulfur in the following order: andic (allophanic) > oxidic > kaolinitic > smectitic, siliceous. SOM decreases sulfur retention because it can bond with clay surfaces that otherwise retain sulfates. In addition, phosphorus applications can kick sulfate ions out from the sites of retention and subject them to leaching. Ribeiro *et al.* (2001) showed how differing textures and SOM levels affect sulfur retention among 13 Oxisols with similar clay mineralogy.

The two sulfate retention mechanisms (anion exchange and sorption) put sulfate ions in an intermediate but good position for plant uptake – they are not too easily displaced from subsoil anion exchange sites, as nitrate
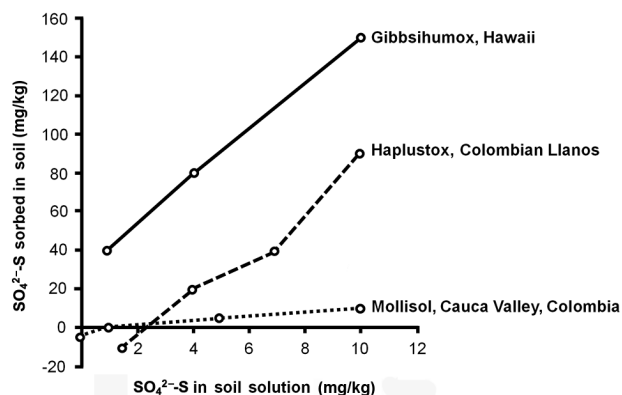
Fig. 15.4 Sulfate sorption retention curve of a permanently charged, clayey Mollisol shows negligible sorption, in contrast with strong sorption by two clayey Oxisols. The strength of sorption depends on the Oxisols' mineralogy, being higher in the oxidic Gibbsihumox than in the kaolinitic Haplustox. Adapted from Fox *et al.* (1971) and Fox 1974)
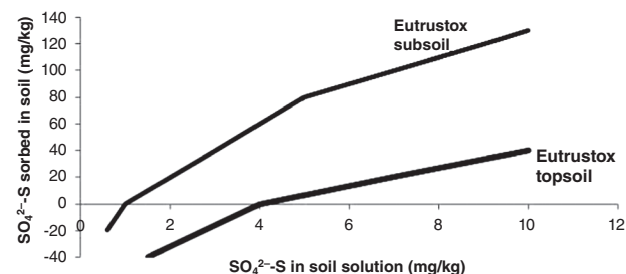
Fig. 15.5 Topsoils sorb much less sulfur than subsoils. Adapted from Fox *et al.* (1971)
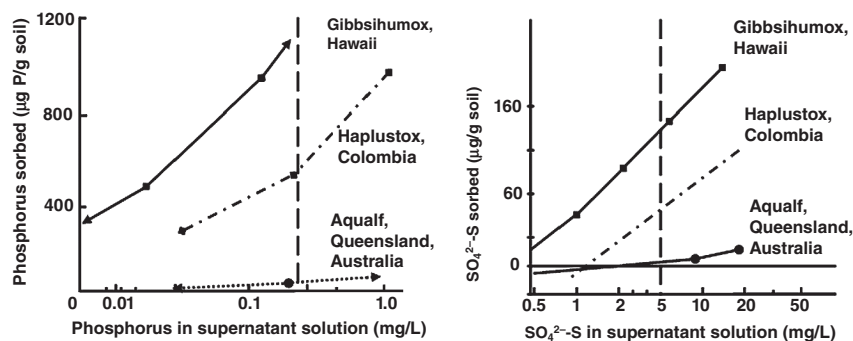
Fig. 15.6 Comparison of phosphate and sulfate retention curves in soils of different mineralogies. Adapted from Fox *et al.* (1971)

ions are, and they are not so strongly retained, like phosphate, which makes the uptake of sulfate by plant roots easier.

15.3 Crop Requirements

Sulfur uptake levels by crops are similar to those of phosphorus (Table 15.3). Therefore, sulfur is a macronutrient and should be considered in the same group as nitrogen, phosphorus and potassium.

Sulfur concentrations in plant tissue are also similar to phosphorus concentrations, ranging from 0.1 percent to 0.3 percent S, as is the range of nutrient uptake by crops (7–45 kg S/ha and 6–29 kg P/ha). A good indication of sulfur deficiency is a decline in the N:S ratio of tissues below 17:1 because the ratio of protein nitrogen to protein sulfur is 15:1.

The sulfur requirements of crops varies among crops, their cultivars, plant parts and the stage of growth, often decreasing as the crop matures. Cereals and root crops have the lowest sulfur contents, while oilseeds, legumes and the *Brassica* genus have the highest. Table 15.3 shows there is considerable variability in this generalization.

15.4 Nutrition

Crop yields and nutritional quality are affected by sulfur, with important effects on animal and human nutrition. I use data from Kanwar and Mudahar (1986), Malavolta and Moraes (2007), Brady and Weil (2008) and Kovar and Grant (2011) to summarize the nutritional effects as follows:

- Deficiencies in the sulfur-containing amino acids methionine, cysteine and cystine, caused by inadequate sulfur uptake, can result in serious malnutrition in monogastric animals such as humans and pigs.
- Sulfur increases the methionine content in cereal proteins, increasing their nutritional value.
- Sulfur also increases the protein content of grain legumes, important in the diets of humans.
- Baking quality and loaf volume decreases with sulfur deficiency in wheat when used in bread-making. The critical level is an N:S ratio of 16:1.
- Sulfur fertilization often increases yields and protein content of grass and legume pastures, as well as vitamin A content in alfalfa and the chlorophyll content of red clover, thereby improving feed quality and ruminant performance. Sulfur contents of feed should range from 0.18 percent S to 0.25 percent S in ruminant diets.
- The joint additions of nitrogen and sulfur help reduce high nitrate levels in animal feed.
- Several sulfur compounds are responsible for the flavors of garlic, onion, asparagus, lettuce and cabbage.
- Vegetables that are low in sulfur are hard, with low commercial value.

- Good sulfur nutrition of plants enhances several secondary metabolites, which improves defense mechanisms against pests and diseases.

15.4.1 Sulfur Fertilization

Sulfur fertilization in sulfur-deficient Entisols and Inceptisols of the Indo-Gangetic Plain increases protein and oil content in various oilseed crops (Khurana *et al*. 2008), with concomitant general increases in the amino acids methionine and cysteine, as shown in Table 15.4. Considering that hundreds of millions of people inhabit this region, sulfur fertilization has a major positive effect on these people's well-being.

15.5 Soil Testing

Water, 1 M potassium chloride (KCl), 0.01 M calcium chloride (CaCl$_2$), 0.01 M calcium phosphate [Ca(H$_2$PO$_4$)$_2$], 0.5 M sodium bicarbonate (NaHCO$_3$), ammonium acetate in acetic acid, and the Mehlich 3 double acid are the main extractants used to estimate available sulfur in soils (Fox *et al*. 1971, Ribeiro *et al*. 2001, Dick *et al*. 2008). The first three provide variable results because they extract mostly sulfate in the soil solution. Calcium phosphate also extracts some sorbed sulfur and has provided the best correlations with plant growth (Probert 1976). Using the isotope ^{35}S in five topsoils of North Queensland grown with *Stylosanthes guianensis* in pots, Probert also found a near full recovery of the sulfur extracted by calcium phosphate in the plants' tissue in four of the five soils. The exception was a sodic, permanent-charge soil, probably a Natraqualf, with little sulfur sorption capacity. Research by Ribeiro *et al*. (2001) in Brazil and Weil and Mughogho (2000) in Malawi indicated a less clear advantage of the calcium phosphate extractant.

Nevertheless, the calcium phosphate extraction is the most common soil test for sulfur. In general, the critical levels are 5–10 mg/kg S (Dick *et al*. 2008), while in Brazil it is mainly 10 mg/kg S (Malavolta and Moraes 2007), and in Hawaii, 8–10 mg/kg S (Hasan *et al*. 1970), all with the calcium phosphate extraction.

A soil test performed in the topsoil, however, tells only part of the picture. In sandy Ultisols, where the topsoil is deficient in sulfur, crops show symptoms of sulfur deficiency until the roots penetrate clayey, oxidic or kaolinitic subsoils that are loaded with sulfate, retained by anion exchange or sorption. Sulfur deficiency gradually disappears as the roots come in contact with the SO$_4^{2-}$-rich subsoil. This was first observed in North Carolina Ultisols by Kamprath *et al*. (1957), although it happens all over the tropics. Therefore, subsoil sampling may be a good management practice in Ultisols and Alfisols of contrasting textural profiles, or in Oxisols and Andisols in general. Since sulfur retention is not as tight as phosphorus retention, plants can tap much of the retained sulfates.

Species	Uptake (kg S/ha)	Uptake (kg P/ha)	Yield (t/ha)
Table 15.3 Sulfur uptake of tropical crops as compared with phosphorus uptake. Adapted from Howeler (2002), Oliveira *et al.* (2005), Vitti and Heirinchs (2007), Fancelli and Tsumanuma (2007), Khurana *et al.* (2008), Dick *et al.* (2008).			
Cereals (grain):			
Maize	7	10	2.1
	4	10	2.6
	21	34	9.0
Rice	7	12	2.7
	4	9	3.1
	13	–	7.8
Wheat	3	9	1.9
	12	26	3.9
Sorghum	25	–	9.4
Root crops:			
Cassava (roots)	7	3	11
	1	4	13
Potato (tubers)	6	5	16
	38	27	28
Grain legumes:			
Beans	3	2	0.7
	25	9	1.0
Soybeans	8	12	2.4
Peanut	15	19	1.9
Chickpea	13	6	1.5
Lentil	6	13	2.0
Pigeon pea	9	8	1.2
Other crops:			
Rapeseed = canola (*Brassica napas*)	45	25	2.6
Cauliflower (*Brassica oleracea*)	21	9	9.0
Cabbage (*Brassica oleracea* var. *capitata*)	64	31	84.0
Sunflower	17	26	2.3
Cotton (lint)	33	8	1.3
	16	8	2.1
Sugar cane	58	21	10.0
	14	14	68.5
	26	29	88.0
Coffee (beans)	2	2	1.5
	27	9	2.0
Cacao (beans)	0.3	2	0.3
Citrus (fruit)	1	2	12.1
Pineapple (50 000 plants/ha)	41	33	-
Forages (dry mass):			
Guinea grass (*Panicum maximum*)	45	44	23
Elephant grass (*Pennisetum purpureum*)	75	64	25
Alfalfa (*Medicago sativa*)	24	21	5
	34	-	13
Trees (wood):			
Eucalypt	24	5	47

15.6 Sulfur Fertilization

15.6.1 Sources

Most of these sulfur requirements are small enough that many nitrogen and phosphorus carriers can supply them. An application of 50 kg N/ha as ammonium sulfate provides 12 kg S/ha, while an application of 50 kg P/ha as single superphosphate provides 6 kg S/ha. When urea and diammonium phosphate are used, there is no sulfur added. Although triple superphosphate should contain zero sulfur, an actual analysis that was conducted by Weil and Mughogho (2000) using commercial triple superphosphate fertilizers showed that it contained 2–3 percent.

The ability to return crop residues or to incorporate manure may add enough sulfur to a crop without mineral fertilization. An application of 5 t/ha of high-quality cattle manure containing 0.3 percent S would provide 15 kg S/ha, but the same application using low-quality manure would provide only about 5 kg S/ha.

Elemental sulfur and gypsum are also used to reduce the pH and ameliorate sodic soils, those with the *n* FCC attribute. Gypsum is used extensively in Oxisols to bring calcium (Ca^{2+}) ions into the subsoil (Chapter 9) and supply calcium to peanuts and other high-calcium-requiring crops. Ammonium thiosulfate is used in fertigation and in blends with other fertilizers (Dick *et al*. 2008).

The main fertilizer sources of sulfur are shown in Table 15.5.

15.6.2 Rates

In general, rates on the order of 5–50 kg S/ha are sufficient to overcome sulfur deficiencies. The average sulfur application rate for crops in Brazil is 20 kg S/ha (Malavolta and

| Table 15.4 | Sulfur fertilization increases protein, methionine and cysteine levels in mungbean grain (*Phaseolus aureus*) that is grown in a sulfur-deficient alluvial soil of the Indo-Gangetic Plain. Adapted from Kamat *et al*. (1981). |

Applied sulfur	Protein	Methionine	Cysteine
kg S/ha	(%)	(% total protein)	
0	24.4	2.42	2.63
10	24.5	2.45	2.25
20	24.8	3.02	4.58
30	26.3	3.13	3.80

| Table 15.5 | Main sulfur fertilizers (Vitti and Heirinchs 2007, Dick *et al*. 2008, Chapter 13, Kirchmann and Pettersson 1995 for urine). |

Fertilizer	Formula	Element content
Gypsum	$CaSO_4 \cdot H_2O$	18.6% S, 23.3% Ca
Elemental sulfur (sulfur flour or flower)	S	88–98% S
Ammonium sulfate	$(NH_4)_2SO_4$	21% N, 24% S
Malawi planting fertilizer blend	23 N–21 P–0 K–4 S	4% S
Single superphosphate	$Ca(H_2PO_4)_2 + 2CaSO_4 \cdot H_2O$	9% P, 12% S
Magnesium sulfate (kieserite)	$MgSO_4 \cdot H_2O$	14–20% S, 16% Mg
Magnesium sulfate (Epsom salt)	$MgSO_4 \cdot 7H_2O$	11% S, 9% Mg
Potassium magnesium sulfate	$K_2SO_4 \cdot 2MgSO_4$	22% K, 18.2% S, 11% Mg
Potassium sulfate	K_2SO_4	18% K, 41.5% S
Ammonium thiosulfate	$(NH_4)_2S_2O_3 \cdot 5H_2O$	12% N, 26% S
Maize stover, wheat straw	–	0.1–0.22% S
Cattle manure (US)	–	0.3–0.5% S
Cattle manure (Zimbabwe)	–	0.11–0.14% S
Sheep manure	–	0.35% S
Poultry manure	–	0.5% S
Pig manure	–	0.32% S
Urine	–	2.2% S
Biosolids	–	~ 0.44% S

Moraes 2007). Jones and Quagliato (1970) showed that 10–20 kg S/ha is sufficient for most tropical pasture legumes and alfalfa. For coffee, an annual rate of 30 kg S/ha increased yields by 82 percent over a 10-year period in Brazil (de Freitas *et al.* 1972).

In Brazil, a country with a majority of variable-charge soils, deficient in sulfur, the generally recommended rates are as follows, all in bands or close to trees at planting time (Vitti and Heirinchs 2007):

- annual crops: 30 kg S/ha
- perennial crops: 30–40 kg S/ha
- sugar cane: 50 kg S/ha per cut
- vegetable crops: 40–50 kg S/ha
- reforestation: 30 kg S/ha.

In Africa, with lower crop yields than Brazil, the recommended rates are lower. Weil and Mughogho (2000) conducted replicated trials in 20 farmer fields for two years in four major agroecolgical zones of Malawi. Nineteen of the 20 trials showed yield responses to sulfur. They also found that a critical N:S ratio of 11.5:1 in maize ear leaves was the best predictor of sulfur deficiency. Rates of 5–6 kg S/ha were found to be best, with few differences among agroecological zones, two of them dominated by variable-charge red Alfisols, Oxisols and Ultisols, while the other two, closer to Lake Malawi, had permanent-charge soils (Fig. 15.7). They also noted that nitrogen had to be applied before sulfur responses were observed, a classic "law of the minimum" situation where nitrogen deficiency has to be overcome before
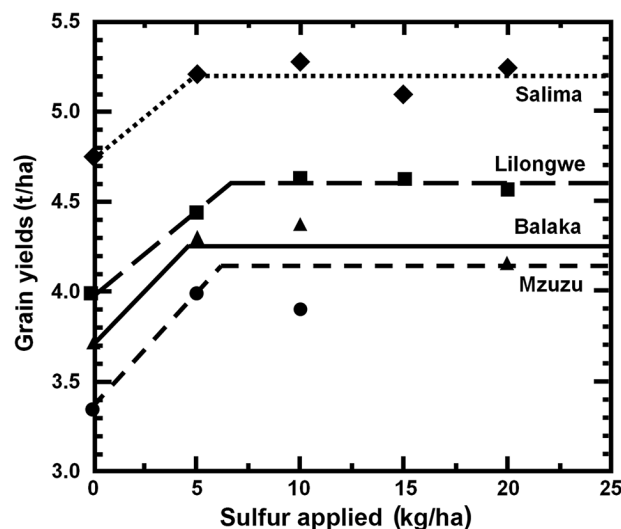
Fig. 15.7 Maize responds to 5–7 kg S/ha in four agroecolgical zones of Malawi. Salima and Balaka regions have mainly permanent-charge soils and are close to Lake Malawi. Lilongwe and Mzuzu are upland areas with mainly variable-charge Alfisols (Weil and Mughogho 2000). Permission granted from the *Agronomy Journal*

addition of sulfur. Results from many previous field experiments in Malawi convinced the Ministry of Agriculture to add four units of sulfur in their special blend, imported by the Malawian government (23 N–21 P–0 K–4 S). This undoubtedly has reduced sulfur deficiency in this country.

15.6.3 Timing and Placement

All sulfur fertilization should be incorporated at planting time for food crops because it helps in root development and the early synthesis of amino acids, as well as in stimulating biological nitrogen fixation in legumes (Fancelli and Tsumanuma 2007). When elemental sulfur is used it should be applied 2–4 weeks before planting so it oxidizes into SO_4^{2-} by the time seeds are planted. Gypsum is also applied at the pegging time for peanuts because of the high demand for calcium at this time. In cases where sulfur deficiency is diagnosed during plant growth it is possible to correct it by fertilizing while the plant is growing (Kovar and Grant 2011).

15.6.4 Agronomic Efficiency and Fertilizer Recovery

The agronomic efficiency of sulfur fertilization (AE_S) was in the range 3–13 kg grain/kg S applied to oilseed crops, and 17–19 kg grain/kg S applied to rice and wheat in India (Khurana *et al.* 2008). These values are lower than the agronomic efficiency of nitrogen (AE_N) reported in Chapter 13.

The fertilizer recovery of sulfur (RE_S) by the first crop is rather low, ranging from 7 percent to 23 percent in India, but higher recoveries (37–73 percent) have been recorded with cotton in temperate North Carolina, according to a compilation by Kanwar and Mudahar (1986). This may be due to soil differences. Most of the Indian data comes from Entisols and Inceptisols of the Indo-Gangetic Plain, which do not have a subsoil with sulfur retention capacity and thus much of the sulfur applied may be lost by leaching. North Carolina Ultisols usually have an argillic B horizon, rich in iron and aluminum oxides, which, as mentioned before, when the crop roots reach it, can take up much of the sorbed sulfur (Kamprath *et al.* 1957).

Residual effects of sulfur fertilization are likely to be better than those of nitrogen (most of it in the first crop and a small amount in the second crop – Chapter 13). Khurana *et al.* (2008) reported that in the rice–wheat rotations in the Indo-Gangetic Plain the first crop recovered 33–82 percent of the applied sulfur while the subsequent crop recovered the remaining 18–67 percent. In one case, the residual effect of sulfur was felt up to the fourth crop of an annual rice–wheat rotation. In general, this is much better than nitrogen even though these soils usually do not have subsoil sulfur retention.

The only long-term trial I was able to find in the literature is the work of Donald and Williams (1955) and Williams and Donald (1957) in which they sampled grazed paddocks with introduced subterranean clover with periodic single superphosphate applications, for up to 26 years of

sheep grazing, located in a "podzolic soil" (probably an Ultisol) in the Crockwell District of New South Wales, Australia. Amazingly, they found that all the sulfur applied as single superphosphate (156 kg S/ha over 26 years) was accounted for in the top 10 cm of soils, presumably in an organic fraction. Being an efficient grazing system, the sheep excreta generally recycles about 70–80 percent of the nutrients they ingest (more on that in Chapter 18). The soils must have an argillic, sulfur-retaining B horizon, where the pasture species certainly tapped inorganic sulfur. This is probably the best example I have read of the synchrony principle. Obviously, more research is needed on the long-term effects of sulfur applications.

15.7 Summary and Conclusions

- Sulfur should be considered a macronutrient, along with nitrogen, phosphorus and potassium. The reason for this proposal is that the sulfur content of plants is similar to that of phosphorus (0.1–0.3 percent in both cases), as is the range of nutrient uptake by crops (7–45 kg S/ha and 6–29 kg P/ha). Most importantly, the current response to sulfur fertilization is as frequent or probably more so than that of phosphorus. The NPK paradigm should be updated to NPKS in practical agronomy.

- Most sulfur requirements are small enough that many nitrogen and phosphorus carriers can supply them. An application of 50 kg N/ha as ammonium sulfate provides 12 kg S/ha, while an application of 50 kg P/ha as single superphosphate provides 6 kg S/ha.

- Sulfur deficiencies are increasing throughout the tropics as well as worldwide. The main reasons are the increasing use of high-analysis fertilizers that contain no sulfur, the increasing use of higher-yielding crop cultivars that require more sulfur, and the decreased atmospheric deposition downwind from industrial urban centers that have air-pollution control.

- Sulfur deficiency in crops occurs in a wide variety of soils. They are often sandy, well-drained, subject to leaching, with variable- or permanent-charge mineralogy and low in soil organic matter (SOM). They generally occur in unpolluted, inland areas where the atmosphere is low in sulfur. Unlike nitrogen deficiency, which starts as chlorosis (yellowing) of the older leaves, sulfur deficiency starts as chlorosis of the younger leaves.

- The sulfur cycle resembles the nitrogen cycle in that the atmosphere plays an important role, that most of the topsoil's sulfur is in the organic form, that sulfur undergoes similar mineralization–immobilization processes and as sulfate anions can be retained in subsoils by anion exchange and also leached, similarly to nitrates. The sulfur cycle resembles the phosphorus cycle in that the original sources of sulfur are primary minerals and that sulfur retention is important in soils that are high in iron and aluminum oxides. It differs from both cycles in that microbial oxidation–reduction (redox) reactions play a central role.

- The main sulfur inputs to soils are primary minerals (gypsum and pyrite), organic inputs and atmospheric deposition of sulfur gases. Organic inputs of plant origin, including manures, generally contain about 0.3 percent S in dry mass, except for low-quality cattle manures in Africa, which contain about 0.1 percent S.

- The atmosphere contains various forms of sulfur gases. These gases are eventually oxidized to sulfuric acid, which along with nitric acid causes acid rain. Atmospheric deposition rates were as high as 200 kg S/ha per year downwind from industrial areas with no pollution controls. Atmospheric deposition rates are 8–15 kg S/ha per year around industrial areas with effective clean-air controls in rich countries, but not around rapidly developing industrial areas in the tropics. Atmospheric deposition in Africa is about 1–4 kg S/ha per year.

- Total topsoil sulfur in the tropics varies from very high in Andisols (1280 mg/kg S) to very low (40 mg/kg S) in sandy Ultisols. Unlike phosphorus, the subsoil often contains significant quantities of sulfur, which are very relevant to soil fertility management in the tropics.

- Most (> 95 percent) of the sulfur in topsoils outside of arid climates is in the organic form. In subsoils with variable-charge clays, the relationship often flips over, with the vast majority being inorganic sulfur because of sulfate retention processes.

- Soil organic sulfur stocks can be grouped into three fractions depending on their redox status and turnover rates: ester sulfates, carbon-bonded sulfur and inert organic sulfur. Ester sulfates are easily hydrolyzed into sulfates. Carbon-bonded sulfur comprises complex reduced forms that include the amino acids methionine, cysteine and cystine. Inert organic sulfur can range from 3 percent to 59 percent of the organic sulfur and has a very slow turnover.

- Mineralization of organic sulfur occurs at C:S ratios lower than 200, while organic compounds with a C:S ratio > 400 produce net immobilization. Organic compounds with a sulfur concentration less than 0.15 percent S are immobilized into microbial biomass but eventually mineralized. The processes could go either way in ratios between C:S values of 200 and 400.

- Flushes of sulfur mineralization upon wetting of previously dried soils have also been observed in the tropics. The processes involved are similar to those governing nitrogen flushes – the Birch effect.

- There are two mechanisms of sulfur retention in subsoils that are high in iron and aluminum oxides: anion exchange and sulfur sorption. The first process is similar to that for nitrates (NO_3^-) – anion exchange; and the second one, sorption, is similar to what happens to phosphate ($H_2PO_4^-$) anions. Because sulfate ions (SO_4^{2-}) are subject to leaching, like NO_3^- but unlike $H_2PO_4^-$, many of these processes take place primarily in the subsoil.

- Anions are held by positive charges and sorption sites at different bonding strengths. Among the macronutrients, $H_2PO_4^-$ is held the tightest, followed by SO_4^{2-}, and last by NO_3^-. Adsorbed sulfates are readily available to plant roots in sharp contrast with adsorbed phosphates, which are not readily available. Sulfate anions are retained more tightly by sorption than by anion exchange.
- Sulfur retention curves resemble phosphorus retention curves, but the amounts of sulfate sorbed are an order of magnitude lower than sorbed phosphate, while the critical level in the soil solution that approaches maximum yield (1.6 mg/L S) is two orders of magnitude higher than that of phosphorus (0.01 mg/L P). This shows that sorbed sulfur is held much less tightly than sorbed phosphorus by the same soils.
- Sulfur retention is affected by the three core soil properties – texture, mineralogy and SOM, with mineralogy playing the dominant role. Since retention takes place in the clay fraction, the finer the texture the higher the potential to retain sulfur. Mineralogy is paramount, retaining sulfur in the following order: andic (allophanic) > oxidic > kaolinitic > smectitic, siliceous. SOM decreases sulfur retention because it can bind with clay surfaces that otherwise retain sulfates. This is why sulfur retention is lower in topsoils than subsoils. In addition, phosphorus applications can kick sulfate ions out from the sites of retention and subject them to leaching.
- The two sulfate retention mechanisms (anion exchange and sorption) put sulfate ions in an intermediate but good position for plant uptake – they are not too easily displaced from subsoil anion exchange sites, as nitrate ions are, and thus leached, and they are not so strongly sorbed like phosphate, which makes the uptake of sulfate by plant roots easier.
- The sulfur requirement of crops varies among crops, their cultivars, plant parts and the stage of growth, but it depends on the seed protein content. Cereals and root crops have the lowest sulfur contents, while oilseeds, legumes and the *Brassica* genus (canola, cabbage) have the highest.
- Crop yields and nutritional quality are affected by sulfur, with important effects on animal and human nutrition. Deficiencies in the sulfur-containing amino acids methionine, cysteine and cystine, caused by inadequate sulfur uptake, can result in serious malnutrition in monogastric animals. Sulfur increases the methionine content of cereal proteins, thereby increasing their nutritional value. Sulfur also increases the protein content of grain legumes.
- Baking quality and loaf volume decreases with sulfur deficiency in wheat when used in bread making. The critical level is an N:S ratio lower than 16:1.
- Sulfur fertilization often increases yields and protein content of grass and legume pastures, improving feed quality and ruminant performance. Sulfur content of feed should range from 0.18 percent to 0.25 percent S in ruminant diets. The joint additions of nitrogen and sulfur help reduce high nitrate levels in animal feed.
- Several sulfur compounds are responsible for the flavors of garlic, onion, asparagus, lettuce and cabbage. Vegetables that are low in sulfur are hard, with low commercial value.
- Good sulfur nutrition of plants enhances several secondary metabolites, which improves defense mechanisms against pests and diseases.
- Sulfur fertilization in sulfur-deficient Entisols and Inceptisols of the Indo-Gangetic Plain increases protein and oil content in various oilseed crops, with concomitant increases in the amino acids methionine and cysteine. Considering that hundreds of millions of people inhabit this region, sulfur fertilization has a major positive effect on these people's well-being.
- Calcium phosphate extraction is the most commonly used soil test for sulfur. In general, the critical levels are 5–10 mg/kg S. Other methods can be used.
- A soil test performed in the topsoil, however, tells only part of the picture. In sandy Ultisols, where the topsoil is deficient in sulfur, crops show symptoms of sulfur deficiency until the roots penetrate the clayey, oxidic or kaolinitic subsoil, loaded with sulfate that is retained by anion exchange or sorption. Sulfur deficiency gradually disappears as the roots come into contact with the sulfate-rich subsoil.
- The ability to return crop residues or to incorporate manure may add enough sulfur to a crop, without mineral fertilization. An application of 5 t/ha of high-quality cattle manure containing 0.3 percent S would provide 15 kg S/ha, but the same application using low-quality manure would provide only about 5 kg S/ha.
- In general, rates on the order of 5–50 kg S/ha are sufficient to overcome sulfur deficiencies. The average sulfur application rate for crops in Brazil is 20 kg S/ha. In Africa, where there are lower crop yields, the recommended rates are lower, 5–6 kg S/ha. In Malawi, nitrogen had to be applied before sulfur responses were observed, a classic "law of the minimum" situation.
- Results from many previous field experiments in Malawi convinced the Ministry of Agriculture to add four units of sulfur in their special blend, imported by the Malawian government. This undoubtedly has reduced sulfur deficiency in this country.
- All sulfur fertilization (organic or mineral) should be incorporated at planting time for food crops because it helps in root development and the early synthesis of amino acids, as well as in stimulating biological nitrogen fixation in legumes.
- When elemental sulfur is used, it should be applied 2–4 weeks before planting so it oxidizes into SO_4^{2-} by the time seeds are planted.
- Gypsum is also applied at the pegging time of peanuts because of the high demand for calcium at this time. In cases where sulfur deficiency is diagnosed during plant growth it is possible to correct it by fertilizing while the plant is growing.

- The agronomic efficiency of sulfur fertilization (AE_S) was in the range of 3–13 kg grain/kg S applied in oilseed crops, and 17–19 kg grain/kg S applied in rice and wheat in India. These values are lower than the agronomic efficiency of nitrogen (AE_N) reported in Chapter 13.
- The residual effect of sulfur fertilization seems to be better than that of nitrogen. Sulfur recovery by the first crop is higher when a sulfur-retaining subsoil is present.
- The long-term effect of periodic single superphosphate applications for up to 26 years of sheep grazing an Ultisol in Australia resulted in all the applied single superphosphate (156 kg S/ha over 26 years) being accounted for in the top 10 cm of the soil, presumably as organic sulfur. This is probably due to the high recycling rate of sulfur as it goes through the sheep. This the best example I have read of the synchrony principle.

References

Aita C and SJ Giacomini. 2007. Materia orgánica de solo, nitrogénio e enxofre nos diversos sistemas de exploração agrícola. *Nitrogênio e Enxofre na Agricultura Brasileira*, T Yamada, SR Stipp and GC Vitti (eds.). IPNI, Piracicaba, pp. 1–41.

Barrow NJ. 1961. Studies on the mineralization of sulfur from soil organic matter. *Australian Journal of Agricultural Research* 12: 306–391.

1974. The slow reactions between soil and anions. 1. Effects of time, temperature, and water content of a soil on the decrease in effectiveness of phosphate for plant growth. *Soil Science* 118: 380–386.

Bolle-Jones EW. 1964. Incidence of sulfur deficiency in Africa: A review. *Empire Journal of Experimental Agriculture* 32: 241–248.

Bornemisza E and R Llanos. 1967. Sulfate movement, adsorption and desorption in three Costa Rican soils. *Soil Science Society of America Proceedings* 31: 356–360.

Brady NC and RR Weil. 2008. *The Nature and Properties of Soils*, 14th edition. Pearson Prentice Hall, Upper Saddle River, NJ.

Buri MM, T Masunaga and T Wakatsuki. 2000. Sulfur and zinc levels as limiting factors to rice production in West Africa lowlands. *Geoderma* 94: 23–42.

Cooper PJM. 1972. Aryl sulfatase activity in northern Nigeria soils. *Soil Biology and Biochemistry* 4: 333–337.

de Freitas LMM, T Tanaka, E Lobato and WV Soares. 1972. Experimentos de adubação de milho doce e soja em solos de campo cerrado. *Pesquisa Agropecuária Brasileira Série Agronomia* 7: 57–63.

Delfosse T, P Delmelle and B Delvaux. 2006. Sulphate sorption at high equilibrium concentration in Andosols. *Geoderma* 136: 716–722.

Dick WA, D Kost and L Chen. 2008. Availability of sulfur to crops from soil and other sources. *Sulfur: A Missing Link between Soils, Crops and Nutrition. Agronomy Monograph 50*, J Jez (ed.). American Society of Agronomy, Madison, WI, pp. 59–82.

Donald CM and CH Williams. 1955. Fertility and productivity of a podzolic soil as influenced by subterranean clover (*Trifolium subterraneum*) and superphosphate. *Australian Journal of Agricultural Research* 5: 664–687.

Ensminger LE. 1954. Some factors affecting the adsorption of sulfate by Alabama soils. *Soil Science Society of America Proceedings* 18: 259–264.

Fancelli AL and GM Tsumanuma. 2007. Nitrogênio e enxofre nas culturas de milho e feijão. *Nitrogênio e Enxofre na Agricultura Brasileira*, T Yamada, SR Stipp and GC Vitti (eds.). IPNI, Piracicaba, pp. 445–486.

Fitts JW. 1970. Sulfur deficiency in Latin America. *Sulphur Institute Journal* 6: 14–16.

Fox RL. 1974. Examples of anion and cation adsorption by soils of tropical America. *Tropical Agriculture (Trinidad)* 51: 200–210.

Fox RL, SM Hasan and RC Jones. 1971. Phosphate and sulfate sorption by Latosols. *Proceedings International Symposium on Soil Fertility Evaluation (New Delhi)* 1: 857–864.

Greenwood M. 1951. Fertilizer trials with groundnuts in northern Nigeria. *Empire Journal on Experimental Agriculture* 19: 225–241.

Haneklaus S, E Bloem and E Schnug. 2008. History of sulfur deficiency in crops. *Sulfur: A Missing Link between Soils, Crops and Nutrition. Agronomy Monograph 50*, J Jez (ed.). American Society of Agronomy, Madison, WI, pp. 45–55.

Hasan SM, RL Fox and CC Boyd. 1970. Solubility and availability of sorbed sulfate in Hawaiian soils. *Soil Science Society of America Proceedings* 34: 897–901.

Hesse PR. 1957. Sulphur and nitrogen changes in forest soils of East Africa. *Plant and Soil* 9: 86–96.

Howeler RH. 2002. Cassava mineral nutrition and fertilization. *Cassava Biology, Production and Fertilization*, RJ Hillocks, JM Thresh and AC Bellotti (eds.). CABI Publishing, Wallingford, pp. 115–147.

Itanna F. 2005. Sulfur distribution in five Ethiopian Rift Valley soils under humid and semi-arid climate. *Journal of Arid Environments* 62: 597–612.

Jez J (ed.). 2008. *Sulfur: A Missing Link between Soils, Crops and Nutrition. Agronomy Monograph*. American Society of Agronomy, Madison, WI.

Jones MB and SL Quagliato. 1970. Respostas de quatro leguminosas tropicais e da alfalfa a varios niveis de enxofre. *Pesquisa Agropecuaria Brasileira* 5: 359–363.

Kamat VN, VG Kankute, RB Puranik, WS Kohadkar and RP Joshi. 1981. Effect of sulfur and Mo on yield, protein and S-amino acid contents in green gram. *Journal of the Indian Society of Soil Science* 29: 225–227.

Kamprath EJ, WL Nelson and JW Fitts. 1957. Sulfur removed from soils by field crops. *Agronomy Journal* 49: 289–293.

Kanwar JS and MS Mudahar. 1986. *Fertilizer Sulfur and Food Production*. Martinus Nijhoff, Dordrecht.

Khurana MPS, US Sadana and B Singh. 2008. Sulfur nutrition of crops in the Indo-Gangetic Plains of south Asia. *Sulfur: A Missing Link between Soils, Crops and Nutrition. Agronomy Monograph 50*, J Jez (ed.). American Society of Agronomy, Madison, WI, pp. 11–24.

Kirchmann H and S Pettersson. 1995. Human urine: Chemical composition and fertilizer use efficiency. *Fertilizer Research* 40: 149–154.

Kovar JL and CA Grant. 2011. Nutrient cycling in soils: Sulfur. *Soil Management: Building a Stable Base for Agriculture*, JL Hatfield and TJ Sauer (eds.). American Society of Agronomy, Madison, WI, pp. 103–115.

Lilienfein J, W Wilcke, MA Ayarza, L Vilela, SC Lima and W Zech. 2000. Chemical fractionation of phosphorus, sulphur, and molybdenum in Brazilian savannah Oxisols under different land use. *Geoderma* 96: 31–46.

Malavolta E and MF Moraes. 2007. Fundamentos do nitrogênio e do enxofre na nutrição mineral das plantas cultivadas. *Nitrogênio e Enxofre na Agricultura Brasileira*, T Yamada, SR Stipp and GC Vitti (eds.). IPNI, Piracicaba, pp. 189–249.

McClung AC, LMM de Freitas and WL Lott. 1959. Analysis of several Brazilian soils in relation to plant responses to sulfur. *Soil Science Society of America Proceedings* 23: 221–224.

Muller LE. 1965. Deficiencia de azufre en algunos suelos de Centro America. *Turrialba* 15: 208–215.

Munévar F and AG Wollum. 1977. Effects of the additions of phosphorus and inorganic nitrogen on carbon and nitrogen mineralization in Andepts from Colombia. *Soil Science Society of America Journal* 41: 540–544.

Neptune AML, MA Tabatabai and JJ Hanway. 1975. Sulfur fractions and carbon–nitrogen–phosphorus–sulfur relationships in some Brazilian and Iowa soils. *Soil Science Society of America Proceedings* 39: 51–55.

Oke OL. 1971. Sulfur in relation to soil organic matter in Nigerian soils. *Journal Indian Society of Soil Science* 19: 309–311.

Oliveira RP de, PLOA Machado, ACC Bernardi and A Naumov. 2005. Considerações sobre o uso do solo e a regionalização do balanço de potássio na agricultura brasileira. *Potássio na Agricultura Brasileira*, T Yamada and TL Roberts (eds.). IPNI, Piracicaba, pp. 119–164.

Olson RA and OP Englestad. 1972. Soil phosphorus and sulfur. *Soils of the Humid Tropics*. National Academy of Sciences, Washington, DC, pp. 82–101.

Parton WJ, RL Sanford, PA Sanchez and JWB Stewart. 1989. Modeling soil organic matter dynamics in tropical soils. *Dynamics of Soil Organic Matter in Tropical Ecosystems*, DC Coleman, J Oades and G Uehara (eds.). University of Hawaii, Honolulu, HI, pp. 153–171.

Probert ME. 1976. Studies of 'available' and isotopically exchangeable sulfur in some North Queensland soils. *Plant and Soil* 45: 461–475.

Ribeiro ES Jr., LE Dias, VH Alvarez, JWV Mello and WL Daniels. 2001. Dynamics of sulfur fractions in Brazilian soils submitted to consecutive harvests of sorghum. *Soil Science Society of America Journal* 65: 787–794.

Schoenau JJ and SS Malhi. 2008. Sulfur forms and cycling processes in soil and their relationship to sulfur fertility. *Sulfur: A Missing Link between Soils, Crops and Nutrition. Agronomy Monograph 50*, J Jez (ed.). American Society of Agronomy, Madison, WI, pp. 1–11.

Solomon D, J Lehmann, M Tekalign, F Frizsche and W Zech. 2001. Sulfur fractions in particle-size separates of the subhumid Ethiopian highlands as influenced by land use changes. *Geoderma* 102: 41–59.

Stevenson FJ. 1986. *Cycles of Soil*. Wiley, New York, NY.

Vitti GC and R Heirinchs. 2007. Formas tradicionais e alternativas de obtenção do nitrogénio e do enxofre: Uma visâo holíística. *Nitrogênio e Enxofre na Agricultura Brasileira*, T Yamada, SR Stipp and GC Vitti (eds.). IPNI, Piracicaba, pp. 109–160.

Vogt JBM. 1966. Responses to sulfur fertilization in northern Rhodesia. *Agrochimica* 10: 105–113.

Weil RR and SK Mughogho. 2000. Sulfur nutrition of maize in four regions of Malawi. *Agronomy Journal* 92: 649–656.

Weil RR. 2011. *Sulfur Deficiency and Ammonia Volatilization in Ethiopian Agricultural Soils. Report to the Ministry of Agriculture*. University of Maryland, College Park, MD.

Weil RR and NC Brady. 2017. *The Nature and Properties of Soils*, 15th edition. Pearson Prentice Hall, Upper Saddle River, NJ.

Williams CH. 1972. Sulfur deficiency in Australia. *Sulphur Institute Journal* 8: 5–8.

Williams CH and CM Donald. 1957. Changes in organic matter and pH in a podzolic soil as influenced by subterranean clover and superphosphate. *Australian Journal of Agricultural Research* 8: 179–189.

Williams CH and A Steinbergs. 1958. Sulphur and phosphorus in eastern Australian soils. *Australian Journal of Agricultural Research* 9: 483–491.

Yamada T, SR Stipp and GC Vitti (eds.). 2007. *Nitrogênio e Enxofre na Agricultura Brasileira*. IPNI, Piracicaba.