



International  
Fertilizer Industry  
Association



# Sulphur and Sustainable Agriculture

A.R. Till



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**A.R. Till**

International Fertilizer Industry Association  
Paris, May 2010

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Sulphur and Sustainable Agriculture

By A.R. Till

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# Contents

<b>About the book and the author</b>	<b>5</b>
<b>Acknowledgements</b>	<b>6</b>
<b>Symbols, acronyms and abbreviations</b>	<b>7</b>
<b>1. Sulphur in agriculture: setting the scene</b>	<b>9</b>
<b>2. Introduction</b>	<b>12</b>
<b>3. The global sulphur cycle</b>	<b>13</b>
<b>4. Importance of sulphur in agriculture</b>	<b>16</b>
4.1. Boundary conditions	16
4.2. Farming systems: sulphur cycling and balance	16
4.3. Forms of sulphur	19
4.4. Management of inputs and losses	20
4.5. Nutrient balances and sustainability	21
<b>5. Soil sulphur</b>	<b>23</b>
5.1. General description	23
5.2. Sulphur fractions	23
5.3. The carbon cycle and balanced nutrition	26
5.4. Sulphur mineralization and fixation	27
<b>6. Sulphur in plants</b>	<b>29</b>
6.1. Needs and deficiencies	29
6.2. Uptake processes and metabolism	30
6.3. Plant sulphur and product quality	32
<b>7. Sulphur deficiency detection and correction</b>	<b>34</b>
7.1. Plant testing	34
7.2. Soil testing	35

<b>8. Sulphur in animal production</b>	<b>39</b>
8.1. Sulphur metabolism in ruminants	39
8.2. Body sulphur content and turnover in sheep	41
8.3. Wool production	42
8.4. Sulphur metabolism in monogastrics	42
8.5. Animal production systems	43
8.6. Fertilizers and ruminant diet quality	43
8.7. Protected protein in ruminant diets	44
8.8. Sulphur in excreta	45
<b>9. Sulphur interactions and processes</b>	<b>46</b>
9.1. General	46
9.2. Glucosinolates and cyanogenic glycosides	46
9.3. Micronutrient interactions in ruminants and man	47
<b>10. Sulphur sources</b>	<b>48</b>
10.1. Application	48
10.2. Sulphur fertilizers	48
10.3. Predicting the release of sulphate from fertilizers	50
10.4. Effect of placement and form on plant uptake and residual value	51
10.5. Organic sulphur sources	53
<b>11. Concluding remarks</b>	<b>56</b>
<b>References and further reading</b>	<b>59</b>
References	59
Further reading	62
<b>Appendix 2. Advantages and disadvantages of various sulphur-containing fertilizers</b>	<b>65</b>
<b>Appendix 3. Plates</b>	<b>68</b>

## About the book and the author

This publication has brought together the many aspects of sulphur in agricultural systems. It is important to do this at this time as intensification of food, fibre and animal production is escalating to feed the ever increasing world population. The move from sulphur-containing single superphosphate and ammonium sulphate to “high-analysis” fertilizers such as diammonium phosphate (DAP) and monoammonium phosphate (MAP), which contain little sulphur (S), has led to increasing deficiencies of S which must be overcome.

A.R. (Ray) Till is a retired agricultural scientist who holds a M.Sc. from the University of Melbourne and a Ph.D. from the University of New England (UNE). He commenced his career in 1949 as a laboratory assistant in the Tracer Elements Investigation Unit in CSIR (later CSIRO - Commonwealth Scientific and Industrial Research Organisation) in Australia, and joined the CSIRO Division of Animal Physiology at Prospect in 1957 as an experimental officer, his main role being the application of radiotracer techniques to research in sheep and wool production. In 1963, he commenced studies on the application of radiotracers in grazing systems and, in 1967, he joined the CSIRO Animal Production Division at Armidale in New South Wales (NSW), as head of a research group applying radiotracer techniques to grazing systems, particularly in studying the pool sizes and flow rates of S in soils, plants and animals.

Upon retirement from CSIRO in 1991, he joined the Department of Agronomy and Soil Science at UNE in Armidale with a large commitment to international projects that utilized his considerable prior experience. He was also heavily involved in post-graduate training.

Ray Till's name appears on a wide range of publications dealing with many aspects of S, and he has been a speaker at many national and international conferences dealing with S.

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## Symbols, acronyms and abbreviations

(as used in this publication)

<sup>35</sup> S	Radioactive S isotope where superscript is the mass number
APS	Adenosine-3-phosphosulphate
AS	Ammonium sulphate
ATP	Adenosine triphosphate
C	Carbon
CH <sub>3</sub> SH	Methyl mercaptan
CN <sup>-</sup>	Cyanide
COS	Carbonyl sulphide
CP	Crude protein
CS <sub>2</sub>	Carbon disulphide
CSIRO	Commonwealth Scientific and Industrial Research Organisation
Cu	Copper
DAP	Diammonium phosphate
DM	Dry matter
DMS	Dimethyl sulphide
EB	Empty body
GSH	Glutathione (reduced form)
GSSG	Glutathione (oxidized form)
ha	Hectare
HI-S	Hydriodic acid reducible S / mainly ester sulphate
HS <sup>-</sup>	The charged part of H <sub>2</sub> S taken up from the rumen
H <sub>2</sub> S	Hydrogen sulphide
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
IFA	International Fertilizer Industry Association
IFDC	International Fertilizer Development Center
K	Potassium
KCl	Potassium chloride
kg	Kilogram
KMnO <sub>4</sub>	Potassium permanganate
K <sub>2</sub> SO <sub>4</sub>	Potassium sulphate
M	Mole
MAP	Monoammonium phosphate
MCP	Monocalcium orthophosphate
mM	Millimole
μM	Micromole
Mo	Molybdenum
MoO <sub>4</sub> <sup>2-</sup>	Molybdate
Mt	Million metric tonne (=Tg)
N	Nitrogen

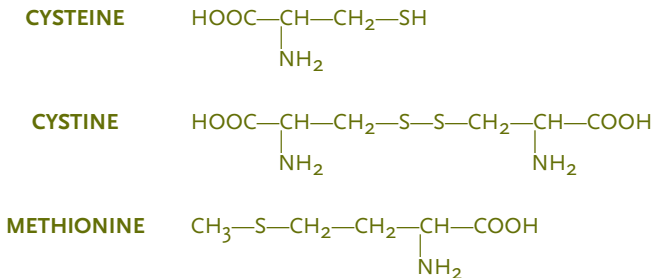
## 8 Sulphur and sustainable agriculture

$\text{Na}_2\text{SO}_4$	Sodium sulphate
$\text{NH}_3$	Ammonia
$(\text{NH}_4)_2\text{SO}_4$	Ammonium sulphate (=AS)
$\text{NO}_3^-$	Nitrate
OM	Organic matter
P	Phosphorus
PAPR	Partially acidulated phosphate rock
PAPS	5'-phospho-adenosine-3'-phosphosulphate
PR	Phosphate rock
S	Sulphur
$\text{S}^0$	Elemental sulphur
$\text{S}^{2-}$	Sulphide
Se	Selenium
$\text{SO}_2$	Sulphur dioxide
$\text{SO}_3^{2-}$	Sulphite
$\text{SO}_4^{2-}$	Sulphate
$\text{SO}_4^{2-}\text{-S}$	Sulphate sulphur
SOM	Soil organic matter
SR	Specific radioactivity
SSP	Single superphosphate
t	Metric tonne
$T_{1/2}$	Half-life
Tg	Teragram (=Mt)
TSI	The Sulphur Institute
TSP	Triple superphosphate
TVA	Tennessee Valley Authority
yr	Year
Zn	Zinc
$\text{ZnSO}_4$	Zinc sulphate

## 1. Sulphur in agriculture: setting the scene

In nature, sulphur (S) occurs as inorganic and organic forms, ranging from reduced states such as hydrogen sulphide ( $\text{H}_2\text{S}$ ) gas through elemental sulphur ( $\text{S}^0$ ), to complex organic compounds and enzymes that contain S in various valency states. Elemental S is widely used in industry, mainly for sulphuric acid ( $\text{H}_2\text{SO}_4$ ) production, with a significant proportion of the acid used in various phases of fertilizer production. In 2008, total S consumption was 74.1 million metric tonnes (Mt) of which 34.5 Mt were used to produce fertilizers (IFA, 2009).

The S-containing amino acids, methionine and cystine (Figure 1), are essential for production of proteins; without them and other S-containing materials, there would be no life as we know it. Higher animals cannot produce the essential amino acids and depend on predation, plants and/or the microflora and microfauna for their supply. Ruminants overcome this problem by having a symbiotic relationship with microorganisms in their gut.

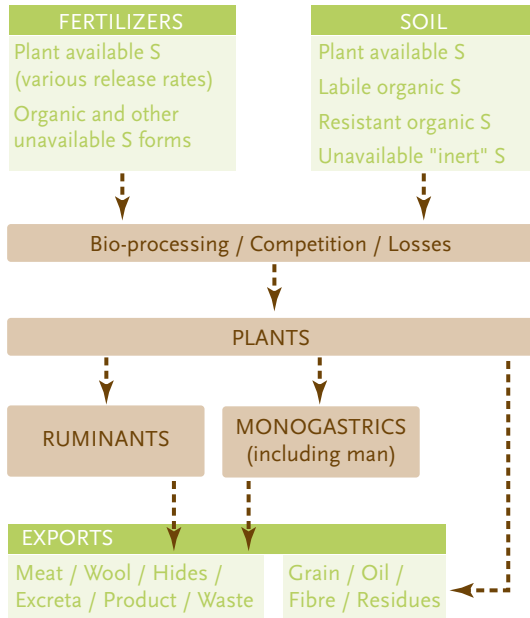


**Figure 1.** Essential S-containing amino acids. Cystine is two cysteine molecules joined by a S—S bond. There is ready interchange between these two and it is often written as cyst(e)ine.

A simplified flow diagram illustrates the use of S in crop and animal production (Figure 2). Plants require S in inorganic forms, normally as sulphate ( $\text{SO}_4^{2-}$ ) from the soil, but can also use sulphur dioxide ( $\text{SO}_2$ ) from the atmosphere. Sulphur is transported to the leaves, where it is incorporated into essential amino acids, proteins, oils and other organic compounds.

Some of the plant products are used directly by man, while others are used by animals to yield an extended range of products. Most of the S used by animals is excreted as  $\text{SO}_4^{2-}$ , which is readily available for reuse by plants. The remaining S, and that from crop residues, is mainly organic and must be converted to  $\text{SO}_4^{2-}$  by the microflora and microfauna to complete the cycle.

In some areas, the S input from the atmosphere can be high enough to supply the S needed for growing crops. However, as more and more stringent limits are enforced on



**Figure 2.** Basic diagram of S use in farm systems (For simplicity, the pathways involving input, loss or recycling are not depicted).

the emission of  $\text{SO}_2$  and other S-containing compounds by industry, and the change towards the use of low-S fuels progresses, S deficiencies will inevitably increase. Some S-containing fertilizers will be required to replace the S removed in or with the final product and other losses due to residue management and leaching, if current production levels are to be maintained or increased.

Several S-containing fertilizers are commercially available, and there is a potential to develop more appropriate ones for specific crops. Fertilizers containing soluble  $\text{SO}_4^{2-}$  provide S that is readily useable by plants, but the plants have to compete with soil microbes and loss processes for the pool of available S. Techniques such as using controlled-release fertilizers, and banding and split applications can improve the plant's ability to compete and reduce leaching losses. Elemental S and organic forms of S in fertilizers must undergo mineralization to  $\text{SO}_4^{2-}$ , as does the crop residues, before being available to plants. Thus, the soil biota play a crucial role in relation to S in agriculture.

How a particular farm is managed can have a big effect on the loss and recycling of S and, consequently, on the fertilizer S requirements. Under low-intensity grazing, the requirement is 5–10 kg S/ha/yr, while a high S-demanding crop like rapeseed might need 50–80 kg S/ha/yr, depending on the crops used in the rotation and their requirements. Care should be taken to select the appropriate fertilizer and S application rate, timing and placement to minimize leaching losses and/or adverse interactions with other nutrients.

Soil and plant testing can be used to estimate the probability of a deficiency occurring but, in specific locations, their most likely value will be in monitoring changes and the stability of the system. In rotations, especially those involving a pasture phase, there may be different depths and volumes of soil explored by plant roots, and this has a direct bearing on the soil testing method and its interpretation in relation to fertilizer use and the residual value for subsequent crops.

In grazing systems, the interaction between animals and pasture in general and the management of the excreta in particular are important. For example, mature wool-growing sheep only retain about 10% of the S that they ingest, i.e. the fate of the 90% that they excrete can greatly influence the amount of fertilizer S needed.

Likewise, the S in the marketable proportion of the crop is frequently less than half of that in the harvested plant, and the fate of the residues after processing may significantly influence total S losses. In addition, the management of crop rotations, including forage crops, and the interaction between any cropping phases and grazing and/or supplementary feeding of animals has significant effects on the redistribution of S and the form and timing of application of the fertilizer.

The calculation of a simple nutrient balance gives a good indication of how much fertilizer is needed for a system somewhere near equilibrium and whether there are potentially damaging effects on the environment, but it cannot readily account for changes in management.

## 2. Introduction

Elemental S (brimstone, S<sup>0</sup>) is often found in the vicinity of volcanoes and hot springs, and so has been known to man for centuries. Together with other naturally occurring S-containing materials, S<sup>0</sup> has been used for medicinal purposes, as a crop protection product and in explosives, among others. Estimates of the amount of S in the Earth's crust range from about the 10<sup>th</sup> to 16<sup>th</sup> most abundant element (95% as the <sup>32</sup>S isotope).

The issue of acid rains has led to many cities and countries introducing increasingly stringent controls on the amounts of SO<sub>2</sub> that can be released into the atmosphere but, especially in the cases of poor and developing countries, there is no universally accepted international standard. The reduced emission has some benefits but it has contributed to increasing S deficiencies in many agricultural crops. If production levels are to be sustained or increased, the S deficit must be made up by some form of fertilizer.

With the exception of ruminants, which have a symbiotic relationship with microorganisms in their gut, no higher animals can metabolize inorganic S to synthesize the essential S-containing amino acids. Consequently, the interactions between the environment, microflora, microfauna and plants form the basis of the initial part of the food chain for survival of all the higher animals.

Excluding cataclysmic events, changes in nature take place slowly and the various biological entities evolve and/or become extinct as the global and local environments change. In the evolution of man, critical changes have been the movement from living within the confines of nature as nomadic hunter-gatherers, to establishment of small communities with the development of primitive agriculture, followed by technological development, cities, population explosion and the ever increasing demand for food and consumer products.

Until recently, when serious problems have emerged, agriculture and industry have paid scant respect to the global or local environment, and this is particularly true for control of atmospheric emission of S and the use of fertilizers with little regard for their S content. However, agriculture is now battling to maintain food supplies, using nutrients efficiently and management strategies appropriate to sustainable agriculture.

One fundamental requirement for a sustainable agriculture is that there must be at least a balance of nutrients between the inputs, removal in products and other losses. Any deficit between indigenous inputs and outputs must be corrected by changes in management and/or some form of fertilizer. Animal manures and waste materials contain various forms of S, and their value as fertilizers can be influenced by management practices. The wide range of S-containing compounds that exist in nature, and are involved in various biological processes, emphasize the potential for developing new and more efficient S fertilizers.

There are ten isotopes of S, four of which are stable and occur naturally as <sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S and <sup>36</sup>S, accounting for 95.02, 0.75, 4.21 and 0.014% of the total, respectively. The rest are radioactive forms with half-lives ranging from approximately 0.2 seconds to 3 months. In many situations, isotopic tracers provide vital information on the pathways and dynamics of S utilization, which cannot be studied by other methods. For such studies, the only isotopes that are of significant value are the stable isotope <sup>34</sup>S, and a low energy β emitter <sup>35</sup>S that has a half-life of 87.4 days.

### 3. The global sulphur cycle

In a survey of 11 world regions for global emissions, SO<sub>2</sub> levels were similar from 1980 to the present time, but showed marked differences at the regional level. In 1980, the North Atlantic region contributed 60% of global emissions but, by 1995, this had fallen to less than 40%, and it will probably continue to decrease in the future. The total global SO<sub>2</sub> emissions in 1990 were estimated at about 72 million tonnes (Mt). Actual emissions may be higher, with 56% from coal, 24% from oil, 15% from industrial processes, and 3% from biomass burning (Smith *et al.*, 2001). China is believed to be the largest contributor to global SO<sub>2</sub> emissions.

Biomass burning is only a small part of the global emission but, together with losses from some of the industrial processes, it should be studied with a view to recycling more of the S directly back into agriculture.

These figures suggest that the overall amounts in the global SO<sub>2</sub> cycle have not changed dramatically as far as agriculture is concerned, but that the distribution of anthropogenic emissions has changed and, especially in relation to agricultural production, there will have to be thorough monitoring of all regions to check for changes.

There are many global cycle models with varying degrees of refinement, mainly aimed at predicting and/or interpreting the results of man's activities on various components of the cycle, and the changes that they may produce on the whole of the Earth's environment.

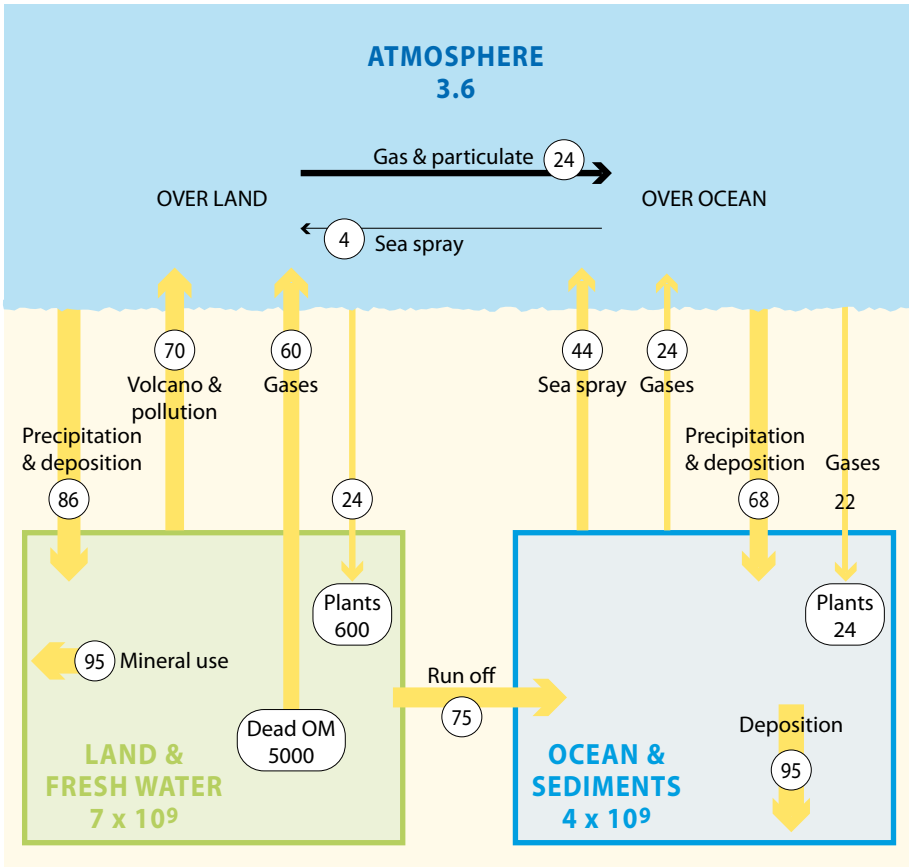
The very simple cycle (Figure 3) and gross fluxes (Table 1) show approximate amounts and transfers of S for some of the components. These estimates emphasize

**Table 1.** Examples of estimated S fluxes between the global pools.

Pathway	Action	Flux <sup>1</sup> (Mt/yr)	Flux <sup>2</sup> (Mt/yr)
Atmosphere to land	Precipitation/deposition	86	49+4
Atmosphere to land	Vegetation intake	24	18
Atmosphere to ocean	Precipitation/deposition	68	56
Atmosphere to ocean	Gas absorption	22	16
Land to atmosphere	Volcanoes	10	3
Land to atmosphere	Biological decay (H <sub>2</sub> S)	60	3
Land to atmosphere	Pollution (SO <sub>2</sub> )	60	65
Ocean to atmosphere	Sea spray	44	44
Ocean to atmosphere	Biological decay (H <sub>2</sub> S)	26	28
River to ocean	Runoff	75	
Ocean to land	Spray via atmosphere	4	

<sup>1</sup>Davey (1980); <sup>2</sup>Granat *et al.* (1976). Most of the values are similar and variations depend largely on estimated S levels and the boundaries used.

the magnitude of the amounts and flows with respect to the requirement in ‘local’ agriculture, especially the inputs to and from the atmosphere and the effect it has on S availability to plants.



**Figure 3.** Simplified global S cycle showing the approximate amounts of S (Mt) and the annual flows (Mt/yr) between basic components. Based on data from Ericsson (1960), Granat *et al.* (1976), Davey (1980) and Smith *et al.* (2001).

In terms of agriculture, the most important influence of the global S cycle is exchanges with the atmosphere. The major natural inputs to the atmosphere are the reduced S compounds: dimethyl sulphide ((CH<sub>3</sub>)<sub>2</sub>S; 75%) and hydrogen sulphide (H<sub>2</sub>S; 15%). Carbon disulphide, carbonyl sulphide and aerosols, mainly from the sea as SO<sub>4</sub><sup>2-</sup>, make up practically all the rest, with a very small input of natural SO<sub>2</sub> (Noggle *et al.*, 1986; Ryaboshapko, 1983; Trudinger, 1986; Kelly and Smith, 1989).

The total SO<sub>2</sub> input to the atmospheric cycle is about half of the total S input and is practically all anthropogenic from combustion of fossil fuels and smelting of ores. The large amount of dimethyl sulphide is formed and catabolised by many biogenic processes in soil and water, but the largest contribution to the atmosphere is from the ocean. However, all the reduced S compounds are rapidly oxidized in the atmosphere and the S is recycled as sulphuric and sulphurous acids and sulphate salts (Trudinger, 1986).

Relative to air, SO<sub>2</sub> is a dense gas and does not mix rapidly. Thus, in combination with the non-uniform distribution of anthropogenic emission sites, the direction of the prevailing winds and rainfall, the return of S is very uneven. These factors result in S input levels ranging from toxic acidification, through adequate supply, to virtually no influence depending on the distance from the emission source.

The total estimated input to the atmosphere in 1976 was about 200 Mt/yr, comprising 70 Mt/yr from the ocean, 70 Mt/yr naturally from the land, and about 60 Mt/yr from human activities (Table 1). Over the years, the anthropogenic input to the atmosphere has been greatly reduced in some regions, allowing for plants to recover in some areas where the deposition levels were leading to toxicity problems. In many other areas, reduced opportunities for plants and soil to derive sufficient S from the atmosphere, together with the use of S-free 'high-analysis' fertilizers, resulted in more widespread S deficiencies

## 4. Importance of sulphur in agriculture

### 4.1. Boundary conditions

Currently, the major consideration in agriculture is the overall profitability of producing sufficient crop and animal products to meet market demand. This is rarely the same as global needs; management of surpluses, deficits and impacts on the environment are the result of the current political and economic pressures on both producers and consumers. Meeting demand generally involves “highly improved” systems using management practices designed to give maximum economic return.

Within these constraints, the system is largely regarded as a simple linear progression from fertilizer to crop, and then either to crop products processed directly for consumption by man and/or fed to animals that are in turn used by man. All too often, the focus in these systems is the dry matter yield of plant products without due regard to the appropriateness or quality of the product for the end user, or the cost to environment stability.

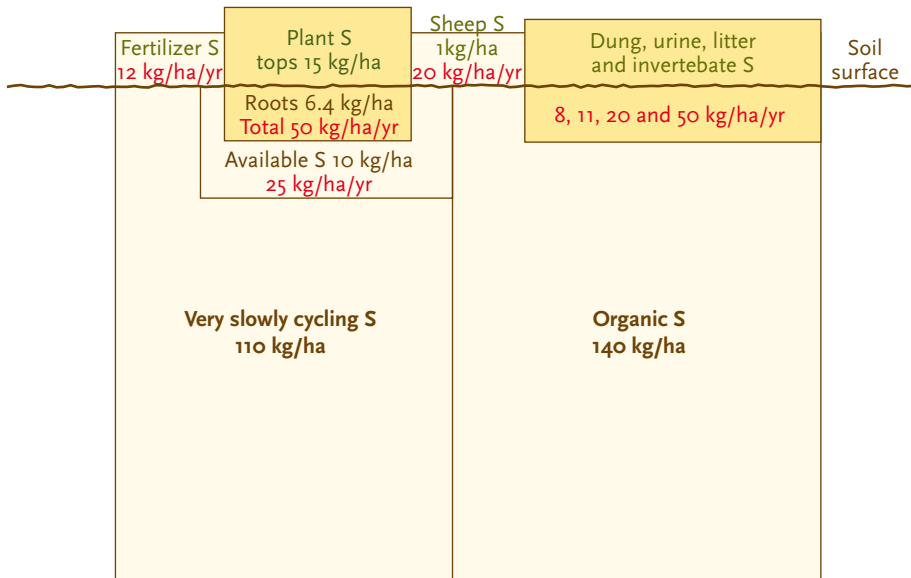
Compared to the total amounts of S in the global cycle, the amounts in agriculture are minuscule, e.g. the S in plant and animal pools is a tiny fraction of the global S pool and it is often assumed that agriculture, unlike anthropogenic  $\text{SO}_2$ , would have no impact on the global cycle. However, the rapid rates of turnover of some of the components in agriculture can cause significant changes to the local inputs and losses.

For example,  $7 \times 10^{15}$  metric tonnes (t) of metamorphic and igneous rocks with a half-life of 50 million years would release about  $10^7$  t S/yr, while a similar amount would be recycled from  $10^8$  t of plant material if it had a half-life of four years. If the plant material occupied 50% of the land area, this release would be about 13 kg S/ha/yr, an amount readily exceeded by S applications and recycling in agriculture. Considering that many of the soil organic S materials have a half-life very much less than four years, it is important that S in agriculture, as well as that used in industry, is recycled efficiently and that significant amounts are not allowed to enter the atmosphere and waterways and alter the natural cycle.

### 4.2. Farming systems: sulphur cycling and balance

As with the global cycle, the amounts and forms of S in the component parts of a farming system vary enormously and do not necessarily give any indication of their relative importance. A simple representation of the relative amounts of S in some components of a sheep grazing system is given in Figure 4.

In this example, only the top 10 cm of the soil are considered, and the amounts are for a wool-producing enterprise stocked at 10 mature sheep per hectare. The important soil “bio-processing” microflora and microfauna are so numerous and varied that they



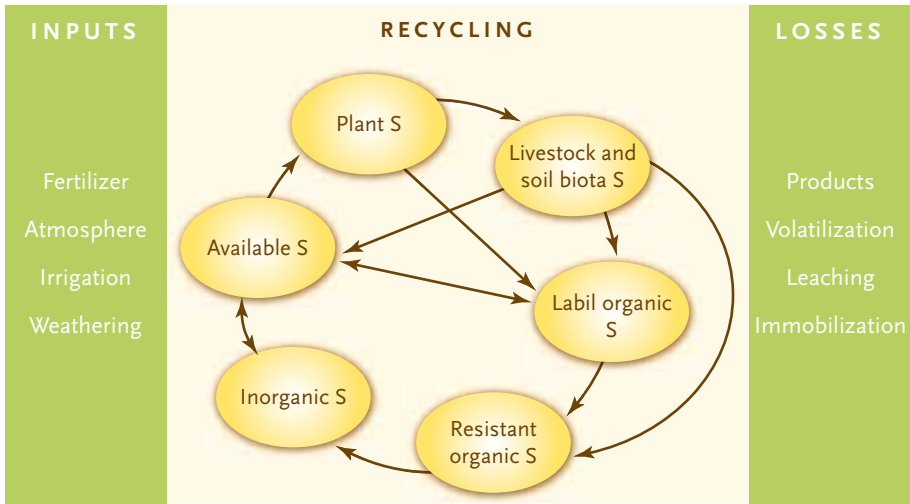
**Figure 4.** Relative sizes of S pools in a grazed pasture. The boxes show the approximate sizes of the S pools (kg/ha), their positions relative to the soil surface at the time of fertilizer application and, for some, the annual flows (kg/ha/yr). Most fertilizer S enters the cycle via the soil-available pool, but some of it and other above-ground S is taken up directly by the plant before it can enter the soil pools.

cannot be readily grouped into a single pool and are assumed to be spread throughout the appropriate components. Individual animals only contain a very small proportion of the total S in the system, but their management can exert a strong influence on the amounts in the other components and involved in the different processes.

The sheep consume between 50 and 90% of the above-ground plant production and only retain 10% of the ingested S. The rest of the S is excreted and its management strongly influences how much fertilizer is needed to maintain the level of production. In this situation, the available pool is too small to provide the amount of S needed for the total plant uptake over the year, and the only way the system can be maintained with a low S input is by mineralization and recycling from the residues and organic pools. Some of the numerous interacting pathways that are influenced by management of such an enterprise are shown in Figure 5.

Apart from animal health control and the seasonal changes in pasture production/availability, the major differences between pure grazing and cropping enterprises are the timescale required to obtain a product and the effect of crop residue management on the amounts of S in some components and the overall S requirement.

Crops have higher short-term demands for S, with the plant pool going from zero to maximum in a few months. Total plant uptake is determined by crop type, nutritional S status, and crop yield. Reported values range from a few kilograms to almost 100



**Figure 5.** A simple representation of the S cycle and the input and loss boundaries. The boxes represent pools of S. The arrows show flows of material in cropping or animal production systems.

The S cycle in that figure is essentially that used in the radiotracer and simulation studies described by Till *et al.* (1970). In real situations, the pools do not have clearly defined boundaries. The pools mainly contain a loosely grouped mixture of S materials and the agents for S transformations. A brief listing of the important components and flows follows in section 4.3.

kg S/ha but, in temperate regions, it is usually less than 50 kg S/ha (e.g. Duke and Reisenauer, 1986; Tabatabai, 1984). Especially for crops with a high S demand, the uptake frequently exceeds the amount of available  $\text{SO}_4^{2-}$  in the soil. Consequently, if the rate of mineralization is too slow, fertilizers must be used.

The efficient use of any fertilizer requires that it must be able to supplement the current soil-available S to a level that will be able to match the changing demand of the particular crop as it develops and matures. As well as the wide variation in the total S uptake by different crops, the proportion of the total plant S that is in the final product also varies. Management of the residual/waste S thus has a significant effect on the need for fertilizer.

In the section on boundary conditions, it was shown that the turnover rates ( $T^{1/2}$ ) of the system components can be more important than the actual amount in that component and, again for the grazed pasture, the management of the amount of S that goes through the animal is far more important in terms of production than the actual amount in the animal.

To really manage any of these complex multi-component agricultural systems, it is not only essential to know how much S is there but also the rates with which the different transformations and transfers proceed along the multiplicity of interacting pathways.

This requires an appreciation of the possible recycling pathways for the particular production system and identification of key processes that limit the availability of S to the plant and/or lead to the loss of S from the productive system.

Apart from fertilizer, the major S inputs are largely controlled by the global cycle, but they can be influenced to some extent by the local management. For example, any S input from irrigation water depends on the S concentration in the water, which can be measured. However, the overall S input as the result of irrigation may be positive or negative because it also depends on other factors such as when and how much water was used, the solubility of the fertilizer, and soil properties such as infiltration rate, adsorption and profile depth.

Sulphur losses are partly controlled by the environment and product removal, but they are significantly modified by other factors, e.g. fertilizer solubility and returns from crop residues and animal wastes.

### 4.3. Forms of sulphur

#### 4.3.1. Available

The available S pool, consisting of the soil solution and adsorbed  $\text{SO}_4^{2-}$ , is probably the simplest in the cycle. It is usually 3-10% of the total soil S and is depleted by plants and other competing processes. Recharging this pool is mainly by mineralization of various organic materials and application of fertilizers. Soluble S fertilizers can increase the pool directly, but  $\text{SO}_4^{2-}$  is susceptible to leaching. Sulphur as  $\text{S}^0$  or in organic fertilizers is less susceptible to losses because it must be oxidized, usually by microorganisms, before the  $\text{SO}_4^{2-}$  becomes available to plants.

#### 4.3.2. Plant

The plant pool is essentially a pool of organic S, in particular the S-containing amino acids and proteins in plants. Plants compete with other processes to take up  $\text{SO}_4^{2-}$  from the available pool and translocate it to the leaves, where practically all of it is converted into a range of organic materials. Apart from leaching and erosion, plants provide the major route for removal of S from the farm.

#### 4.3.3. Livestock and soil biota

This is the most complex and diffuse pool in the cycle. As well as domestic livestock, it includes an enormous range of microflora and microfauna, and other consumers that occupy various niches and are spread throughout the system. The range of their specific functions combines to provide all the necessary transformations and transfers that maintain the S recycling through the other pools.

#### 4.3.4. Labile organic

This consists of a pool of organic S, plus the labile fractions of the plant and soil biota. In some situations, it may constitute up to half of the total S pool, and it has a fairly rapid turnover (e.g.  $T_{1/2}=35$  days). Because of its large size and rapid turnover, the

management of the labile organic matter pool is critical for the flow of  $\text{SO}_4^{2-}$  into the available pool. In the cropping system, a significant portion of the crop residues and soil biota are included in this pool.

#### 4.3.5. Resistant organic

The resistant organic pool is a mixture of materials derived from the more resistant carbon-bonded-S fractions in the residues of various plants and in the soil biota. Depending on the land use, the combined components of this fraction is frequently larger than the labile pool. It ranges from about 50 to 90% of the total soil S. The turnover of some components can be very slow but, under cropping, most fractions will have a half-life of 1-3 yr.

#### 4.3.6. Inorganic

This pool does not include the available pool, but contains materials from many sources and with a wide range of turnover rates, most of which are very slow. The sources are small amounts of strongly adsorbed S, leached  $\text{SO}_4^{2-}$  that may accumulate as gypsum at some depth in the soil profile, reduced S in anaerobic flooded soils, and various mineral deposits that release S very slowly.

### 4.4. Management of inputs and losses

Efficiency of fertilizer use depends on fertilizer placement, release rates of nutrients, timing of application and interactions between nutrients.

Agricultural products (grain, livestock, etc.) are unavoidable losses of S from the cycle, while the management of residues removed with product, and those left in the field also influence nutrient losses/requirements. Management of residues left in the field influences water infiltration, soil aggregate stability, erosion, and rates and amounts of nutrients recycled and/or lost.

Consideration of the preceding figures and outlines of pools and flows emphasizes some important points:

- In most circumstances, any S inputs to the plant are via the available  $\text{SO}_4^{2-}$  pool.
- The plant must compete with other processes for the available S.
- Very different rates of S supply are needed for the cropping and grazing situations.
- For intensive animal production systems such as feedlots, pigs and poultry, the primary crop production sources should be geared to quality products having the appropriate balance of protein, energy and nutrients to suit the specific animal needs.
- The management of residues and waste from the various enterprises is critical in minimizing fertilizer requirements and reducing nutrient losses to the environment.

## 4.5. Nutrient balances and sustainability

If the overall production system is to be sustainable, the minimal requirement is a balance between the total S inputs and outputs. Whether bringing new land into production or changing cropping systems, the initial problem that the farmer faces is to know if his system is, or will become, S-deficient what measures he must take to reach his required level of production.

It is difficult to get an early enough warning of crop S deficiency to take corrective measures based on plant visual symptoms or tissue tests, while problems exist with many soil S tests for predicting relationships between fertilizer requirements and levels of production.

The starting point in this assessment is an educated guess based on local experience and backed up by whatever technical information that can be obtained. Any fertilizer trials carried out on the way to reaching an acceptable level of production are valuable in the final estimation of fertilizer requirements to reach a sustainable S balance.

The inputs from the atmosphere are virtually beyond the control of the local farmer and will come through rain, dry fall and gaseous absorption. In the long term, they are unlikely to change significantly unless there are big changes in local industry and large scale burning of crop residues, fossil fuels and organic waste.

Depending on the crop or farming enterprise, the atmospheric S input may be adequate or virtually insignificant, but it is important to know how much S is supplied. If crops are irrigated, the potential input from water can be calculated, but it will not always be easy to estimate how much of the S is actually available to the crop. The S in drinking water can also be a valuable input to ruminants.

The ease of predicting removals with products is subject to seasonal variability and the processing that separates the disposable product from the residues, but long-term experience may help in estimating the magnitude of errors in estimating S loss. The management of residues from processing of products and any left in the field may significantly reduce S loss. Leaching and surface flows can remove significant amounts of S from the root zone, and there may be very small losses of volatile S compounds from some soils and plants. Any discrepancy between the inputs and losses must be made up by inputs from appropriate fertilizer materials (organic, inorganic or a combination of both).

Assuming that the release rate of  $\text{SO}_4^{2-}$  from the fertilizer is known, the amount of fertilizer needed is determined by the efficiency with which the plants compete for the available  $\text{SO}_4^{2-}$ , and by any losses of fertilizer S. The efficiency with which plants compete for nutrients can be modified by strategic placement of fertilizers and using fertilizer sources that supply a balanced suite of nutrients at rates that match the demand by the plant. This stage requires an intimate local knowledge and/or an understanding of any other factors that influence the loss, utilization and recycling processes.

If the S balance is negative, the system cannot be sustained, but the converse is not necessarily true. Even with a positive balance over a short term, the system can still be in a decline if changes in the various processes allow the relative sizes of some pools to change. For example, a change in management could change the relative amounts of labile and resistant organic matter in residues or soil. A build-up in resistant organic

matter would send the system into a decline due to a fall in the supply of S to the available pool, while an increase in labile organic matter could allow production to rise or a reduced fertilizer input.

A major problem in finding some of the required information is that once S from a particular source has entered the system, it becomes mixed with S already in the cycle and it is not possible to know where the fresh S goes to or whether any response is due directly to the added S or some secondary change.

Various isotopic techniques have been used to study the input, recycling and loss of S in sites ranging in size from small pots to pastures of over one hectare (e.g. Blair and Till, 2003). Usually, in the smaller-scale studies, radioactive  $^{35}\text{S}$  or stable  $^{34}\text{S}$  were applied to the system being studied, while, on a larger scale, it is sometimes possible to exploit the naturally occurring differences in the ratio of  $^{34}\text{S}$  to  $^{32}\text{S}$  ( $\delta^{34}\text{S}$ ) in materials from different sources to estimate transfers and turnover rate. While it is unlikely at present that isotopic studies will be developed on a commercial scale, they are essential for scientific validation of key processes and the development of testing methods.

It is the unenviable job of the farmer and his advisors to find answers to these questions and integrate their effects with the probability of having a “good” season and profitable markets. Various computer models ranging from simple local regression types to mechanistic ones including economics and risk analysis have been developed to help answer some of these questions. However, the wide range in the levels of sophistication needed to explain individual processes together with the enormous amount of data that is still needed to drive the models makes the chances of an all-seeing model that spans all the critical variables very remote. Different types of models can help with specific tasks, but there needs to be great care to ensure that the results are realistic and not pre-determined by the model construction.

The minimum requirements for any particular cropping and/or livestock production enterprise to be sustainable are:

- There must be energy and nutrient balances between the inputs to, and losses from, the system as a whole. Some form of fertilizer and/or a change in management must make up any S deficit.
- It must be financially viable, i.e. the overall management and productivity must be profitable.
- For efficient production of plants and animals, it is necessary to have a balanced supply of all the essential nutrients for each process, and the quality of the product must be aimed to suit the end-user.
- If an overall S balance is achieved, the productivity of the system is controlled by the relative sizes of the pools in the cycle and the rates of transfer of S along the competing pathways between the pools.

## 5. Soil sulphur

### 5.1. General description

The soil is not just a collection of minerals but it is a living, breathing complex of inorganic and organic materials, plus the myriad of microflora and microfauna that coexist within it. The proportions in various components and the biological activity are dictated by the environment and agricultural practices. Biological processes are responsible for most of the mineralization, essentially oxidation of organic fractions to  $\text{SO}_4^{2-}$ .

The term “fixation” is used freely for different processes depending on the nutrient and the situation. In the case of S, it can be considered as removing S from the soil available pool by physical or chemical processes such as adsorption and precipitation, but also incorporation into a wide range of organic S forms in nature (e.g. soil biota and plants). The time scale over which the changes take place ranges from a few minutes to several million years. Biological processes can be very rapid and are mainly limited by temperature and the supply of substrates containing minerals and energy.

In conventional agriculture and natural systems with higher plants and animals, the soil is the primary source and/or intermediate reservoir of the raw materials that provide the energy and nutrients for the soil biota and of the available nutrients for plants. Plants take up virtually all their S from the soil solution as  $\text{SO}_4^{2-}$ .

In all productive soils, the predominant S storage is in organic matter: about 95% in temperate soils and somewhat lower in weathered tropical soils. In the soil solution,  $\text{SO}_4^{2-}$ , like nitrate ( $\text{NO}_3^-$ ), is highly mobile and, as it is only weakly adsorbed onto the surface of soil particles. It is vulnerable to displacement by strongly adsorbed ions such as phosphate and/or to leaching from the soil layer explored by plant roots.

This process may result in precipitation of  $\text{SO}_4^{2-}$  too deep for retrieval by plants and/or complete loss from the profile into groundwater and river systems. The interactions between the environment, microorganisms and plant uptake can cause very large seasonal fluctuations in the extractable  $\text{SO}_4^{2-}$  levels. Consequently, the rates of the biological mineralization and fixation processes are major determinants in the supply of  $\text{SO}_4^{2-}$  to plants.

### 5.2. Sulphur fractions

The complexity of transformations in the mixture of inorganic and organic components in the soil is not clearly understood, and detailed studies of the interactions are very difficult in real agricultural situations. There is a good understanding of some inorganic components and processes such as adsorption, diffusion and leaching. However, the

very important, mainly biological, processes responsible for the two-way conversions between SOM and the inorganic fractions are poorly defined.

In attempts to get more orderly studies of the pathways and processes, researchers have used various approaches to group materials and/or processes into fractions with known composition or common attributes. Based on simple chemical processes, there are four most commonly determined fractions:

- **Total S** is determined after digestion of the soil with a mixture of nitric and perchloric acid.
- **Available S** is commonly considered as the fraction extracted by various soil test reagents, which remove mainly soluble  $\text{SO}_4^{2-}$  plus different proportions of other S fractions (See Figure 9). Results from the different methods are then correlated with yield responses, and they give estimates of fertilizer requirements.

An example of a test that has been increasingly used in Australia is the KCl-40 extraction (Blair *et al.*, 1991), which removes adsorbed  $\text{SO}_4^{2-}$  and some labile organic S.

- **Hydriodic acid-reducible S (HI-S)** is roughly 50% of the S in SOM, and is considered as fairly labile as it contains some very labile components.

The analytical method is based on the release of  $\text{H}_2\text{S}$  from certain classes of compounds and is adapted from Johnson and Nishita (1952). The organic matter reduced is comprised mainly of the ester sulphates (-C-O-S-) plus smaller amounts of sulphamates (-C-N-S) and complexes with ester bonds (-C-S-S-). Depending on the actual sequence for handling the soil analysis, the HI-S value may have to be corrected for  $\text{H}_2\text{S}$  from the “available”  $\text{SO}_4^{2-}$ .

- **Carbon-bonded S** is the rest of the organic S, comprising materials with S covalently bonded to carbon (C) plus some small peptides and free and adsorbed S-containing amino acids.

Additional fractions that are sometimes used are:

- **Rainey-Ni reducible S** is a portion of the C-bonded S, probably from the free and adsorbed S-containing amino acids, which may be up to 30% of the C-bonded S.
- **Soil solution S** is extracted either directly using porous cups or microtubes in the soil, or by centrifugation of soil samples, to monitor the concentration of S in the solution that is available to plants and soil biota.
- **Cycling S pool:** If isotopic tracers are being used in a system that has time to approach equilibrium, it is sometimes possible to calculate the cycling S pool and input rates for small inputs and very slowly cycling pools. The S cycling pool has no clearly defined boundary but shows the amount of S actually taking part in the recycling during the length of the study. The difference between the total S and the cycling S shows the amount of intractable S (i.e. S with very long turnover rates). It may also be possible to measure the S in the SOM labile C fraction.

Alternative fractionation methods have been described (Janzen and Ellert, 1998), such as:

- Physical fractionation of soil based on particle size, and then chemical determination of S in the fractions as outlined above (Anderson *et al.*, 1981).

- Separation of organic S into non-protected S, protected S and insoluble S fractions (Eriksen *et al.*, 1995a, 1995b). It showed that there was a large pool of passive organic S (52-82% of the total organic S in the soils studied), which probably contributed very little to S mineralization; this is of similar size as the resistant fraction that was identified as only playing a minor role in the  $^{35}\text{S}$  grazed pasture studies of May *et al.* (1968).

Although the chemically-separated fractions described above are useful for exchange of information between different groups, further refinement to allow focus on particular critical entities is needed. Some studies aimed at achieving a more critical focus have concentrated on fractionation of organic S into biotic and abiotic components and, although the microbial biomass may be less than 5% of organic S, its high turnover rate may be responsible for much of the S cycling in some soils (Gupta and Germida, 1988). The microbial biomass almost certainly represents a vital component of the SOM, but the role that it plays in the overall production needs to be clarified, and this probably requires the use of isotopic techniques.

Possible support for the importance of such a rapidly turning over S pool comes from simulation studies with  $^{35}\text{S}$  (May *et al.*, 1968, 1972), where the existence of such a pool was clearly indicated but could not be identified by them. Other studies of the turnover rates of specific fractions of the SOM depend on complete specification of the fractions and of the fate of the S from them and, so far, this has only met with limited success (Ghani *et al.*, 1991). Studies of the mineralization of  $^{14}\text{C}$  in SOM have also shown the presence of a fraction of soil carbon that turns over rapidly (Blair, 2004).

It is not possible to generalize on the total amounts of S required in various soil fractions for plant production due to differences in the depth and density of plant roots ranging from pastures to arable land. Also, the amount of S fertilizer required for a particular crop will depend on the influence of management practices, S recycling and loss and the form and the release processes of S from the chosen fertilizer. The best that can be done at this stage is probably to consider an arbitrary soil depth and an uncomplicated soil profile. Soil testing depths range from about 7.5 cm to over 1 m depending on nutrient and soil but, for many crops and pastures, most of the root biomass is in the top 10 cm. If we consider this depth, the range in total S is about 100-1000 ppm. Except for highly weathered soils, with high proportions of 1:1 clays, or inorganic and saline soils, most of the S is in various organic forms, with the remainder occurring as inorganic  $\text{SO}_4^{2-}$ .

The inorganic forms are mainly solution and adsorbed  $\text{SO}_4^{2-}$ , precipitated  $\text{SO}_4^{2-}$  and, depending on the degree of water saturation, very small amounts of S in reduced states.

The ester sulphates, sometimes termed HI-S, are usually about 50% of the SOM and are more labile than the C-bonded S. However, the C-bonded S can contain a small proportion of free and/or adsorbed S-amino acids, which may be readily available for metabolism.

Radiotracer studies of S cycling using  $^{35}\text{S}$  fertilizer applied to temperate pastures showed that S from the fertilizer could still be detected two years after the initial application (May *et al.*, 1968). The results showed rapid incorporation of the fertilizer S

into SOM and emphasized the role of organic matter as the major storage of S and the supplier of mineralized S to plants.

The SOM is composed of a wide range of materials from inputs such as plant residues and animal excreta, and the multitude of living and dead intermediates in the processes and pathways for recycling S via the soil biota. Although the importance of these processes is obvious, it is difficult to study them in a fully functioning production system.

There are countless microfauna and microflora species that exist in the soil and, together with the macrofauna and others which populate the organic matter-rich upper soil horizon, they play key roles in mixing and metabolizing organic matter. In a sheep grazing system stocked at 10 sheep/ha, Till *et al.* (1980) estimated that there was some 395 kg/ha of underground micro and macro organic matter consumers and that this compared with a sheep biomass of 513 kg/ha.

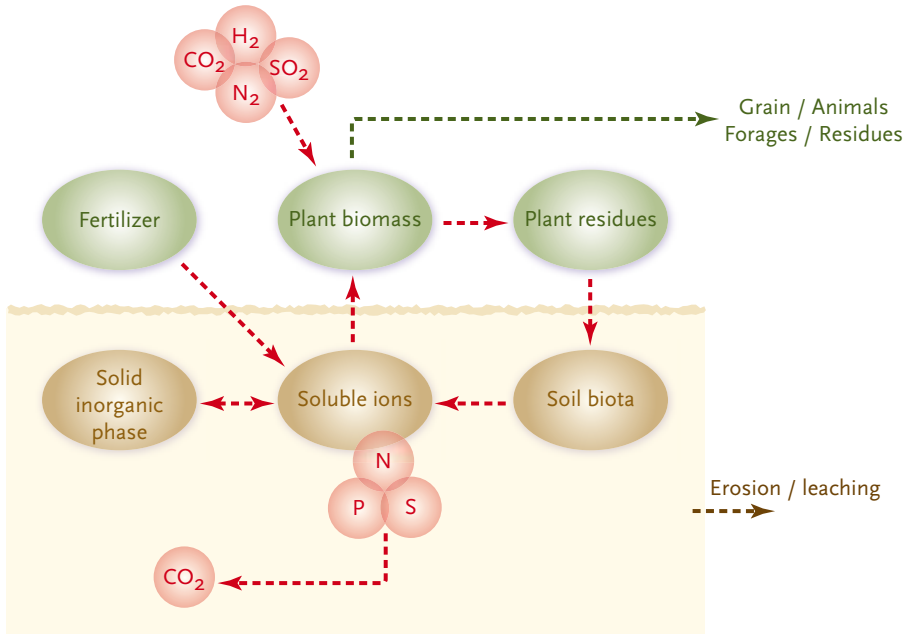
The management of the particular production system interacts strongly with the soil biota and has the potential to significantly influence the productivity and nutrient storage or loss. In terms of S metabolism, some of the important species have been identified and there is also some information on their numbers, and how management influences the populations. However, the integration of these studies with S mineralization in various cropping and grazing management systems is difficult and requires collaboration of researchers with a very wide range of skills.

### 5.3. The carbon cycle and balanced nutrition

Given the dominance of the organic matter in the storage and recycling of S and the need for a balanced supply of plant nutrients, it is appropriate to consider the carbon cycle in relation to nutrient release rates and balances (Figure 6). The cycle shows the release of N, P and S but, even if they were initially in perfect proportions in a particular SOM fraction, the differences between nutrients in their mineralization rates, and their adsorption, uptake and loss processes will make it unlikely that the nutrients remain available to the crops in optimum proportions (e.g. Till *et al.*, 1982). Some of the important factors are:

- Sulphate is only weakly adsorbed in most soils and may be displaced by applied phosphate;
- Nitrate and  $\text{SO}_4^{2-}$  are very mobile and are susceptible to leaching;
- If S is deficient, N cannot be used efficiently for protein production, and *vice versa*;
- Legumes cannot fix N efficiently without an adequate supply of S and P.

In studies of SOM, the separation into different classes or pools has been carried out on the basis of molecular weight, particle size, microbial biomass and their oxidation by reagents of graded strengths. At this stage, progressive oxidation with potassium permanganate ( $\text{KMnO}_4$ ) appears to be the most useful approach to assess the lability of OM and nutrient turnover rates, especially if it is combined with isotopic tracer studies. Such an approach might resolve some of the observed differences in plant-available S between the HI-S and C-bonded S fractions.



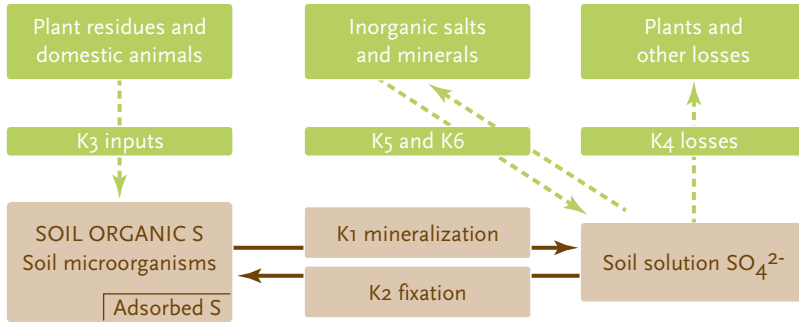
**Figure 6.** The C cycle and nutrient recycling.

## 5.4. Sulphur mineralization and fixation

In order to restrict the number of variables, most S mineralization studies are carried out as isolated incubations under controlled conditions. The results obtained depend on the difference between the forward ( $k_1$ ) and backward ( $k_2$ ) process rates. Depending on the duration and number of parameters in the experiment, these are very variable. Certain key factors such as pH, temperature and moisture play an important part in the  $k_1$  and  $k_2$  rates but, in practice, the final equilibrium values are controlled by other sources and sinks as shown in Figure 7.

Another problem with many of these studies is that they are carried out in soils where the agents responsible for the competing processes of mineralization and fixation are not clearly identified. In such studies, it is essential that the soil biota is either as close as possible to that existing in the field or comprised of known organisms, and that plants or sinks that compete for the liberated  $\text{SO}_4^{2-}$  are used to obtain realistic estimates of the availability of the mineralized S and of a net equilibrium value.

The mineralization and fixation of other nutrients from the SOM follows similar processes to those shown in Figure 7, but the amounts in the different pools and the processes rates will almost certainly not be the same. The differences in the net mineralization of the elements will alter the balance in the concentrations in the soil



**Figure 7.** Mineralization and fixation interactions.

The boxes and arrows represent pools and flows. Brown boxes and arrows show the situation commonly studied, while green boxes and arrows give examples of some of the missing inputs and losses.

solution and, for optimum value, the fertilizer will need to have appropriate release rates for each nutrient.

Soil organic matter tends to have an N:S ratio of about 8:1 compared to about 15:1 to 17:1 in most plants and 10:1 for plants that have a high S demand (Cowling and Jones, 1970). The enrichment of S in SOM relative to plants is in agreement with the results of Till *et al.* (1982), who isotopically labelled clover, using <sup>14</sup>C, <sup>15</sup>N and <sup>35</sup>S, and found different release/re-utilization rates for N and S.

Other studies found that organic N is often mineralized faster than organic S in the early stages of plant decomposition (Barrow; 1961, Freney and Spencer, 1960). Presumably, the proteins, which comprise most of the S in plants and soil microorganisms, are more rapidly broken down than the S-containing compounds in them, the amino acids being recycled. This suggestion is supported by the fact that Rainey Ni-reducible S, mainly cysteine and methionine, represents only 20 to 30% of the organic S in soils (Williams, 1975) and the rest is roughly divided about equally between HI-S and C-bonded S fractions. The HI-reducible S is a very diverse mixture of organic materials that collectively incorporate applied <sup>35</sup>S at a greater rate than the C-bonded soil S fraction (e.g. Freney and Swaby, 1975).

Improved fractionation procedures and a greater knowledge of what happens to specific S-compounds in soils are clearly prerequisites to a better understanding of the nature, role and dynamics of organic S in soils. There is a need for more isotopic studies in 'normal' functioning systems, where specific components are labeled and elements traced.

## 6. Sulphur in plants

### 6.1. Needs and deficiencies

The concentration of S in plants is similar to that of P, but both nutrients have very different roles. Phosphorus is mainly involved in energy and lipid production. Both S and N are necessary for the production of essential S-containing amino acids. Sulphur is also essential for many enzymes and other important S-rich products. Plants such as brassicas and oil palm have high requirements for S, while others can accumulate  $\text{SO}_4^{2-}$ . The total amounts of N and S in plants can vary widely, with common values of N:S ranging from about 10:1 to 20:1.

Sulphur is essential for processes such as:

- synthesis of essential S-containing amino acids and proteins,
- synthesis of coenzyme A, as well as biotin, thiamine and glutathione,
- synthesis of chlorophyll, lipids and volatile oils, and
- biological N fixation by bacteria living in symbiosis with legumes.

For many years, little attention has been paid to S as a plant nutrient, mainly because it has been supplied incidentally to soil through rainfall and volcanic emissions and as a component of some fertilizers. In some early studies, in order to correct what was perceived as specific nutrient deficiencies using fertilizers such as ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ), sulphate of potash ( $\text{K}_2\text{SO}_4$ ), zinc sulphate ( $\text{ZnSO}_4$ ) and superphosphate, the responses attributed to N, P, K and Zn may have been partially due to S, or its interactions with other nutrients. Any such unobserved interactions emphasize the need to accurately detect deficiencies and provide plants with a balanced supply of nutrients.

Plants predominantly use  $\text{SO}_4^{2-}$  from the soil, but some can utilize  $\text{SO}_2$  and/or  $\text{H}_2\text{S}$  from the atmosphere. In the past, atmospheric inputs have often supplied sufficient S for plants and masked the need for S. Other reasons for the increasing incidence of S deficiencies are changes in the crops grown, increasing yields and more short-season cropping with decreasing recycling of residues, especially in developing countries. For example, just changing crops from cereal to oilseed can increase S demand by 50 kg/ha or more (Table 2).

The amount of S applied to crops as fungicides and insecticides have also declined. Meat and wool production and greater emphasis on high protein crops have increased demand, while the use of “high-analysis” fertilizers reduces inputs of S relative to the other nutrients. Crops can be classified into three groups according to their S requirement (Spencer, 1975):

- high S requirements: rapeseed, alfalfa and cruciferous forages;
- moderate S requirements: coconut, sugarcane, clover, grasses, coffee and cotton;
- low S requirements: sugar beet, cereals and peanut.

The S requirements of some crops and the proportion of the S that is contained in the useable product (Table 2) show values in line with the broad grouping by Spencer (1975). The proportions of S in the useable product emphasize the need for good management of the crop residues in order to reduce losses.

**Table 2.** Crop S uptake and amounts in harvested product and residues (adapted from Zhao *et al.*, 2002).

Crop	Uptake kg S/ha	Exported		Residues	
		kg S/ha	% uptake	kg S/ha	% uptake
Brussels sprouts	73.5	29.8	40.6	43.7	59.4
Broccoli	60.4	14.3	23.7	46.1	76.3
Oilseed rape	58.3	14.6	25.1	43.7	74.9
Cabbage	55.1	22.9	41.5	32.3	58.5
Swede	50.5	27.3	54.0	23.2	46.0
Onion	41.1	31.7	77.2	9.4	22.8
Leek	37.2	14.0	37.5	23.2	62.5
Red beet	19.9	8.3	41.4	11.7	58.6
Sugar beet	16.5	5.1	30.8	11.4	69.2
Wheat	15.9	9.5	60.0	6.3	40.0
Peas	15.9	9.5	60.0	6.3	40.0
Beans	14.6	8.1	55.7	6.5	44.3
Carrot	11.3	5.3	47.2	6.0	52.8
Lettuce	11.0	4.3	39.1	6.7	60.9

## 6.2. Uptake processes and metabolism

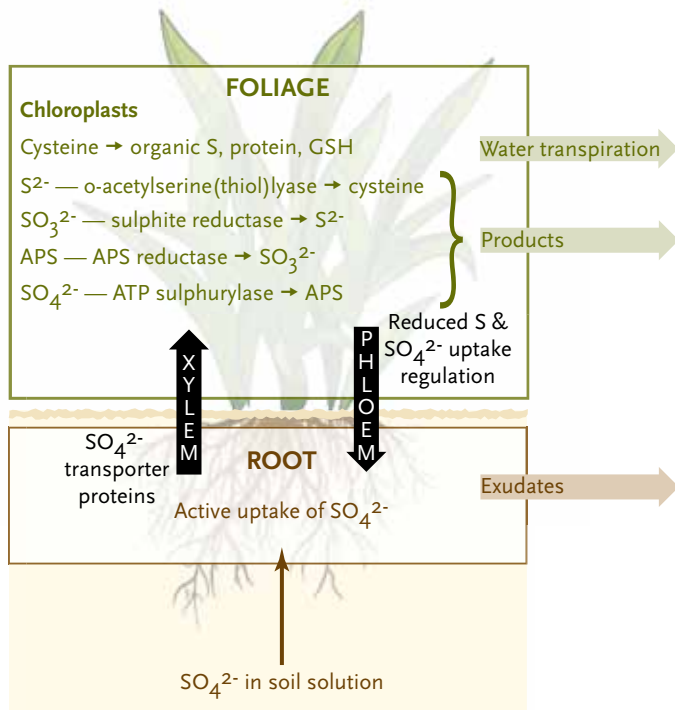
The usual source of S for plants is  $\text{SO}_4^{2-}$ , which is actively taken up from the soil solution by the root cells. Sulphate is then moved by transporter proteins through the xylem to the leaves in the water transpiration stream. Although proteins can be synthesized in the roots, the common site for  $\text{SO}_4^{2-}$  reduction to  $\text{H}_2\text{S}$  is in the chloroplasts in the leaves. In most plants, S is used mainly to synthesize cyst(e)ine and methionine, which are incorporated into proteins. Smaller amounts of S are needed for the synthesis of other essential molecules such as coenzyme A, biotin, thiamine, glutathione and sulpholipids.

Some brassicas (e.g. rapeseed) use significant proportions of the S to produce glucosinolates, while onions and garlic (*Allium* sp.) have high S-alkylcysteine sulphoxides (allins) contents. The production of allins appears to be a sink for  $\text{H}_2\text{S}$  and the levels of glucosinolates and allins depend on the availability of S.

In situations of excess S supply, some plants accumulate modest amounts of  $\text{SO}_4^{2-}$  and, in a control mechanism, may eliminate excess to the atmosphere as  $\text{H}_2\text{S}$ , while

others such as tomato and cotton can accumulate large amounts of  $\text{SO}_4^{2-}$ , which is apparently held in relatively unavailable forms. The total S: $\text{SO}_4$ -S ratio is sometimes used to indicate the sufficiency of S supply, but the diversity of the S forms and their differences in mobility in the different crops make it very difficult to have general guidelines for “critical” S levels.

The basic uptake of  $\text{SO}_4^{2-}$  and sequence of metabolic processes in the plant (Figure 8) are as follows: Sulphate is transported to the leaves. In the chloroplasts, it is transformed to adenosine 5'-phosphosulphate (APS) prior to its reduction. The reaction is catalyzed by ATP sulphurylase, but its affinity for  $\text{SO}_4^{2-}$  appears to be rather low, and the  $\text{SO}_4^{2-}$  concentration in the chloroplasts is probably one of the rate-limiting steps in the regulation of the  $\text{SO}_4^{2-}$  reduction pathway (De Kok and Stulen, 1993; Stulen and De Kok, 1993). The APS is first reduced to sulphite ( $\text{SO}_3^{2-}$ ) by APS reductase, which probably has the lowest activity of the enzymes involved in the assimilatory  $\text{SO}_4^{2-}$  reduction pathway. It may be the key regulation point, responding rapidly to S concentration, with sulphide ( $\text{S}^{2-}$ ), O-acetylserine, cysteine or glutathione being the likely regulators. Sulphite is then reduced to sulphide by sulphite reductase, with reduced ferredoxin as reductant. The incorporation of sulphide into cysteine is catalyzed by O-acetylserine(thiol)lyase, with sulphide and O-acetylserine as substrates (For detailed descriptions on S metabolism, see Thompson *et al.*, 1970, and De Kok *et al.*, 2002).



**Figure 8.** Simple diagram of  $\text{SO}_4^{2-}$  uptake and metabolism by plants.

Methionine, an essential S-containing amino acid present in plants, is the most important compound derived from cysteine. It is synthesized via the bi-directional trans-sulphurylation pathway between cysteine and homocysteine, the cysteine to methionine direction in fungi and higher plants and the reverse in animals and fungi. The homocysteine in plants is converted into methionine using the methyl group derived from serine (Thompson *et al.*, 1970) as indicated: *Cysteine + O-acetyl homoserine* → *cystathione* → *homocysteine* → *methionine*.

Most of the cysteine and methionine is usually incorporated into plant proteins and lesser amounts in glutathione, enzymes, phytochelatins and other “secondary” S-compounds, such as sulpholipids, glucosinolates and allins. The ability of the –SH side to cross link in S–S bonds plays a significant role in the structure and properties of proteins, while the –SH is also important in binding enzymes and metals, e.g. in thioredoxins and ferredoxins.

Glutathione (GSH) and its homologues have important roles as regulators and in redox reactions in plants and animals. The glutathione homologues have the same N-terminal  $\gamma$ -glutamyl moiety and central cysteine residue but have a variable C-terminal amino acid. They are widely distributed in plant tissue in concentrations ranging from 0.1–3 mM.

Glutathione is predominantly present in its reduced form and the ratio of reduced glutathione (GSH) to oxidized glutathione generally exceeds a value of 7. Reduced glutathione may function as a carrier and reductant in the assimilatory  $\text{SO}_4^{2-}$  reduction pathway and it appears to be the major transport control for shoot to root transfer of reduced S via the phloem.

Unconsumed plant material and crop residues are the major suppliers of organic S to the soil with significant inputs from animal excreta in some areas. There are also additions of S to the soil from root exudates, which may be significant (Lynch and Whipps, 1990). However, it is difficult to get details of the amounts and role of these sources, probably because of the difficulties in separating roots from soil and the recycling of S within the soil biota, although the presence of amino acids in these exudates (Rovira, 1969) suggests that some S may enter the soil via this route.

If a crop has a high demand for S, the application of a particular S fertilizer at high rates may not supply the S to the plants efficiently, and can lead to undesirable changes in the rest of the system, e.g. increased leaching losses and antagonism between different forms and amounts of S, selenium (Se) and molybdenum (Mo). The stage of the crop growth when S demand is highest, the proportions of nutrients in the fertilizers, their form, site of application and rates of nutrient release will all influence the efficiency of S use by the crop.

### 6.3. Plant sulphur and product quality

When dealing with a large number of interacting processes, at any level of sophistication, there is the problem of where to break into the various interlocking cycles because, ultimately, a perturbation at one point will inevitably have some consequences in another part of the metabolism. Considering the absolute dependence of all higher animals on

microorganisms and plants for their supply of essential S-containing materials and the ever-increasing demand for food by man, this section concentrates on the effects of S supply on the beneficial components of crops and forages.

There are other interactions between S, Mo and Se that occur to varying extents and are very important to different processes in soils, plants and animals. Natural systems gradually adapt to changes in their environment but, in the quest for more food, agricultural production has been intensified and this has resulted in large-scale changes to nutrient balances over large areas. To maintain current levels of production, the nutrient balances must be restored and this can only be achieved by fertilization with the appropriate combination of inorganic and organic materials.

### 6.3.1. Sulphur responses in crops and forages

The range of S uptake for various crops is from about 11 to 74 kg/ha (Table 2). Maintaining levels of production requires a fertilizer to supply sufficient S to balance the overall inputs and losses imposed by the management system. Consequently, the form and amount of fertilizer required for each production system will vary significantly. General or “average” recommendations can rarely be more than a rough guide. This becomes even more uncertain and difficult when there are crop rotations with different S requirements.

The values of residual S may change dramatically with fertilizer and residue management. If an appropriate source of S is applied, then, provided other severe constraints are not operating, there will be an increase in biomass production and/or in the amounts and distribution of quality components such as proteins, essential amino acids and vitamins. Exceptions to this may arise when excess S applications lead to accumulation of  $\text{SO}_4^{2-}$  and/or compounds with anti-nutritional properties, especially glucosinolates, and disproportionately low N:S ratios in animal feeds.

When the economics of applying average levels are considered, it often appears to be worthwhile to add extra S “to be on the safe side”, but such actions can be a dangerous or detrimental practice. It is important to get the application right (*right product(s) at the right rate, right time and right place*) in order to ensure that the product will be the best for the next stage in the production chain and ultimately for the end user.

### 6.3.2. Bread quality

Variable results have been obtained in New Zealand for studies of the effect of fertilization on bread quality. A change from fertilizers containing S to urea for wheat nutrition can lead to a decline in the quality of wheat flour for bread-making, expressed in dough rheological properties by increased farinograph, dough work input and extensigraph resistance. The choice of cultivar seemed to be the single best option for obtaining the quality desired, but each of the cultivars tested showed a linear increase in work input with increasing N:S ratio.

Under high N management, the application of S fertilizer can significantly improve dough and baking characteristics (De Ruiter and Martin, 2001). In Australia, Europe and the USA, the poorer bread-making qualities have been attributed to S deficiency (Moss *et al.*, 1981, Zhao *et al.*, 2002).

## 7. Sulphur deficiency detection and correction

### 7.1. Plant testing

#### 7.1.1. Visual Symptoms

The visual detection of S deficiency is fairly straightforward, although in young plants it may be confused with N deficiency. Symptoms include a yellowing of the younger leaves, as a result of a low chlorophyll production and poor remobilization of S within the plant (Yoshida and Chaudhry, 1972) and a marked reduction in plant height and tiller number in cereals (Blair *et al.*, 1979). Photographs of S deficiency in crops provide an excellent reference source for the visual detection of S deficiency in plants (see plates in Appendix 3).

There are two main problems with the visual detection:

- By the time the deficiency is obvious it is usually too late to correct it in that crop;
- The observation does not give an accurate indication of how much S is needed or the best form to apply.

#### 7.1.2. Chemical analysis

Many chemical analyses of plant tissues have been used to detect and/or estimate the degree of deficiency such as: total S,  $\text{SO}_4\text{-S}$ , total S: $\text{SO}_4\text{-S}$  ratio and N:S ratio. Sometimes they are useful, especially for particular crops in regions where there is a good agronomic background and experienced extension officers but, similarly to visual symptoms, by the time results are available, it is usually too late for the crop, and no precise recommendation can be given on how much S is needed. Another problem with these tests is actually sampling the precise part of the plant at exactly the right time and, then, using a standard method of preparation for analysis.

A rice growers' cooperative in the Murrumbidgee Irrigation Area of Australia provides an example of the coordinated use of modern technology and local experience/cooperation to manage crop nutrition, especially S. In conjunction with researchers and extension officers, the cooperative has adopted a diagnostic package developed by the New South Wales Department of Agriculture. This involves specified sampling at a known stage of plant development, immediate drying in a microwave oven, same day dispatch to the laboratory and Near-Infrared estimation of plant S. The combination of standardized sampling methods and local experience provides good recommendations for management and/or remedial treatment of the current crop.

Recent work at Rothamsted Research in the UK resulted in a simple and rapid method for determining the malate:sulphate ratio in a hot water extract of plant materials (Blake-Kalff *et al.*, 2002). It has been tested on plants grown in the field with different levels of applied S fertilizer and it appears that this test can give an early enough warning of S deficiency for corrective measures to be taken. However, the developers point out that there are many factors involved in arriving at the required plant product and no precise

recommendation of the amount of S needed for correction can be made at present. The interpretation also needs information on the stage of development of the roots in relation to the distribution of S in the soil profile, and needs to be backed up by the experience of the farmer and the local agronomic adviser.

In glasshouse studies of rice, S deficiency was indicated when the grain S content was less than 0.1% and the N:S ratio was wider than 14:1. Application of S after anthesis, to previously deficient plants increased grain S from 0.08% to 0.2%, well above the highest level achieved by applying S at sowing, and suggests that the use of grain analysis for retrospective diagnosis warrants further testing in the field (Randall *et al.*, 2003).

Much information is available on critical nutrient concentrations and ratios of nutrients in different parts of crops and trees (e.g. Reuter and Robinson, 1997). However, in many cases it is probably better just to leave it up to readers to consult local agronomists or books such as those in the references.

## 7.2. Soil testing

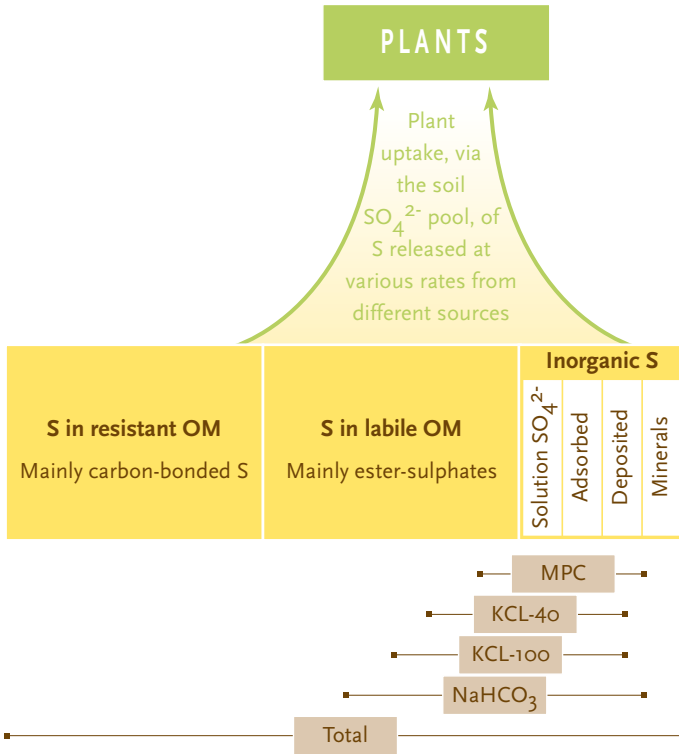
Over the years, many extractants have been used on soils to predict the likely occurrence of a deficiency in a particular cropping or pasture situation and, more importantly, estimate the amount of fertilizer needed to obtain optimum production. The objective has usually been to estimate the amount of soil solution  $\text{SO}_4^{2-}$  plus adsorbed  $\text{SO}_4^{2-}$  that make up the pool of plant-available  $\text{SO}_4^{2-}$ , and relate that to the plant requirements.

This approach has not been successful, the main problem becoming clear if the uptake and cycling of S is considered (Figure 9). Even in that simplified representation, there are many interacting alternative pathways and processes, and the relative sizes of the S pools (e.g. the extracted plant-available pool) are only part of the story, and it is the process rates that complete the picture.

The proportion of the total S as available  $\text{SO}_4^{2-}$  in the cycle is about 5% and, subject to large seasonal variations; the rest is in organic forms such as ester and C-bonded S. Even without competition, the available  $\text{SO}_4^{2-}$  pool is usually less than the amount required by the plants throughout the growing season.

The proportions of the  $\text{SO}_4^{2-}$  initially available and of  $\text{SO}_4^{2-}$  mineralized from the organic matter, mobilized from inorganic sources and applied in fertilizer that the plant can retrieve depend on such factors as the placement of the fertilizer and the mineralization rates of the various organic fractions. Consequently, except in a few specialized situations, the various soil extractants either under- or over-estimate the availability of S from SOM. Without a better understanding of the importance of the process rates and of the critical factors which control them, universally applicable soil tests are unlikely.

Bardsley and Lancaster (1960) attempted to overcome the problem by estimating “reserve” S but, as with most of the proposed methods, the main difficulty in evaluating the soil tests is that, without isotopic tracers, there is no way of measuring the efficiency of the fertilizer in supplying S to the plant, and whether the extractant recovered S from the same pool as that used by the plant.



**Figure 9.** Diagrammatic representation of the main soil S fractions and of the proportions of them that are removed by different extractants. Based on isotopic S studies at the University of New England, Australia.

Using standardized soil sampling methods at appropriate times of the year, and integrating these with local experience of the magnitude and persistence of plant responses to particular fertilizers, their methods of application and other management practices, it has sometimes been possible to use regression relationships and statistics to estimate soil critical S levels, and to develop response curves suitable for recommending fertilizer rates for specific crops. Such regression relationships can work for particular areas where there is enough background experience and data, but none of them have had rigorous investigation to establish what fractions, pathways and processes actually supply the S used by the plant, and the efficiency with which the plant competes with other users and loss processes. These difficulties do not preclude the possibility of other extractants being developed, but it is preferable that future work should pay more attention to the dynamics, processes and management of the whole soil-plant system.

From pot studies in which rice was grown in <sup>35</sup>S-labelled soil, the relationships between the specific radioactivities (SR) of the S in the plants and those of S recovered from the soil by various extractants show the relative merits of the extractants (Table 3).

The KCl-40 test, where 0.25 M KCl is added to the soil and extracted at 40°C for three hours was the most promising (Blair *et al.*, 1991).

**Table 3.** Degree of association between the SR of the extracted S and that in the S taken up by rice (The nearer to 1, the closer the S used by the plant is to that extracted).

Extractant	System	
	Non-flooded	Flooded
H <sub>2</sub> O	0.88	0.85
MCP	0.83	0.79
KCl-40	0.92	0.92
NaHCO <sub>3</sub>	0.27	0.19

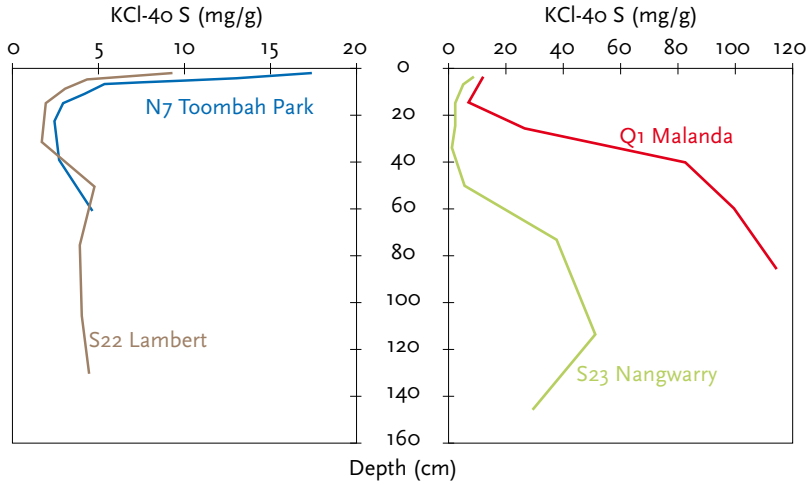
Soils from 18 pastures in northern New South Wales, Australia, were used in pot trials to test the relationship between plant responses to applied S, expressed as percentage of maximum yield, and the available S determined by various extractants. The results presented in Table 4 show that the best relationship was with the available S extracted by the KCl-40 test. The results from the KCl-40 test are a pointer to what may be achieved through a fundamental approach. However, they are by no means universally applicable tests and, in some situations, the locally tried and adapted tests will give better results.

**Table 4.** Coefficient of determination ( $r^2$ ) between S recovered by various extractants and the percent of maximum yield for 18 pasture soils collected from northern New South Wales, Australia (Blair *et al.*, 1991).

Extractant	$r^2$
H <sub>2</sub> O	0.47
MCP	0.48
KCl-40	0.74
NaHCO <sub>3</sub>	0.15
Total S	0.03

A number of other factors, such as the forms and distribution of S in the soil profile and the changes in volume of soil explored by roots as the plant develops, also have to be taken into account when using soil samples to assess the probability of S deficiency being a problem for different plants.

Some examples of large variations in available S in the soil profiles from four sites in New South Wales are shown in Figure 10. The variation in S demand with plant growth, the type of crop and management would have a significant effect on the occurrence and persistence of S deficiencies.



**Figure 10.** Sulphur distribution down the profile for some New South Wales soil sites (Blair *et al.*, 1997).

Care must also be taken when collecting the samples because the results could be biased due to previous treatments such as burning of crop residues and animal grazing habits and management. For example, there are important differences in the pathways and forms of S excretion by ruminants with inorganic S mainly in urine and organic forms in dung.

Reutilization of S by plants from these materials occurs by different pathways at different rates, which can be altered by management. In pastures, there can be high S concentrations under sites of earlier dung or urine excretion. The redistribution by cattle is fairly random, while the camping of sheep leads to the development of gradients of increasing concentration of S towards the camp.

## 8. Sulphur in animal production

Sulphur is essential for growth of virtually all organisms. Plants and microorganisms can utilize inorganic sources of S and N in the synthesis of S-containing amino acids and many enzymes and vitamins. Higher animals cannot synthesize the essential amino acids and, except for ruminants which have a symbiotic relationship with the microorganisms in their gut, they depend on plants or predation for their supplies of energy, proteins and the essential amino acids, among others.

The focus of this section is on the metabolism of S in animals, the interactions between animals and the rest of the S cycle, the metabolism of S in terms of the quality of an animal's diet, the removal of S in products, and recycling from excreta.

### 8.1. Sulphur metabolism in ruminants

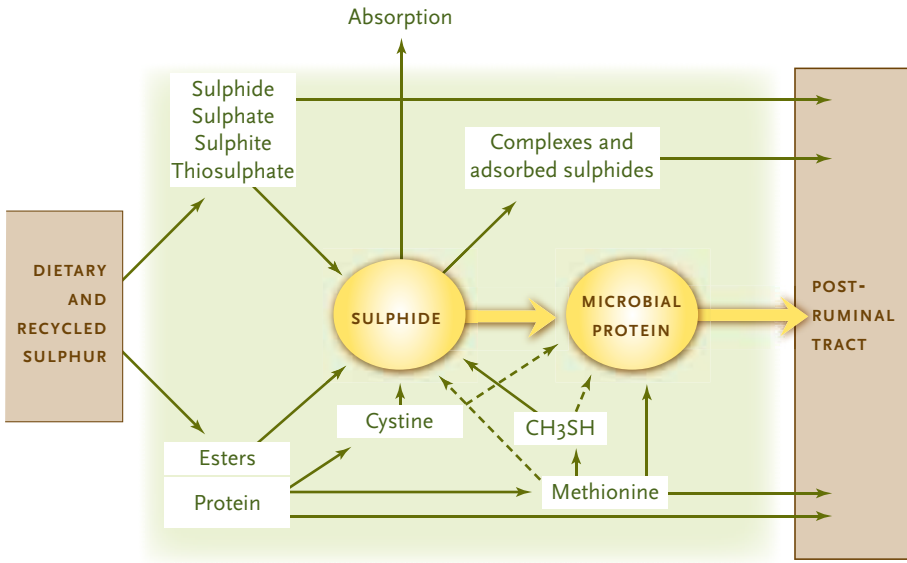
The ability of ruminants to utilize low quality roughage and inorganic forms of N, P and S to supply proteins and other products and services enable them to play an important role in most farming systems and food chains. The metabolism of S in ruminants has been reviewed in some detail (Bray and Till, 1975; Underwood and Suttle, 1999), but the focus here is on the role that the rumen plays in dealing with diets of very different quality that result from variations in S supply and management of pastures, crops and feed supplements. In terms of S metabolism, the gut of a ruminant can be divided into two main systems:

- *The reticulo-rumen*, in which S in feed and secretions is largely reduced to  $H_2S$  and converted into microbial proteins or absorbed directly as  $HS^-$  (Figure 11 );
- *The post-ruminal section*, in which the overall processes are the digestion of proteins and other S-containing materials, and the absorption of amino acids, peptides and inorganic and organic sulphates.

In addition, there are several interactions in the animal that regulate the levels of S in various body components. The undigested organic S, plus a small amount of inorganic S are excreted in the dung, and the rest of the inorganic S is excreted as  $SO_4^{2-}$  in urine.

The metabolism of S appears to be via ATP (adenosine triphosphate) to APS (adenosine-3-phosphosulphate), which either interacts with ATP to produce PAPS (5'-phospho-adenosine-3'-phosphosulphate), or releases  $H_2S$  by the action of dissimilatory-reducing bacteria, which derive reduced S from PAPS. These processes can be disrupted by competitive inhibition of APS formation by molybdate, selenate, tungstate or chromate and, although the results are variable, this inhibition has been used to show that microbial reduction is the major, if not sole, method of  $SO_4^{2-}$  reduction in the rumen.

Radiotracer studies have shown that  $^{35}S$ -labelled APS and PAPS are formed from  $Na_2^{35}SO_4$  in mixed cultures of rumen bacteria, and subsequent incubation of  $^{35}S$ -labelled APS and PAPS with mixed rumen bacterial cultures results in the formation of  $H_2^{35}S$ .



**Figure 11.** Diagram of S utilization in the rumen.

As with plants, which synthesize proteins from inorganic sources, there are many similarities between the metabolism of S and N in ruminants so, at times, it is advantageous to consider the relative retention of N and S by the animals.

Bray and Till (1975) used data for 51 sheep with a wide range of N:S ratios in their diets from ten different sites. They showed that N and S retention was related by  $N = 10.37 S - 0.038$  with a correlation of  $r = 0.952$ .

The desirable dietary N:S ratio is about 10:1 for sheep and about 13.5 to 15:1 for cattle (Bird, 1974; Kennedy, 1974). Thus, the supplementation of diets with non-protein N, e.g. urea, may entail the provision of additional S and energy. Sulphur supplements commonly used are various  $SO_4^{2-}$  salts,  $S^0$  and, to a lesser extent, S-amino acids and the hydroxy analogue of methionine.

In addition, feed additives that supply energy, such as molasses, may contain appreciable amounts of S. Provided there is sufficient energy available, the synthesis of microbial protein from non-protein N and S will enhance the nutritive value of a poor quality diet but, on protein-rich diets, fermentation in the rumen can lead to wastage of N and S via the production and absorption of ammonia ( $NH_3$ ) and sulphide ( $S^{2-}$ ).

The S content of drinking water from different locations can vary widely and its potential nutritional value is frequently ignored. Its value can range from insignificant amounts to the situation where the S intake from this source may be large enough to produce adverse effects due to microbial production and subsequent absorption of large quantities of  $S^{2-}$ , which can result in loss of appetite (Bird, 1972).

## 8.2. Body sulphur content and turnover in sheep

The incorporation of S into wool, various body components, and its excretion in urine and faeces has been studied using  $^{35}\text{S}$  to help in estimating the effects of grazing on fertilizer requirements and S recycling (Till *et al.*, 1970). The concentration of S in various body components ranged from 0.12% dry matter in blood to 0.23% in liver, while the total S in the components, as a percentage of the body S, ranged from 0.3% in brain

**Table 5.** Composition of an "average" sheep (Till *et al.*, 1970).

Component	Sulphur		Pathway <sup>1</sup> (x-y)	Run B (T½ days)	Run D (T½ days)
	Concentration (% DM)	Proportions (% empty body S)			
Blood (p)	0.12	5.3	a-p	1.4	1.7
Skin (s)	0.19	12.3	p-g	15	15
Liver (l)	0.23	2.6	g-p	26	26
Heart (h)	0.16	0.7	g-a	30	30
Lungs (m)	0.17	2.3	p-l	31	31
Kidney (k)	0.17	0.4	l-p	16	16
Brain (b)	0.13	0.3	p-h	286	338
Gut wall (g)	0.10	5.5	h-p	38	38
Spleen (r)	0.17	0.3	p-m	65	89
Carcass (c)	0.15	70.3	m-p	24	33
Gut contents (a)	0.29	6.2	p-b	877	877
Total	0.15	106.5	b-p	49	50
Empty body	0.15	100.0	p-r	582	647
			r-p	34	34
			p-c	3.9	4.8
			c-p	25	31
			p-s	10	13
			s-p	20	24
			p-k	274	413
			k-p	24	35

<sup>1</sup>Sulphur content of an "average" 40 kg Merino wether sheep and component T½ estimated using a simulation model for the  $^{35}\text{S}$  data.  $T\frac{1}{2} = 0.693/k$ , where k is the rate constant for the flow of  $^{35}\text{S}$  from component x to component y, i.e. along pathway x-y. The two runs (B and D) are presented to show the variation of estimated T½ in the simulations.

to 12.3% in skin and 70.3% in the carcasses. The excretion pathway and proportions depend on the diet quality. In this study, it was 61% in urine and 21% in faeces.

The turnover rates for S transfer between the different pools were estimated by a computer analysis of the  $^{35}\text{S}$  measurements (Table 5). The observed half-life for the  $^{35}\text{S}$  flow into wool was 28 days, and similar half-life (about 30 days) were estimated for the blood, carcasses and skin, which are the other pools of major influence. Consequently, it appears that, in the field, most of the sheep's S equilibrates with the pasture with a half-life of about 28 days and, although there were differences between body components in S contents and concentrations, there were no large S-rich components that would be likely to produce unusual turnover rates within the sheep.

### 8.3. Wool production

Production of wool and some hair has a high demand for S but, unlike hair, wool is a continuously growing fibre. This is a reason for the lower N:S ratio needed in sheep feed than in cattle. Another reason is that cattle are more efficient at recycling S through saliva.

Wool contains about 3.5-4% S due to the high proportion of S-containing amino acids in the protein. The cross-linking of S-S bonds in the protein is responsible for some of the important properties of wool. Supplementing the supply of cysteine and methionine by sub-cutaneous injection or infusion into the gastro-intestinal tract immediately after the rumen may increase wool growth. On the contrary, feeding sheep with high quality proteins via the rumen is inefficient due to microbial degradation.

### 8.4. Sulphur metabolism in monogastrics

In their natural state, monogastrics have to obtain their essential S-containing food by grazing and/or predation. The main animals that are farmed for human consumption in this group are pigs, poultry and rodents. These animals cannot synthesize the essential S-containing amino acids from inorganic sources. Therefore, they must obtain them from plant, animal and synthetic sources.

The farmed animals are sometimes free-ranged or tethered, but are mostly kept in enclosures or cages and are fed with prepared feedstuffs and/or cut pasture and crop residues. Consequently, it is factors such as the suitability of the housing, the management of disease and the composition of the diet in terms of protein, energy, vitamins and minerals that determine the productivity of the animals.

If the protein-energy balance of the feed is acceptable, the only unexpected problems that may emerge would probably be due to mineral imbalances such as Se deficiencies or toxicities, as a result of the origin of feed components (e.g. toxicity due to the use of feed from high-seliniferous plants or areas, or deficiency due to plant and animal feeds from low Se areas or antagonism through the overuse of S fertilizer). The results of Se deficiency and toxicity in monogastrics are similar to those in ruminants when the effect of the rumen processes is ignored.

## 8.5. Animal production systems

### 8.5.1. Animals on natural pastures and woodlands

These may be changing cyclically or be in a fairly stable state with a balance of herbivores and predators but, in terms of exportable food and fibre products for human consumption, their output per unit area is usually low. If any nutrient balance exists, it depends on natural recycling. Within these areas, there is the occasionally-managed system, mainly subsistence farming where large ruminants provide draft power and manure for the farm and/or milk and fuel.

These farms sometimes provide limited management of nutrient recycling from crop residues, animal excreta and small inputs of nutrients from fodder supplements and fertilizers. In these systems, economics dictate that the large ruminants are rarely used for meat, while small ruminants and monogastrics give more flexibility in their use for food and fiber products.

### 8.5.2. Managed improved pastures and intensive production systems

These systems range in size from extensive farming, which provides a major source of exportable meat and fibre (sometimes integrated with forage cropping), to smallholder farming systems where the ruminants provide power, manure and sometimes meat. Dairying frequently involves rotational grazing, dietary supplements and fertilizer inputs to maintain production.

Intensive systems for ruminant meat, pigs, poultry, etc., are usually smaller and depend largely on imported feed and require specialized processing of excreta. They also tend to be more readily incorporated into, or associated with, mixed farming operations, and the management of the overall nutrient balance can be very complex.

In all these systems, there must be significant inputs of fertilizer (organic and inorganic) in order to balance the removal in products. The management of the residual nutrients in excreta after supplementary feeding may reduce the fertilizer requirements in some cases but, as the supplements are designed to replace additional demands by the intensively managed animals, their contribution are probably small and the nutrients are not in the required proportions.

## 8.6. Fertilizers and ruminant diet quality

The feature that makes ruminants so important is their ability to survive on poor quality (low-protein) roughage-based diets. This is due to their symbiotic relationship with microorganisms in the rumen, which can use the feed and inorganic sources of nutrients to produce microbial proteins that are subsequently digested by the ruminant. However, as the quality of the diet increases, the microbial processes readily degrade digestible proteins, with the end result that the ruminant eventually becomes less efficient than a monogastric animal.

In an extensive survey of the relationships between S supply and the quality of forage in ruminant nutrition, Tisdale (1977) found that, when S is deficient, its application

increases the quality of forage crops by improving the content of important components such as vitamin A, chlorophyll and plant proteins, while, at the same time, lowering the non-protein N level and the N:S ratio. He concluded that dietary levels of 0.20-0.25% S and N:S ratios of 10:1 to 12:1 are adequate, and that levels below 0.15-0.18% S and N:S ratios wider than 13:1 require improvement. He suggested that a better estimate of diet quality than crude protein (CP;  $CP = N \times 6.25$ ) was needed.

Although fertilization can change the N:S ratio by altering the proportion of amino acids, proteins and other S-containing constituents in the plants, it is not always possible to predict the effects of fertilizer on the efficiency of animal production or on the environment. Moderate S fertilization is essential to overcome plant S deficiencies, but large application rates are often required to increase protein levels. In some cases, this only results in "luxury consumption" and accumulation of  $SO_4^{2-}$  in the plant. Rumen microorganisms reduce  $SO_4^{2-}$  to  $S^{2-}$  for protein synthesis. Moderate levels of  $SO_4^{2-}$  can improve animal performance, but high levels of  $S^{2-}$  are toxic.

Once fertilizers have overcome the basic S deficiencies in plants, supplementation of the animals with S is probably a better option vis-à-vis the environment because it reduces the opportunity for antagonism between S and Se and  $SO_4^{2-}$  and molybdate ( $MoO_4^{2-}$ ).

Additional work by both agronomists and animal nutritionists is needed to compare the merits of forage fertilization vs. feed supplementation as a means of most efficiently supplying ruminants with their S requirements (Tisdale, 1977). The main limitations in the quality of the diet for ruminants are the degree of protection of the ingested proteins from degradation in the rumen and, especially in the case of poor quality feed, the availability of sufficient energy substrates and nutrients for microbial growth.

## 8.7. Protected protein in ruminant diets

Ruminants do not use highly digestible protein diets efficiently because the microorganisms in the rumen break down the protein and, in its place, only a lower amount of microbial protein passes on down the digestive tract. For fresh forages containing less than about 130 g crude protein/kg dry matter (DM), the rumen processes can increase the quantity of amino acids absorbed from the intestine, but a net loss of amino acids occurs with forages high in crude protein.

Supplements of non-protein N alone can only convert a sub-maintenance forage diet into one that will maintain ruminants. The crude protein of forage can be increased by applying fertilizer N a few weeks before it is grazed or cut, but this will be of little benefit to the animal, unless there is also sufficient S.

A potentially better method of improving the quality of the forage pastures is to include a legume. If already harvested, the crude protein content of conserved forages can be increased by adding urea or ammonia, but their value to the animal is usually limited, unless adequate S and energy are also provided.

The ingested protein can be used more efficiently if it can be protected from degradation in the rumen (a by-pass protein) and can be digested further down the

gastro-intestinal tract. Consequently, the challenge is to provide just the right level of protection to the protein in the diet. The possibilities for this are:

- Feeding supplements that have natural protection or appropriate pre-treatment, e.g. fish meal heated in processing and cottonseed meal treated with formaldehyde;
- Selecting and/or breeding plants to obtain the required degree of protection of the essential amino acids and protein, e.g. plants with manageable levels of tannins;
- Incorporating other materials into the diet that give protection to the protein.

In some countries the degradation of forage protein in the rumen can also be reduced by selective defaunation using various products approved by the appropriate health and safety authorities.

## 8.8. Sulphur in excreta

The previously noted separation of the pathways for S excretion by ruminants into relatively intractable organic S and the readily useable or leachable inorganic S applies in varying extents to all domestic animals, except poultry. The fate of the excreted S is not only controlled by the animal's metabolic processes and excretion pathways, but also by their natural habits and the management of the farming systems.

At pasture, cattle tend to distribute their excreta at random and, subsequently, avoid dung pat areas until the solid matter has virtually all disappeared. Sulphur loss from the dung-affected area is minimal, but there can be considerable loss from areas receiving urine due to leaching.

Sheep are more gregarious and are more likely to graze in groups and camp each night in the same small area. This frequently results in areas of high nutrient concentration that are sparsely vegetated. There can be significant nutrient losses from camps. Studies using <sup>35</sup>S have shown significant S movement out of the camp and recycling through pasture on other areas.

For animals housed at night or maintained in pens or cages, the fractionation between available and resistant S materials is more critical. The dung, which contains largely resistant organic S, is more easily managed and can be returned to pasture or crop areas, while the urine and soluble available S components are more difficult to contain and the S is more likely to be lost into drains and/or leached into surface and sub-surface water flows.

The magnitude of this problem becomes more apparent when the distribution of the other nutrients in the excreta is considered. For example, P is mainly excreted in dung, while available S is mainly in urine. Consequently, the management of excreta can significantly change the balance in the recycling of S and P and the amounts of fertilizer needed. Poultry has combined excreta, and the management of this may be easier.

## 9. Sulphur interactions and processes

### 9.1. General

In the current situation where industrial emission of S and acid rains are largely under control, the dominant problem is awareness of the frequent lack of an adequate input of S. Much greater attention has been given to other nutrients, the end result being that S deficiency and/or an imbalance in the application and recycling of S is a major problem. Once recognized that there is S deficiency, and that real gains in production can be obtained, there is the problem of knowing how to correct it without going into overuse just to be on the safe side.

Some examples of useful high applications of S are: gypsum to improve water infiltration;  $S^0$ ,  $H_2SO_4$  or other potentially acidifying S compounds to saline, alkaline and calcareous soils to lower pH, improve infiltration and increase nutrient availability; to combat Se toxicity. However, such problems tend to be in marginal and difficult environments where the use of such materials, especially on irrigated arid lands, is frequently not sustainable.

Unfortunately, when dealing with a large number of interacting processes, where to break into the various interlocking cycles is a problem because, a perturbation at one point will inevitably have consequences in another part. Interactions between S, Mo and Se occur to varying extents and are very important to different processes in soils, plants and animals.

Selenium and S are in the same group in the periodic classification of the elements and are chemically similar and compete in many processes, in some cases via the same enzymes. For instance, glutathione is involved in the reductive assimilation of inorganic selenite into selenocysteine (Anderson and McMahon, 2001), while the  $SO_4^{2-}$  and molybdate ions are antagonistic because of their shape.

### 9.2. Glucosinolates and cyanogenic glycosides

Following successful programmes to reduce glucosinolates in oilseed rape, this crop is now being used extensively for production of edible oil and animal feed supplements. In the European Union (EU), an upper limit for glucosinolates in farm-saved rapeseed was set at  $18 \mu M/g$ ; above this, the seed could not be sown. However, because of advances in breeding, this restriction is no longer considered necessary in some countries.

In the European environment, applications of  $50 \text{ kg S/ha}$  to S-deficient sites more than doubled the glucosinolate levels to about  $20 \mu M/g$  which, therefore, exceeded the EU limit. Trials in Germany showed virtually no increases in seed yield above applications of  $30 \text{ kg S/ha}$  and applications of S at that level would be unlikely to raise glucosinolate levels above the EU limit (Zhao *et al.*, 2002).

Forage sorghums are high yielding plants that can be used for animal supplements under controlled grazing, or as hay and silage. Unfortunately, they contain cyanogenic glycosides which, at various stages of plant growth, can be in high enough concentrations to release toxic to lethal levels of cyanide ( $\text{CN}^-$ ) during digestion. As a consequence, they are frequently under-utilized. Detoxification of  $\text{CN}^-$  released in the rumen from cyanogenic glycosides is achieved by conversion to thiocyanate, which requires about 1.2 g S/g  $\text{CN}^-$ . This additional demand for S can induce S deficiency in the animal, and the by-products of detoxification are goitrogenic.

Goitre is also linked to iodine (I) and/or Se deficiencies, and muscular dystrophy (white muscle disease) is also the result of Se deficiency. Because of the chemical antagonism between S and Se, it is important to only use sufficient S, either as a supplement to animals or as a fertilizer for the forage, to correct the S deficiency without driving Se concentration down to a dangerously low level.

Low Se levels can readily be corrected by giving animals Se supplements. Low levels in crops and pastures are corrected in some countries by using selenized fertilizers. However, there is a fairly narrow range between Se deficiency and toxicity (0.1 to 5 ppm in plants).

The balance between S and N applications can influence the proportions of glucosinolates in rapeseed, cyanogenic glycosides in forage sorghums, and  $\text{NO}_3^-$  levels in both.

### 9.3. Micronutrient interactions in ruminants and man

High S inputs to the rumen can lead to high production of sulphide ( $\text{S}^{2-}$ ) and, if the absorption rate into the blood exceeds the rate with which it is oxidized to  $\text{SO}_4^{2-}$ , loss of appetite and respiratory distress will follow. High  $\text{S}^{2-}$  levels in the rumen, especially if there is too much Mo in the diet, can lead through a series of complex reactions to adverse effects on copper (Cu) retention (Underwood and Suttle, 1999).

Sulphur inputs to the soil have antagonistic effects on Se and Mo levels in plants and can lead to reduced biological N fixation in legumes and depressed Se uptake by plants. The results of low Se in plants can be the increased incidence of white muscle disease and goitre in ruminants and other animals, including man, and a potential higher risk of cancer in man. Low Mo intake is also linked to higher incidence of dental caries in man.

## 10. Sulphur sources

### 10.1. Application

Fertilizers applied to pastures are usually broadcast. Ideally, the time of application and choice of fertilizer should be such that the nutrient release pattern of the fertilizer matches the plant demand. In practice, the environment virtually limits what application methods can operate satisfactorily and, for economic reasons, there is often a need to schedule application to fit in with other routine operations. These conditions may alter the appropriateness of a particular fertilizer and should also be taken into account when selecting a fertilizer.

In row crops, the efficiency of fertilizer nutrient use by plants may be improved by application in bands or via fertigation, but the balance with the other nutrients and their relative placement is critical. Crop residues, animal excreta and wastes from product processing all have varying amounts of nutrients and energy, and their management within the primary production system can have a significant influence on the amounts of fertilizers needed and the physical properties of the soil.

### 10.2. Sulphur fertilizers

The wide range of valency states of S and the natural occurrence and stability of  $S^0$  mean that a large number of fertilizer materials are available, including combination with other essential plant nutrients. Examples of S fertilizers and some of their advantages and disadvantages are presented in Appendixes 1 and 2.

Other potential high-analysis S materials have been proposed, but limited resources and economic considerations have prevented their development. Undoubtedly, new materials will become available for use as technology changes, and the awareness of balanced nutrition and controlled-release rates develops. There are a number of unusual experimental inorganic and organic S fertilizers, but the majority of the commercial fertilizers used are based on  $SO_4^{2-}$  and  $S^0$ , which have some important differences that are outlined below.

For sulphatic fertilizers, the availability is only limited by the rate of release to the soil-available pool and the plant's ability to compete with other processes for the  $SO_4^{2-}$ . Sulphate, like  $NO_3^-$ , is highly mobile and leaching losses of S can be a problem in soils with coarse texture and low S sorption capacity. Depending on the rainfall pattern, any fertilizer that releases  $SO_4^{2-}$  at a rate faster than it can be incorporated into organic matter has the potential for significant losses.

In order to address the release rate and leaching issue, various single (straight) and multi-nutrient (compound) sulphatic fertilizer products have been tested, with release rates controlled by granulation, co-precipitation and/or coating with waxes or polymers.

These materials contain  $\text{SO}_4^{2-}$  in plant-available form, but their S content is unavoidably low, and transportation costs per unit of S are high. Even as the salt of other major nutrients, the relative proportions may not be the best in terms of plant uptake.

Unlike  $\text{SO}_4^{2-}$ ,  $\text{S}^0$  is insoluble in water and does not leach nor become oxidized under normal atmospheric conditions. Therefore, it is not immediately available to plants. However, once  $\text{S}^0$  is applied to the soil, it can be oxidized to  $\text{SO}_4^{2-}$  by numerous microorganisms via various pathways (Trudinger, 1986). The aerobic *Thiobacillus thiooxidans* is probably one of the most important in the soil and is an obligatory S user. The surface area of the  $\text{S}^0$  particles and the environmental variables that control the activity of the  $\text{S}^0$  oxidizing microorganisms influence the rate of  $\text{SO}_4^{2-}$  release.

As the environmental variables controlling microorganism activity are essentially the same as those that control plant growth, the availability of  $\text{SO}_4^{2-}$  from  $\text{S}^0$  tends to be synchronized with plant demand. The lack of leaching and the ability to manipulate the rate of  $\text{SO}_4^{2-}$  release by using mixtures of  $\text{S}^0$  with different particle sizes provide the potential to match the release rate of  $\text{SO}_4^{2-}$  to plant demand at different growth stages.

Elemental S is a 'high-analysis' S source that can be used on its own. It is also ideal for incorporating into other fertilizers or as a coating for N, P and K fertilizers. This can markedly increase the saleable nutrient content of a fertilizer with minimal increase in weight, transport and application costs.

Some almost pure  $\text{S}^0$  fertilizer preparations are available, aimed at improving the safety of handling the fine material needed to present the large surface area required for efficient oxidation. Very fine  $\text{S}^0$  particles (2-5 microns) mixed with a small proportion of wetting/suspending agents are used to produce flowable S that can be applied as an aqueous suspension spray. Other fertilizers are produced by foaming to give a greater surface area or aggregating with other materials such as bentonite, with the aim of dramatic expansion on wetting and dispersion of the fine  $\text{S}^0$  particles in the soil. These can be applied on their own or physically mixed with other fertilizers. However, mixtures are often poor performers in the field due to problems of wide separation of 'granules' at normal S application rates (Table 6), which reduces the opportunity of

**Table 6.** Distribution of fertilizer granules<sup>1</sup> for P and S, each element applied at 10 kg/ha.

Fertilizer	TSP	+	$\text{S}^0$ bentonite or granulated $\text{S}^0$	Fine $\text{S}^0$ -coated TSP
Nutrient applied	P		S	P and S
Broadcast (granules/m <sup>2</sup> )	250		50	250
Drilled* (granules/m row)	50		5	50

<sup>1</sup> TSP granules approx 3 mm diam. 19.6% P and 1% S as  $\text{SO}_4^{2-}$ . Sulphur bentonite pellets of similar size to TSP. Particle sizes of  $\text{S}^0$  in coating can be adjusted to give required  $\text{SO}_4^{2-}$  release rate. Typical  $\text{S}^0$  sizes are 50 to 200 microns. Urea, DAP and TSP have also been successfully coated.

\* Drilled refers to placement of the fertilizer in or near the seed row. The calculation is based on 20 cm between rows and 10 cm between TSP granules.

the beneficial association with other nutrients (Table 7), especially as many S-oxidizing organisms require a high supply of P and/or benefit from the low pH in the immediate vicinity of the P granules. These problems can be avoided if the S<sup>0</sup> is coated onto, or incorporated into, other fertilizers.

An additional advantage of S<sup>0</sup>-coated fertilizers is that, provided there are no adverse effects from the material used to bond the S<sup>0</sup>, the S<sup>0</sup> is immediately exposed to any S-oxidizing microorganisms, and colonization is not hindered by the matrix of the other nutrients.

Some fertilizers use a mixture of SO<sub>4</sub><sup>2-</sup> and S<sup>0</sup> to get an initial high level of available S, but they run the risk of significant leaching losses if rains are heavy before the plant is sufficiently developed to take up enough of the SO<sub>4</sub><sup>2-</sup>. The different properties of S<sup>0</sup> and soluble SO<sub>4</sub><sup>2-</sup> combined with techniques for application, crop requirements and management and environmental conditions must all be considered in selecting the most appropriate fertilizer.

**Table 7.** Effect of S application rate and mixed or separate band application of TSP and S<sup>0</sup> (<0.250 mm particles) on yield and fertilizer S uptake by maize in pots<sup>1</sup>.

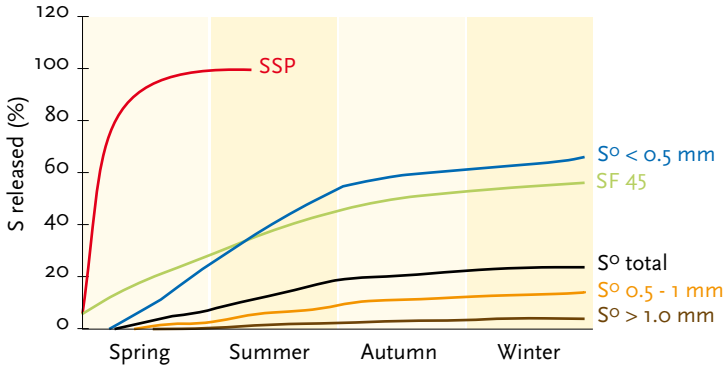
Distance between TSP and S bands (cm)	Relative DM yield		Relative fertilizer S uptake	
	15 kg S/ha	45 kg S/ha	15 kg S/ha	45 kg S/ha
0	71	100	51	100
1	58	74	18	47

<sup>1</sup> Extracted from the data of Friesen (1989).

### 10.3. Predicting the release of sulphate from fertilizers

McCaskill and Blair (1988) used data from <sup>35</sup>S studies of the fate of S from different fertilizers, together with data on the effects of soil moisture, temperature and the surface area of applied S<sup>0</sup> to develop a simulation model that could predict the rate of SO<sub>4</sub><sup>2-</sup> supply to the soil-plant environment. An example is shown in Figure 12. The value of such results is that they provide a basis for the development of fertilizers that release SO<sub>4</sub><sup>2-</sup> at a rate to match the changing requirements of plants as they develop in different environments.

Dana (1992) presented seasonal climate data and estimated plant S requirements for some Australian sites and showed that, using 100 and 200 micron sized S<sup>0</sup>, the proportions of each could be adjusted to give a predicted SO<sub>4</sub><sup>2-</sup> release that was reasonably close to the shape of the plant demand curve.



**Figure 12.** Predicted release of  $\text{SO}_4^{2-}$  from SSP,  $\text{S}^0$ -fortified SSP (SF45) and various sizes of particles isolated from a commercial agricultural grade of  $\text{S}^0$  (McCaskill and Blair, 1988).

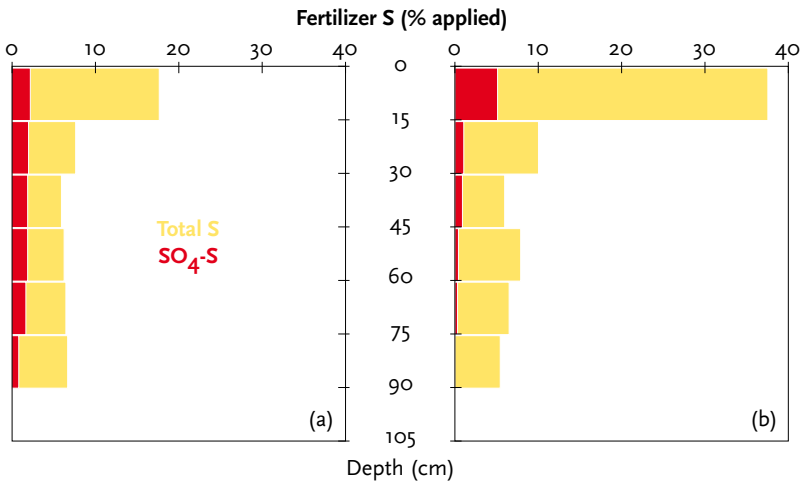
#### 10.4. Effect of placement and form on plant uptake and residual value

The following table and figures are from field and pot trials in which  $^{35}\text{S}$ -labelled fertilizer was used to follow the utilization of the fertilizers in different parts of the system. They demonstrate the importance of form, placement and rate on the uptake efficiency, leaching and residual value in various situations. In a field experiment in Togo, total fertilizer S uptake by maize was 6.4% from SSP and 5.3% from the  $\text{S}^0$ -fortified TSP

**Table 8.** Fate of  $^{35}\text{S}$ -fertilizers containing S as soluble  $\text{SO}_4^{2-}$  (SSP) or  $\text{S}^0$  ( $\text{S}^0$ -fortified TSP) applied to maize in a sub-humid environment in Togo (adapted from Friesen, 1989).

	SSP	$\text{S}^0$ -fortified TSP
	(% of S applied)	
<b>Maize</b>		
Grain	4.1	3.4
Stover	2.2	1.8
Roots	0.1	0.1
Total	6.4	5.3
<b>Soil</b>		
$\text{SO}_4^{2-}\text{-S}$	8.3	7.7
Organic-S	40.8	60.3
$\text{S}^0$	--	7.5
<b>Total</b>	<b>55.5</b>	<b>80.9</b>

with a similar distribution of S between the plant components (Table 8). However, there were large differences in total S from fertilizer remaining in the soil, especially in the forms of S and its distribution in the profile (Figure 13). About 44% of the S could not be accounted for in the SSP treatment, but the loss was only 19% from the S<sup>0</sup>-fortified TSP. In addition, there was twice as much S remaining in the top 15 cm from the S<sup>0</sup> treatment.

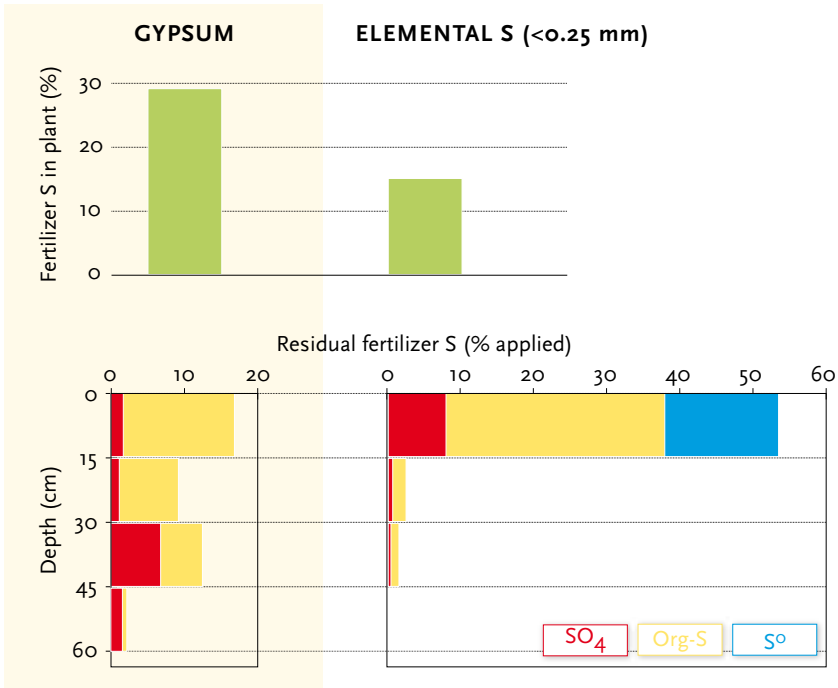


**Figure 13.** Soil profile distribution at harvest of fertilizer S from (a) SSP and (b) S<sup>0</sup>-fortified TSP applied to maize at Amoutchou, Togo in 1987 (Friesen, 1989).

The results in Figure 14 are from a study of maize grown in deep pots under controlled conditions with provision to trap gaseous losses and leachate. The fertilizers were gypsum and S<sup>0</sup>. The total plant uptake from gypsum was 30% and about half as much from S<sup>0</sup>. The difference in S uptake between the treatments indicates that, in this experiment, the particle size of the S<sup>0</sup> was too large. This is supported by the significant amount of free S<sup>0</sup> remaining after the crop. There was no detectable volatile loss of <sup>35</sup>S and the major difference was the distribution and the forms of S in the soil profile. The experiments indicate that:

- In the field trials, there was a small decrease in total fertilizer S uptake from the S<sup>0</sup>-fortified TSP, with a similar distribution pattern for the S in the plant. Losses from SSP were significantly greater than losses from S<sup>0</sup>-fortified TSP. Distribution of the remaining S in the soil profile was much more favorable with S<sup>0</sup>-fortified TSP.
- The higher uptake of S by maize from SSP and gypsum (soluble SO<sub>4</sub><sup>2-</sup> sources) than from S<sup>0</sup> is probably due to different particle sizes of S<sup>0</sup>, which must undergo biological conversion to SO<sub>4</sub><sup>2-</sup> before it can be used by the plant.
- There are similar patterns of incorporation of S into the maize.
- In the soil profile, there were similar average concentrations of available S from each source but, in terms of availability to plants and potential for leaching loss, a much better distribution down the profile was observed with the S<sup>0</sup> treatment.

- There is much more of the S incorporated into organic forms with  $S^0$  than with  $SO_4^{2-}$  sources.
- It is possible to select a range of  $S^0$  particle sizes to tailor  $SO_4^{2-}$  release rates to match plant demand.



**Figure 14.** Plant recovery and distribution to fertilizer S in soil from two sources at harvest (Friesen, 1989).

## 10.5. Organic sulphur sources

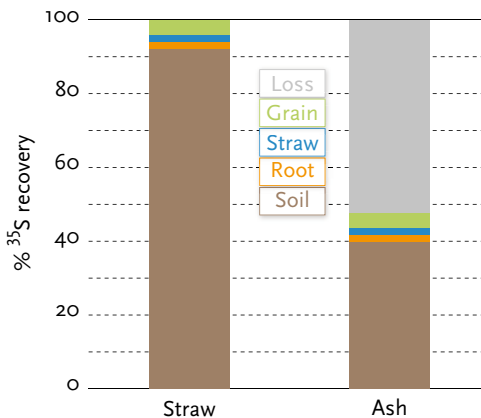
### 10.5.1. Forage and crop residues

There can be a considerable amount of energy and nutrients in the residues of some forage and grain crops. Their management can play a significant part in maintaining the biota and the recycling processes. Depending on the crop, the amount of S that ends up in the harvested product varies from about 25 to 75% of the total S that is taken up by the crop (Table 2).

The removal of residues can constitute a major loss of nutrients and energy, and the management of residues can make a significant contribution towards recycling S through the biological system. As shown in the carbon cycle (Figure 6), the release rates and balance of the nutrients from the residues depend on the quality of the organic matter, especially for S, as the SOM is the major storage of S in the soil.

The increasing incidence of multiple cropping, with very short intervals for soil preparation between crops, has created problems in the management of crop residues. There are many schemes of short rotation cropping, and the growing of three rice crops a year is now quite common. In some cases, practically all of the rice residues are removed and never returned to the field and, in other cases, the crop residues are burnt on site. The burning of the residues causes a loss of virtually all the energy in it, and it is a significant loss of S to the atmosphere. However, any S remaining in the ash will be in a form immediately available to plants.

Field studies in Thailand using  $^{35}\text{S}$ -labelled rice residues, either returned directly or as the ash from the same amount of residues, are presented in Figure 15. They show that, in the short-term, similar proportions of the S were incorporated into grain and roots from each treatment, but there was a large loss of applied S from the ash treatment. If just the grain uptake of returned S was used to evaluate the treatments, they would indicate that there was no difference. However, there were significant losses of S as a result of the burning, which could take several seasons to become evident. Losses should be replaced by fertilizer applications rather than let soil fertility run down.



**Figure 15.** The fate of S from rice straw residues and the ash derived from it (Data from Chaitep, 1990).

The results from the studies using labelled fertilizers and ash emphasize that the rate at which the S becomes available is very important and that losses, as a result of some changes in management strategies, may be difficult to detect. Apart from any physical benefits to the soil structure, the real S nutrient value depends on the management of the residues (e.g. incorporation or crushing) and the lability of the organic matter. A large return of organic matter that is not in a position to be readily colonized by the macro- and micro-flora and fauna, and/or has the S in an intractable or protected form, is of little value and may even aggravate the situation by tying up S from other sources.

### 10.5.2. Recycling animal excreta and industrial wastes

The different distribution of nutrients in dung and urine, together with management options, indicate the potential problems from imbalances with other nutrients and rates of availability. These differences in management and contents of nutrients extend beyond the use of excreta to other wastes from animal and industrial processing that are used as soil “conditioners” and sources of nutrients.

Excreta and other wastes constitute potentially valuable sources of nutrients to agriculture, but the problem is that, except for some industrial wastes, there is rarely any real effort to define the balance of nutrients that they contain or their rates of availability for plant production. The data of Eriksen (2002) also suggests that some inorganic S may be retained in inaccessible sites in organic wastes.

The soil organic matter (SOM) content tends to rise under grazing and/or application of manure and to decline under cropping without additional organic matter inputs. Does this rise and fall of SOM really represent both a build-up of fertility and mining of a resource? The answer to this question depends largely on the nutrient balance and on the lability of the various components that are in the recycled matter relative to the nutrient balance, lability and total amounts of the different fractions that make up the SOM.

One possible outcome for recycled material that has a good nutrient balance and reasonable lability is that agricultural production could be maintained or increased as the SOM remains steady, or could fall slowly as the overall lability of the SOM increases. On the other hand, if the lability and/or the nutrient balance are poor, SOM is likely to rise and agricultural productivity will probably fall or, at the best, remain stable for a while. It is probable that the best way to estimate the magnitude of these possibilities (a “fertility index”) would be a computer model based on nutrient contents and the lability of the major fractions in the SOM and in the material being recycled. Unfortunately, this would require significantly more data than is available at present.

The importance of recycling through livestock was shown in an experiment where sheep grazed a pasture fertilized with  $^{35}\text{S}$ -labelled gypsum, in which there were small “hot-spots”. After about one year, the “hot-spots” were fenced to prevent grazing and new sheep were allowed to graze the “cold” pasture. The new sheep immediately started to incorporate  $^{35}\text{S}$  into their wool, showing significant recycling through the animal-soil-plant system. The concentration of the  $^{35}\text{S}$  in the wool made it possible to quantify the amount translocated and recycled (May *et al.*, 1968).

## 11. Concluding remarks

Meeting the food, feed, fibre and bioenergy requirements of a fast growing world population over the long term calls for the increased adoption of sustainable agricultural practices. An important aspect of sustainable agriculture is nutrient management. A sustainable system requires nutrients removed in marketable products and any removed in harvesting or processing to be replaced. In all highly productive systems this requires the application of some form of supplement or fertilizer. These must be applied at the right rate, right time and right place, taking into account the crop- and site-specific requirements in order to minimize nutrient losses to the environment.

Various S-containing compounds are used by microorganisms to produce the amino acids cysteine and methionine, which cannot be produced by higher animals, and are essential for the production of protein. Sulphur is also an essential ingredient in lipids and a wide range of other organic compounds.

Crop residues, animal manure, urban and industrial wastes, irrigation water and aerial deposition contain S and other nutrients in varying amounts, and their management can have a significant influence on the amount of fertilizer needed.

Historically, little attention was paid to S as a plant nutrient since there were inputs to the soil through rainfall (acid rain), volcanic emissions, and as a component of most fertilizers, fungicides or insecticides. However, due to stringent regulations on emission of  $\text{SO}_2$  and other S-containing compounds by industries, and the increased use of “high-analysis” fertilizers, S input has declined and S deficiencies are becoming more widespread.

The global S cycle controls the input of S from the atmosphere and the farmer has virtually no control over this, but it is important to know the magnitude of that contribution. The total S in the agricultural system is minimal, consisting of only a tiny fraction of the global S pool. The S from the atmosphere is mostly anthropogenic, from combustion of fossil fuels and smelting of ores. The reduced S compounds are mostly oxidized in the atmosphere and S is recycled as  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$  and  $\text{SO}_4^{2-}$  salts. If there is any  $\text{H}_2\text{S}$  in the atmosphere, plants can utilize moderate amounts as a source of S.

The S requirement of crops may range from about 10 to more than 70 kg/ha and the N:S ratio in plants varies widely, depending on the balance of the nutrients supplied, but for most plants it is in the range of about 10:1 to 20:1. The stage of crop growth, proportions of nutrients in the applied fertilizer, their form, site of application and rate of nutrient release all influence the efficiency of S used by the crop.

Thus, it is important that farmers know their crop's requirements in terms of both the total amounts and the rate of nutrient supply over the growing period. Supplying high S-demanding crops with a particular S fertilizer at high rates may not necessarily meet the plant's S requirements and can lead to increased leaching losses and/or antagonism between S and some micronutrients, notably Se and Mo. Nutrient imbalances can cause the build-up of toxic substances in plants and, indirectly, cause mineral deficiencies, goiter, muscular dystrophy and loss of appetite (even death) in animals. Optimum

production is achieved by having an appropriate balance of nutrients available at the appropriate rate and time for the particular production systems.

Aside from being a plant nutrient, some S materials are used as fungicides while others are applied to soil to improve water infiltration, adjust soil pH and reduce the toxic levels of Se, among others.

Ruminants, unlike other animals, have the ability to synthesize essential amino acids due to the microorganisms in their stomach. There are many similarities in the metabolism of N and S in ruminants. The optimum N:S ratio in their diets is about 10:1 for sheep and 13.5 to 15:1 for cattle. Dietary levels of 0.20 to 0.25% S are adequate for ruminants. Moderate levels of  $\text{SO}_4^{2-}$  can improve ruminant performance on poor quality diets, but an excess of S can result in high levels of  $\text{S}^{2-}$ , which is toxic. Fertilizer application of S in grazed pasture systems can be used to correct S deficiencies in forage crops, but once the plants deficiency is overcome, supplementation of the animals with S appears to be a better option than overuse of S fertilizer.

In some large-scale crop production areas, “precision agriculture” uses previously-stored data and/or sophisticated electronic estimation of soil and plant nutrient status, together with computer-controlled fertilizer application machinery, to vary treatment rates to suit the estimated “fertility” status of different parts of the farm with the aim of reducing excessive and wasteful application and minimize nutrient losses.

In the case of S, when deficiency is detected, it is usually too late to correct it in the crop and, in the early stages, it can be confused with N deficiency. Soil tests, together with computer models, help in the estimation of soil critical S levels and the establishment of response curves suitable for making fertilizer recommended rates for specific crops.

Fertilizers are still the main source of nutrients for plants. Rate, timing and placement are important considerations for their efficient use. The challenge is to determine how much fertilizer is needed so that the release of S can match the plant's needs, bearing in mind that the plant competes for the S with other processes and losses, its requirements change as it develops, and there are variable S inputs from other sources. A great deal of information on processes, pathways and rates is needed to better understand the mechanisms involved. Elemental S and  $\text{SO}_4^{2-}$  are the main sources of S in fertilizers. Sulphate is directly available to plants but is susceptible to leaching losses. Elemental S must be oxidized in the biota, but has the advantages that the processes that release the  $\text{SO}_4^{2-}$  tend to be synchronized with plant demand, and  $\text{S}^0$  is not lost by leaching. In fertilizers, the  $\text{SO}_4^{2-}$  is chemically combined with other nutrients such as N, P and K during their production, while the  $\text{S}^0$  is physically incorporated into or surface-coated onto fertilizers or other carrier materials.

Since S is a component of plants in the form of amino acids, proteins and oils, there can be a considerable amount of organic S in the residues of forage and grain crops and in animal excreta. Management of these residues can play an important role in maintaining the biota, the recycling process, and the overall balance of the system for sustainability. However, there is a need to determine the S content of these organic nutrient sources, and the rate at which S will become available for plant production.

It is suggested that, in order to improve the efficiency of S use and the sustainability of the system in general, the following actions should be undertaken:

- Greater efforts should be made to better understand the processes and dynamics of S cycling at different scales, the S requirements of individual crops and its evolution over crop's development, and interactions of S with the other nutrients.
- Increased research on the dynamics of S utilization and availability to plants, the accurate prediction of the amount of fertilizer needed to achieve optimum crop production and interactions of S with the other plant nutrients in order to avoid misinterpretation of results and misleading recommendations.
- The development of S fertilizer products that can be integrated with essential farm operations, with nutrient release rates that suit specific crops, and that are economically viable.
- Fertilizer policies and incentives should be developed for greater use of S where S deficiencies are a constraint to higher productivity. In case of fertilizer subsidies, they should be designed to promote balanced fertilization. Where S deficiencies cause a serious threat to national food and nutrition security, and where the use of S-containing fertilizers is not economically viable, subsidies for their wider use might need to be considered.
- Fertilizer producers and agriculturalists should work towards ensuring that S is recognized as an essential plant nutrient and removing regulations that impede the use of S-containing fertilizers. This would allow commercialization of a wide range of S-containing fertilizers, and give farmers the flexibility to choose the fertilizer products best suited to their specific agro-ecological conditions.
- Extension workers and agro-businesses should be involved in providing scientifically-sound advice to the farmers on the best management of S in their farming systems, avoiding blanket recommendations.

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- Various S models and other information on isotopic studies of S can be accessed via [www.une.edu.au/sciences/isotopic-tracer](http://www.une.edu.au/sciences/isotopic-tracer)

## Appendix 1: Sulphur fertilizers

Fertilizer product	Nutrient content (%)			
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	S
Ammonium nitrate with ammonium sulphate or ammonium nitrate sulphate	up to 30	0	0	7-16
Ammonium nitrate with gypsum	24-27	0	0	3-6
Ammonium phosphate sulphate	Variable	Variable	0	6-17
Ammonium polysulphide	20-21	0	0	40-45
Ammonium sulphate	21	0	0	24
Ammonium sulphate, liquid	8	0	0	9
Ammonium thiosulphate, solid	19.5	0	0	43
Ammonium thiosulphate, solution	12	0	0	26
Calcium nitrate with sulphur	15	0	0	1-5
Calcium sulphate (dihydrate gypsum)	0	0	0	17-18
Calcium sulphate (hemihydrate gypsum)	0	0	0	19-22
Calcium sulphate (anhydrite gypsum)	0	0	0	22-24
Fortified SSP	0	5-16	0	28-50
Iron pyrites	0	0	0	54
Magnesium sulphate (Epsom salt)	0	0	0	13
Magnesium sulphate (Kieserite)	0	0	0	10-23
Micronized sulphur <sup>1</sup>	0	0	0	50-99
Mixed-grade NKs with sulphur	Variable	0	Variable	5.2-10
Mixed-grade NPs with sulphur	Variable	Variable	0	2-21
Mixed-grade NPKs with sulphur	Variable	Variable	Variable	2-17
Mixed-grade PKs with sulphur	0	Variable	Variable	2-15
Nitrogen-sulphur solutions	7-35	0	0	2-6
Polyhalite	0	0	13	19
Potassium magnesium sulphate	0	0	22	22
Potassium sulphate	0	0	48-52	17-18
Potassium thiosulphate	0	0	25	17
Single superphosphate (SSP)	0	16-20	0	11-14
Sulphur (elemental) <sup>1</sup>	0	0	0	50-100
Sulphur bentonite	0	0	0	90

## 64 Sulphur and sustainable agriculture

Fertilizer product	Nutrient content (%)			
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	S
Sulphur-coated MAP	8-10	44	0	12
Sulphur-coated TSP	0	38-43	0	10-20
Sulphur-coated urea	38-40	0	0	10-14
Sulphur with micronutrients	0	0	0	2-80
Urea with sulphur	40	0	0	5-6
Urea sulphuric acid	10-28	0	0	9-18
Zinc sulphate	0	0	0	11

<sup>1</sup> Includes wettable/dusting powders (dry powder) and "flowable" sulphur (liquid suspension).

## Appendix 2. Advantages and disadvantages of various sulphur-containing fertilizers\*

Fertilizer	Advantages	Disadvantages
<b>Sulphur sources</b>		
Gypsum (0:0:0:16)	Mined or by-product. Used as S source or soil conditioner.	Low-analysis material. All S is readily leachable $\text{SO}_4^{2-}$ . Can be difficult to handle and uneconomical to transport.
Elemental S ( $\text{S}^0$ ) (0:0:0:100)	High-analysis. Does not leach. Mixtures of different sized particles allow S release rates to be adjusted to suit crop and environment.	Must be finely ground to be effective. Difficult to apply on its own. Fine material, explosive and irritant.
Fine $\text{S}^0$ -aggregated with various binders and/or dispersing materials, e.g. $\text{S}^0$ -bentonite (0:0:0:90) or various "flowable" forms for foliar application	Existing technology. High-analysis product, stable when dry, relatively safe to handle. Can be mixed with other fertilizers to give desired combinations of nutrients. Foliar spray benefits mainly due to control of fungus or other parasites. Sometimes an S nutrient response may be observed from excess spray entering cycle via the soil.	Fine $\text{S}^0$ is released on wetting but not all products perform satisfactorily. Slow oxidation, unless close to soil surface. Relative placement of the different components of the mix can be critical for optimum efficiency. Very fine S from flowable materials is rapidly oxidized to $\text{SO}_4^{2-}$ and potentially lost.
<b>Phosphorus and sulphur sources</b>		
Single super-phosphate (SSP) (0:9:0:11)	Simple manufacturing process.	Low-analysis. High risk of $\text{SO}_4^{2-}$ leaching. Disposal of fluoride may be a problem.
$\text{S}^0$ -fortified SSP, e.g. SF45 (0:6:0:45)	Simple manufacturing process.	P:S ratio unsatisfactory. Need to manipulate P:S ratio by mixing with TSP.
Double super-phosphate (0:16:0:6)	Simple manufacturing. Fairly good P:S ratio.	S all as $\text{SO}_4^{2-}$ .
Triple super-phosphate (TSP) (0:19:0:1)	Established technology using phosphoric acid acidulation, (but usually with wastage of S in by-product).	Higher P, but will exacerbate any S deficiency.
$\text{S}^0$ -granulated TSP	Can manipulate P:S ratio. Minimal capital investment. P and S applied at sowing/transplanting.	Manufacturing problems in run of pile processing (explosion).

S <sup>o</sup> -coated TSP	Minimal capital investment. Simple manufacturing that allows easy adjustment of the P:S ratio. Can be produced on-site by a small-scale portable plant. Can manipulate S <sup>o</sup> oxidation rate. P and S applied at sowing/transplanting.	Need ground S <sup>o</sup> . Need thorough evaluation of products as some coating methods can result in reduced S and P release rates.
S <sup>o</sup> -coated phosphate rock (S <sup>o</sup> -PR)	Simple manufacturing. Good P:S ratio. Minimizes processing. P:S ratio and release rate can vary.	Technology not readily available. May be unsatisfactory on very P and S deficient areas. Need ground S <sup>o</sup> .
S <sup>o</sup> -coated partially acidulated PR (S <sup>o</sup> -PAPR)	P and S release rates can vary. Contains SO <sub>4</sub> <sup>2-</sup> and S <sup>o</sup> . Simple manufacture.	Requires a new plant. Low-analysis if Ca ignored. Need ground S <sup>o</sup> .

### ***Nitrogen and sulphur sources***

Ammonium sulphate (21:0:0:24)	Existing production capacity and marketing structure. High-analysis.	Efficiency of N reduced when applied at transplanting. All SO <sub>4</sub> <sup>2-</sup> .
Ammonium thiosulphate (19.5:0:0:43)	Readily soluble, non corrosive. Can be mixed with other nutrient solutions for irrigation systems.	A wide range of products, but most are unlikely to be readily available or within the economic/production scales of most developing countries.
Urea-S <sup>o</sup> melt (36:0:0:20)	Relatively simple production technology. Can be produced with little modification to existing plants. N:S ratio can vary. High-analysis.	Maximum N efficiency is obtained with either deep placement or delayed top-dressing, both of which reduce S efficiency.
S <sup>o</sup> -coated urea (41:0:0:10)	Technology exists. S <sup>o</sup> "skin" forms partial moisture barrier over urea, slowing N release.	Limited surface area of S <sup>o</sup> coat. Deep placement results in poor efficiency of S uptake.
S <sup>o</sup> -ammonium sulphate granules	Contains both SO <sub>4</sub> <sup>2-</sup> and S <sup>o</sup> as well as N.	Not yet evaluated. Would need to be mixed with other fertilizers to provide a balance of nutrients.

### ***Potassium and sulphur sources***

K <sub>2</sub> SO <sub>4</sub> (0:0:45:18)	Mined.	Generally expensive and of varying quality.
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**Nitrogen, phosphorus, sulphur and other multi-nutrient sources**

S <sup>0</sup> -coated monoammonium phosphate (MAP)	Technology exists for coating commercial products with fine S <sup>0</sup> particles to give controlled release of SO <sub>4</sub> <sup>2-</sup> .	N applied at sowing/ transplanting.
Other potential fertilizers	Many other existing and/or potential fertilizers can be coated by existing technologies and these provide the potential for restoring the S balance needed for most crops. Simple S <sup>0</sup> coating systems could be set up where SO <sub>4</sub> <sup>2-</sup> supplies are needed for particular environments and crops.	

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\* The N, P, K and S contents quoted are the percentage by weight of each element in the fertilizer. To convert the P level to P<sub>2</sub>O<sub>5</sub>, multiply by 2.29; the K times 1.41 gives the K<sub>2</sub>O; and S times 2.50 is the SO<sub>2</sub> equivalent.

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### Appendix 3. Plates



**Plate 1.** S deficiency symptoms in wheat: general and intervenal yellowing (Photo: TSI)



**Plate 2.** S deficiency symptoms in maize: interveinal yellowing, followed by reddening of stems and leaf edges (Photo: TSI)



**Plate 3.** S deficiency symptoms in rapeseed: leaves cupped inwards and reddening on underside (Photo: TSI)



**Plate 4.** S deficiency symptoms in sugar cane: smaller plant, leaf yellowing and striations (Photo: TSI)



**Plate 5.** S deficiency symptoms in alfalfa: reduced tillering, pale yellow-green new leaves (Photo: TSI)



**Plate 6.** S deficiency symptoms in coffee: general and interveinal yellowing, smaller new leaves and plant (Photo: TSI)



