

## ORGANIC SULPHUR AND NITROGEN IN PASTURE-CEREAL MIXED CROPPING SOILS AND RELATED FACTORS –A REVIEW

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### ABSTRACT

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A detailed review was carried out to report the published information on the forms of S and N present in soils as well as their accumulation and mineralisation in a grazed pasture ecosystem under New Zealand condition. Sulphur and N present in soil are mostly in organic forms (about 90% of total). Accumulation of N under intensive heavily stocked grass-clover pastures occurs mainly from the biological N fixation of the legume component of pastures, residue return from pasture crops and return of grazing animal excreta whereas, the build up of organic S in soils is mainly attributed to the addition of fertiliser S as but indirectly it also helped build up of organic N. Cultivation of arable crops, on the other hand, decreased soil organic matter. Mineralisation of S from decomposing organic materials depends on the S content of the decomposing materials in much the same way as mineralisation of N depends on the N content. Although considerable research work has been done on the accumulation and mineralisation of organic S and N in soils under various conditions, there is still considerable uncertainty regarding the biological turnover of organic S and N in soil plant ecosystems.

### INTRODUCTION

Sulphur (S) is the tenth most abundant element in the universe (Stevenson, 1986, Stevenson and Cole, 1999) and ranks thirteenth in abundance in the Earth's crust (Trudinger, 1975). On the other hand nitrogen (N) is one of the most widely distributed elements in nature. The N supply is one of the general decisive factors in crop production. Nitrogen plays a fundamental role as an indispensable elementary constituent of all amino acids, protein coenzymes, nucleic acids, chlorophyll and growth hormones. Plants obtain S and N mainly from soil. In most soils more than 90% of total N is contained in organic compounds (Cornforth, 1968; Stevenson, 1982a; Haynes, 1986; Kelley and Stevenson, 1996). Most non-saline mineral soils contain more than 90% of total S in organic forms (McGill and Cole, 1981; Nguyen and Goh, 1990). The importance of this organic S and N from the standpoint of soil fertility and crop production has long been recognised, and research into the nature and composition of soil organic S and N is extensive. Nevertheless, there is still considerable uncertainty regarding the structure and function of soil organic S and N.

In pasture systems, where fertiliser and atmospheric inputs of S are very low, mineralisation of soil organic S is very important for pasture S nutrition (McLaren et al., 1988; Nguyen and Goh, 1990; Sakadevan et al., 1993). Nguyen and Goh (1990) estimated that the net S mineralisation is around 18-31 kg S ha<sup>-1</sup> yr<sup>-1</sup> in intensively managed grasslands, where soil organic S has reached a steady state condition after long-term pasture development and fertiliser application. Fertiliser phosphorus (P) is required for a desirable rate of pasture production in most soils of New Zealand and superphosphate (9% P, 12% S) provides both P and S when applied to pasture development. Superphosphate is the major source of S that accumulates in the soil organic matter during pasture development (Russel and Williams, 1982; Lewis et al., 1987; Perrott and Sarathchandra, 1987; Nguyen and Goh, 1990). The distribution and forms of organic S accumulated in soils and their availability to plants has become important in recent years because of the increasing use of non-S fertilisers and smaller S fertiliser application rates. Under these conditions, mineralisation of organic S will be the major source of S for pasture production (Walker and Gregg, 1975; Nguyen et al., 1989a; Goh and Nguyen, 1992, 1997).

Accumulation of N under intensive heavily stocked grass-clover pastures occurs mainly from the biological N fixation of the legume component of pastures, residue return from pasture crops and return of grazing animal excreta (Walker et al., 1959; Jackman, 1964; Williams and Haynes, 1990, 1997). Use of high analysis N fertiliser can lead to increased NO<sub>3</sub>-N leaching through the soil profile (Barraclough et al., 1984, 1992). A considerable proportion of applied fertiliser N is also immobilised into organic forms of N in soils (Kelley and Stevenson, 1996; Mengel, 1996). To keep inorganic fertiliser N application to a minimum in mixed cropping farming, understanding the nature of the readily mineralisable pool of N that accumulates under pasture and its mineralisation following ploughing-in of pastures is very important to the fertility of mixed cropping soils (Williams and Haynes, 1997).

Obviously the area of research on the nature and composition of organic S and N and their role in crop production and soil management is very wide. The purpose of this review is to report published accounts confined mainly to the forms of S and N present in soils, their accumulation and mineralisation in a grazed pasture ecosystem and the factors that influence these processes.

**Forms of Sulphur in Soils**

Sulphur in soil occurs generally both in organic and inorganic forms (Figure 1) (Freney, 1986). Soil type, depth and management practices greatly influence the proportion of organic and inorganic S present in the soil. Many authors have reviewed the forms of S in soil and S cycling in great detail (Blair, 1971; Till, 1975). In general most well drained inorganic surface soils contain more than 90% S in the organic forms (Biederbeck, 1978; Metson, 1979b; Freney, 1986; Perrott and Sarathchandra 1987; Goh and Nguyen, 1992).

**Soil Inorganic Sulphur**

Despite the very small amount present in soils, inorganic S is very important because of its water solubility and availability to plants. Soil inorganic S is present in non-calcareous aerated soils entirely as  $SO_4^{2-}$  with very small amounts of reduced S compounds (Freney, 1961). However, under waterlogged conditions sulphides are abundant.

**Soluble Sulphur**

Soluble S is present in the soil solution and is the main form of S available to plants and also the form in which S is leached from the soil. Soluble S can be extracted from the soil with distilled water or salt solutions like lithium chloride or calcium chloride (Spencer and Freney, 1960; Fox et al., 1964). The soluble sulphate may be immobilised by soil microorganisms (Williams, 1974; Biederbeck, 1978). It may represent up to 10% of the total S pool in some soils (Freney and Williams, 1983).

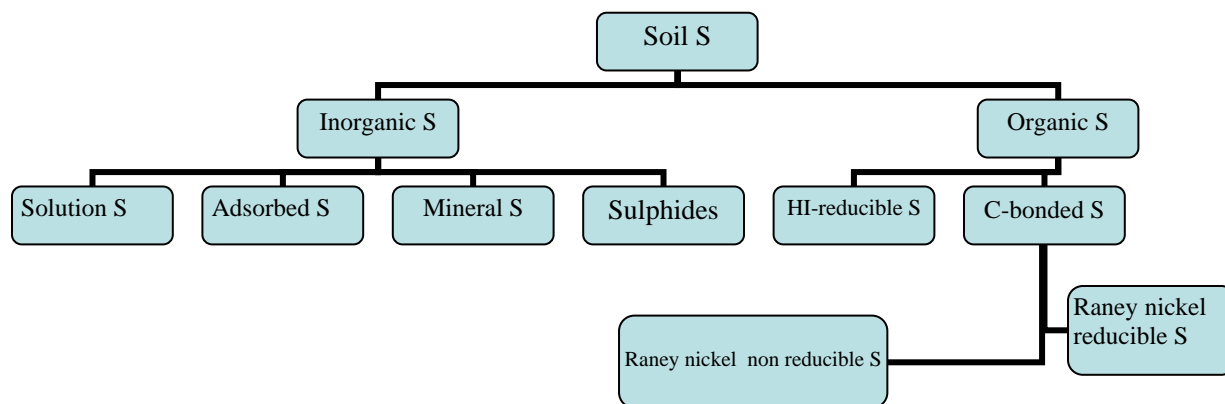


Figure 1. Forms of sulphur in soils (Freney, 1986).

**Adsorbed Sulphur**

The sulphate in solution can be adsorbed on the soil mineral surfaces. The amount of sulphate adsorbed in soils varies greatly and is determined by the sulphate adsorption capacity of the soil (Metson 1979a-c; Bohn et al., 1986). Sulphate adsorption in soil is affected by a number of factors e.g. texture, pH, sesquioxide content, phosphate content, source of sulphate as well as rainfall etc. The mechanism of sulphate adsorption has been explained in detail by Bohn et al. (1986). Sulphate adsorption is fully reversible and concentration dependent (Ensminger, 1954; Metson and Blakemore, 1978; Williams 1974; Williams and Steinbergs, 1962). Adsorbed sulphate is readily available to plants and in many soils provides a major source of S supply to plants.

**Mineral Sulphate**

Mineral sulphates are relatively insoluble and commonly occur in calcareous soils co-precipitated or co-crystallised with calcium carbonate (Williams and Steinbergs 1962). This form of sulphate is relatively unavailable to plants. It is reported that as high as 95% of total S in some Australian soils (Williams and

Steingbergs, 1962, 1964) and 75% of a Scottish soil (Tisdale et al., 1985) occurred as sulphate co-precipitated with calcium carbonate. Small amounts of highly insoluble barium sulphate and strontium sulphate can be found in most soils (Williams, 1975). Some mineral sulphates like BaSO<sub>4</sub>, CaSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> can be present in semi-arid soils.

### ***Sulphide Sulphur***

Considerable amounts of reduced forms of S can be present under anaerobic conditions. Sulphur reduction is generally observed in poorly-drained and waterlogged soils and also in tidal swamplands. Although trace amounts of sulphate, thiosulphate and elemental S are found in anaerobic soils (Smittenberg et al., 1951), sulphides are the principal stable forms of reduced S (Brummer et al., 1971). The sulphide concentration in soil is critical for high water requiring plants like rice, and also crops grown under waterlogged conditions e.g. jute because of its toxicity to these crops. In well aerated soils sulphides hardly exist.

### ***Organic Sulphur***

Organic S in soils originates mainly from plants, animal residues and microorganisms. Over 90% of the total soil S in the surface horizons of well-drained non-calcareous soils of humid, semi-arid, temperate and sub-tropical regions is present in organic forms (Freney et al., 1962; Tabatabai and Bremner, 1972a; Bettany et al., 1973; Tisdale et al., 1985; Perrott and Sarathchandra, 1987; Syers et al., 1987; Nguyen and Goh, 1990).

The proportion of total S existing as organic S depends on the soil type and depth in the soil profile (Freney, 1986). A great range of soil organic S compounds are present in soil but understanding the precise nature of most of these is far from complete (Freney and Williams, 1983). Soil organic S occurs in plants, the microbial biomass and humic substances, with the later being the largest pool (Bettany et al., 1973; Sjoqvist, 1994). A small amount of organic S may also occur in the soil solution (Nguyen and Goh, 1992a, b). Soil organic S has been divided into two broad groups, essentially on their reactivity with hydriodic acid, e.g. Hydriodic acid reducible S and Carbon-bonded S (Figure 2).

### ***Hydriodic Acid Reducible Sulphur***

The fraction of organic S that can be reduced to H<sub>2</sub>S by a reducing mixture of hydriodic acid, formic acid and hypophosphorous acid is generally known as hydriodic acid-reducible S (HI-S). This fraction is not bonded directly to carbon. The reducing mixture can reduce the S in ester sulphates (-C-O-S-), sulfamic acid (-C-N-S) and the second S in S-sulfocysteine (-C-S-S-), where the S and C atoms are separated by O, N, or S atoms, respectively (Cooper, 1972; Freney et al., 1970; Lowe and DeLong, 1963). Inorganic SO<sub>4</sub>-S present in soils is also reduced in this process. HI-S is believed to be composed mainly of ester sulphates. These organic sulphates also appear to be readily hydrolysed to inorganic sulphate by hot acid or alkali. Therefore, this fraction is considered to be mainly associated with active side chain components of humic and fulvic materials (Bettany et al., 1973). Organic S compounds which are reduced to H<sub>2</sub>S by hydriodic acid include arylsulphates, alkylsulphates, phenolic sulphate, sulphated polysaccharides, choline sulphate and sulphated lipids (Tisdale et al., 1985). Some organic sulphites, such as dimethyl sulphite or diethyl sulphite can be also reduced to H<sub>2</sub>S by hydriodic acid.

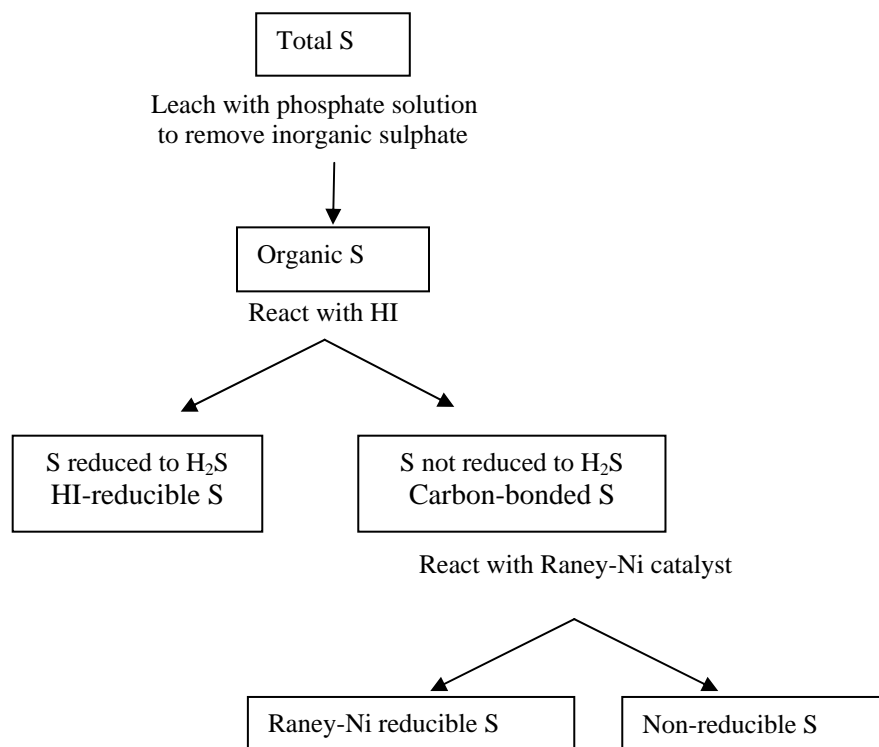


Figure 2. A flow chart showing fractionation of soil sulphur (Zhao et al., 1996)

On average, HI-S accounts for 50% of the total organic S in soils. However, results from a wide range of soils indicate that the percentage may range from 30 to 70% of the organic S in soils (Williams and Steinbergs, 1959; Freney, 1961; Lowe and DeLong, 1963; Cooper, 1972; Tabatabai and Bremner, 1972b; Bettany et al., 1973; Neptune et al., 1975; Stevenson, 1986; Stevenson and Cole, 1999; Sjoqvist, 1994). Values of HI-S as high as 93% have also been reported (Tabatabai and Bremner, 1972b). In some soils, the percentage of organic S present as HI-S remains constant with depth in the profile, but in others, the percentage increases with depth (Tabatabai and Bremner, 1972b; Williams, 1974). Results from Bettany and Stewart (1983) showed that the environment in which a soil is formed is an important factor in influencing the proportion of total S present in HI-S forms. The proportion of HI-S decreases with decreasing temperature and increasing rainfall.

### **Carbon-Bonded Sulphur**

Carbon-bonded S (C-S) is the fraction of organic S in which the S atoms are bonded directly to the C atoms. This fraction represents the difference between the total organic S and HI-S. Sulphur directly bonded to carbon is a major component of soil organic S. Generally, it comprises approximately half of the total organic S in soils (Williams, 1975). In some soils, C-S accounts for up to 70% of organic S (Freney and Williams, 1983). Because of its resistance to some extractants, and correlation with certain humus properties it is suggested that C-S is primarily associated with the aromatic core of humic acids (Bettany et al., 1973).

Many researchers have tried to determine C-S directly by reacting soil with Raney-Ni alloy (e.g., Lowe and DeLong, 1963; Freney et al., 1970; Tabatabai and Bremner, 1972b; Scott and Anderson, 1976). This reagent reacts with all reduced S bonded to C and oxidized S in the form of sulfoxides  $R-C-SO-CH_3$ , sulfinic acids  $R-C-SO-OH$ , or sulfonic acids attached to an aromatic nucleus (e.g. sulfanilic acid,  $H_2N-C_6H_4-SO_2OH$ ). However, Raney Ni does not react with S in the form of aliphatic sulfones (e.g. methionine sulfone or aliphatic sulfonic acids (Freney et al., 1970).

The Raney Ni technique accounted for 46-58% of the total S in organic soils and 12 to 32% in mineral soils from Canada as C-S (Lowe and DeLong, 1963; Lowe, 1965, 1969). Freney et al. (1975) reported values on average of 56% of C-S and 30% of the total S determined with a modified Raney Ni method from a range of Australian soils. Values ranging from 0.4 to 21% of total C-S in soil from different parts of the world have been reported by Freney et al. (1970), Tabatabai and Bremner (1972b) and Scott and Anderson (1976). Some results

of Raney Ni reducible C-S were found to have good agreement with amino acid S as determined in acid hydrolysates of soil (Freney et al., 1975; Scott et al. 1981). It is possible that the Raney Ni method determines mainly amino acid S. Amino acid S may constitute up to 30% of the organic S in soils and approximately 60% of amino acid S is cystine S (Freney and Williams, 1983).

The values calculated by the indirect method (i.e. difference between total organic S and HI-S) are always found to be higher than those obtained by the Raney Ni method. In some cases it was found that Raney nickel alloy failed to reduce aliphatic sulphones and sulphonic acids.

Hence it is obvious that some organic S fractions are not reduced by either the HI-reducing mixture or Raney Ni alloy. This fraction generally represents approximately 30 to 40% of the organic S (Tisdale et al., 1985), and may be in the form of aliphatic sulfones or aliphatic sulfonic acids. Since this form of S resists degradation by strong treatments, it is a very stable fraction of organic S and thus is probably less important as a potential source of S for plant growth (Lowe and DeLong, 1963; Lowe, 1964; Biederbeck, 1978).

#### ***Soil Microbial Sulphur***

The biomass S generally accounts for only 1 to 4% of soil organic S. This fraction is considered to be very important because of its role in S turn-over in soils (Saggar et al., 1981 a, b; McLaren et al., 1985; Nakas, 1986; Germida et al., 1992). Biomass S is generally determined by chloroform treatment (Saggar et al., 1981a) which involves chemical extraction of S before and after chloroform fumigation of the soil. The principle involved is that the chloroform treatment causes lysis of the microbial cells, resulting in the release of the cell bound S. Biomass S is affected by the type of extractant, time of chloroform treatment and extraction period (Banerjee et al., 1993). O'Donnell et al. (1994) reported that the primary mechanism of SO<sub>4</sub>-S incorporation into soil organic S is via the microbial biomass.

#### ***Soluble Organic Sulphur***

Soil organic S exists in organic compounds, mostly insoluble in water. However, some of the soil organic S can be extracted with water or dilute salt solutions. Although soluble organic S in soils accounts for only a small part of the total organic S, it is important because it is readily available to plants as evident by a significant relationship between soluble organic S and SO<sub>4</sub>-S (Watkinson and Perrott, 1990). The amount of soluble organic S increases with the level of extractable organic S.

#### ***Nitrogen in Soil***

Bremner (1965a) reported that the plough layer of most cultivated soils contains between 0.06 and 0.5% nitrogen and it may be as low as 0.02% in the subsoil. New Zealand topsoils (0-15 cm) contain higher amounts of nitrogen ranging from 0.1 to 0.9% (Blakemore and Miller, 1968; McLaren and Cameron, 1996). This can represent between 2000 and 12,000 kg N ha<sup>-1</sup>. However, total N in organic soils may reach 4% (Haynes, 1986). In most soils more than 90% of the total N is contained in organic compounds (Cornforth, 1968; Stevenson, 1982a; Kelley and Stevenson, 1996; Haynes, 1986).

Nitrogen occurs in many different forms in nature, and very large amounts are present in the earth's crust (18 x 10<sup>15</sup> tonnes) and in the atmosphere (3.8 x 10<sup>15</sup> tonnes of N gas) (McLaren and Cameron, 1996). Plant nutrition is dependent on the efficient cycling of N from unavailable forms of N to its available forms such as NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. Atmospheric N can be added to soil through the process of wet and dry deposition (Fraser, 1992). In rural areas of New Zealand, N added through precipitation is estimated as less than 1 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Steele, 1982) but in some parts of the world can exceed 20 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Legg and Meisinger, 1982). In grazed pasture systems, the N cycle is greatly influenced by the presence of grazing animals (Floate, 1981; O'Connor, 1981; Ryden, 1985). The grazing animals return a significant amount of N to the soil-plant system, either directly in the form of urine and dung, or indirectly when the farmers spread slurries from housed animals (Jarvis et al., 1989). A major proportion of energy and N supply to the soil usually comes from above and below ground litter (Staaf and Berg, 1981; Haynes, 1986).

As the plant residues decompose, N and other nutrients are released in soil which may be stored and subsequently used by crops. Hence in the majority of agricultural ecosystems, the process of plant residue decomposition is a very important component of the N cycle (Floate, 1981).

### **Forms of Soil Nitrogen**

Soil N can be present in three major forms:

- i). Organic N - associated with soil humus and also with the dead and decaying plant and animal residues. More than 90% of soil N is in the organic form and only becomes available to plant after being mineralised.
- ii). Ammonium N - held in the 2:1 layers of clay minerals such as vermiculite, illite and montmorillonite, in a non-exchangeable “fixed” form (Bremner 1959).
- iii). Soluble and exchangeable inorganic nitrogenous compounds - “mineral N” such as  $\text{NH}_4^+$ -N,  $\text{NO}_2^-$ -N and  $\text{NO}_3^-$ -N (Young and Aldag, 1982).

At any one time, the major forms of mineral N (soluble and exchangeable  $\text{NH}_4^+$  and  $\text{NO}_3^-$ ) comprises less than 2% of the total N content in soils (Melillo, 1981; Woodmansee *et al.*, 1981). Nonetheless, plants obtain their requirements from this small pool of soil N (Haynes, 1986).

The forms of soil organic N can be divided into two broad categories a) organic residues, consisting of undecayed plant and animal residues and partial decomposition products, and b) soil organic matter or humus (Kelley and Stevenson, 1996). Humus is the dark-coloured major fraction of the soil organic matter, usually stable and relatively resistant to decomposition (Kelley and Stevenson, 1996; Paul and Clark, 1989).

The major known fractions of soil N are amino N (proteins, peptides), polymers of amino sugars, and  $\text{NH}_4^+$  fixed in interlayers of 2:1 minerals (Mengel, 1996). However, only a small percentage of the total soil organic N is easily mineralisable and contributes to the pool of mineral soil N. Recently Schneider (1995, quoted in Mengel, 1996) showed that the most important sources of mineralisable N are peptides and amino sugars.

About 50% of the total soil N remains unidentified. A remarkable proportion of this non-identified N is heterocyclic N. Presumably, most of this heterocyclic N is integrated in humic and fulvic acids (Schnitzer and Spiteller, 1986).

### **Characterisation of Organic Nitrogen by Conventional Techniques**

The most widely used procedure for characterising organic N in soil or humic substances is by acid hydrolysis. The methods for determining the forms of N in hydrolysates of soil or soil organic matter have been described by Stevenson (1982b). In a typical procedure, the soil is heated with 3 N or 6 N HCl for 12 to 24 hours, after which the N is separated into different forms as outlined in Table 2.1.

### **Accumulation of Soil Sulphur and Nitrogen under Pasture**

Pasture establishment and application of S containing fertiliser have been reported to increase the accumulation of soil organic matter (C, N and S) in both New Zealand and overseas soils (Walker *et al.*, 1959; Jackman, 1964; Quin and Rickard, 1981; Russell and Williams, 1982; Lewis *et al.*, 1987; Perrott and Sarathchandra, 1987; Nguyen *et al.*, 1989a; Nguyen and Goh, 1990; Williams and Haynes, 1990; Franzluebbers *et al.*, 2000). The accumulation plays an important role in pasture-cereal S and N nutrition.

Table 1 Fractionation of soil N by acid hydrolysis procedure (Kelley and Stevenson, 1996).

Form	Definition and method	% of soil N
Amino acid-N	-amino acid-N, usually determined by ninhydrin- $\text{CO}_2$ or ninhydrin- $\text{NH}_3$ method	30-40
Amino sugar-N	Steam distillation with phosphate-borate buffer at pH 11.2	5-10
$\text{NH}_3$ -N	Ammonia recovered from hydrolysate by steam distillation with MgO	20-35
Hydrolysable unknown N	(HUN) hydrolysable N not accounted for as amino acids, amino sugars, or $\text{NH}_3$	10-20
Acid insoluble unidentified-N	N remaining in soil residue following acid hydrolysis (boiling 6 N HCl for 12 hours)	20-35

The build up of organic S in soils is mainly attributed to the addition of fertiliser S as superphosphate (Walker *et al.*, 1959; Quin and Rickard, 1981) but indirectly it also helps build up of organic N. Donald and Williams (1954) demonstrated that there was a linear relationship between soil N accumulation in subterranean clover and total superphosphate application. White clover is the most commonly used legume in a grazed pasture and it is a poor competitor for soil P, potassium (K) and S when grown with other grasses (Haynes, 1980). The

application of fertiliser P and S from superphosphate promotes vigorous growth of white clover, which in turn increases N fixation and accumulation in soil. Under legume pasture the major source of N build up in soil is the symbiotic fixation of atmospheric N by the legume component of pastures particularly white clover (Walker, 1956; Williams and Haynes, 1990; Haynes and Williams, 1992). Recently Nyborg et al. (1999) reported that application of N and S fertiliser to grass over 13 years increased total C in soil (0-30 cm) and light fraction C (0-5 cm).

In well-managed grass-clover pastures rates of atmospheric N fixation of 100-300 kg N ha<sup>-1</sup> are not uncommon (Edmeades and Goh, 1978; Hoglund and Brock, 1987; Ledgard, 1989) and when conditions are particularly favourable for white clover, a maximum of up to 700 kg N ha<sup>-1</sup> may be fixed with adequate P and K applications (Sears et al., 1965). The amounts of atmospheric N fixation under short-term pasture in mixed cropping practices in Canterbury, New Zealand is not fully documented (Haynes and Francis, 1990). However, estimated ranges of 106-145 kg N ha<sup>-1</sup> under dry land and 152-226 kg N ha<sup>-1</sup> under irrigated areas have been reported (Crush, 1979). In the New Zealand Ministry of Agriculture and Fisheries (MAF) fertiliser recommendation model for mixed cropping, the rate of N<sub>2</sub>-fixation is considered to be about 200 kg N ha<sup>-1</sup> yr<sup>-1</sup> (Metherell et al., 1989). Such information on the amounts of S accumulated under short-term pastures is rarely available.

Soil organic matter contains C, S and organic P in relatively constant proportions (Walker et al., 1954; Barrow, 1961a). However, the rate of organic matter (C, N, S and P) accumulation and the time taken to reach equilibrium vary considerably at a particular site depending on the initial organic matter content of the soil, soil type, climate and management (Jackman, 1964; Quin and Rickard, 1981; Simpson, 1987; Williams and Haynes, 1990; Whitehead, 1970). Nguyen and Goh (1990) found that application of superphosphate increased the accumulation of organic S, HI-S and C-S fractions in New Zealand soils. The accumulation of organic S reached a steady state after 25-27 years of superphosphate application, whereas, N and C attained a steady state at 3-4 and 9-12 years earlier respectively, thus suggesting that these elements were stabilised independently in soil organic matter. Perrott and Sarathchandra (1987) also reported that fertiliser topdressing and N fixation have led to accumulation of P, S and N in soil organic matter during pasture establishment on a range of New Zealand soils. Total C, N and S build up in soils under legume-grass pasture occurs at different rates. Consequently the C : N and C : S ratios in soils change. Walker et al. (1959) found that the C : N ratio of an under developed scrub soil dropped from 33 to 11 in 25 years due to improved pasture management in that soil.

Under grazing, only small proportions of the nutrients used in pasture production are actually removed from the system compared to grain pasture or arable cropping. In contrast large quantities of nutrients are recycled within the system (Haynes and Francis, 1990). About 90% of the nutrients ingested by grazing animals in pasture herbage are returned to the soil surface in animal excreta (Barrow, 1987; Haynes and Francis, 1990).

Sulphur and N accumulation differ under different pasture crop species. Organic matter supply is closely related to the dry matter (shoot and root) production and residue-return to the soil. Perennial crops generally produce higher dry matter yield than the annual crops (Francis et al., 1999). Haynes et al. (1993) reported the pattern of N accumulation in the above ground dry matter by barley over 60 days (40% of total N) was different than that by lupins (20% of total N). Haynes (1997) indicated that the pool of readily mineralisable soil organic N built up under short-term pasture occurs essentially through decay of grass-clover litter, roots and clover nodules and through immobilisation of N in soil where N is returned after passage through the grazing animal (Williams and Haynes, 1994). The factors affecting long-term rates of organic S accumulation in soils, such as climate, soil characteristics, plant species and addition of fertilisers, are evident from periodic analysis of soil S content in the pastoral soil studies of Walker et al. (1959).

#### ***Cultivation Effect on Soil Organic Matter***

As pasture development increases, soil organic matter builds up. Cultivation of arable crops, on the other hand, decreases soil organic matter. Under arable cropping, the soil is usually tilled at least once a year, which breaks up the soil clods and exposes previously inaccessible organic matter to microbial activity. As a result soil organic matter usually decreases under continuous cropping (Jenkinson, 1988; Haynes and Francis, 1990). Tillage continually exposes new soils to wet-dry and freeze-thaw cycles at the soil surface (Beare et al., 1994; Paustian et al., 1997), thereby increasing the susceptibility of aggregates to disruption. Ploughing changes the soil conditions (e.g. temperature, moisture, and aeration) and increases the decomposition rates of litter (Rovira and Greacen, 1957; Camberdella and Elliot, 1993). The microbial community is affected by ploughing and litter placement (Holland and Coleman, 1987).

Bettany *et al.* (1980) reported that long-term cultivation of Canadian prairie soils decreased the total amount of C, N, S and P held in the soil organic matter. Overall decrease in soil organic matter due to cultivation was also reported by Carter *et al.* (1998), Davidson and Ackerman (1993), and Ellert and Gregorich (1996) in different Canadian soils. During the decomposition of soil organic matter there is a release of organic S and N in mineral forms, a considerable portion of which are taken up by the arable crops and then removed from the system as crop products, e.g. grain (Haynes and Francis, 1990).

### **Soil Sulphur and Nitrogen Mineralisation**

The turnover of S and N between mineral and organic forms occurs through the opposing process of mineralisation and immobilisation. Mineralisation of soil organic matter is a process whereby nutrients are released in inorganic forms by soil microorganisms as they utilise organic compounds as a source of energy (Jansson and Pearsson, 1982; Jarvis *et al.*, 1996; Jensen, 1997). This is a very complex process and involves the activity of non-specific heterotrophic soil microorganisms under both aerobic and anaerobic conditions (Jarvis *et al.*, 1996). Both mineralisation and immobilisation are simultaneously carried out by large numbers of microorganisms. The rate of release of inorganic S and N is the net result of these two concomitant processes (Frenay *et al.*, 1971; Maynard *et al.*, 1983). It is believed that mineralisation of S and N results either from (a) release from organic materials during oxidation of C by soil microbes to provide energy or (b) release controlled by the supply and need of the microbial population. Only the excess SO<sub>4</sub>-S and mineral N which are not required by microbes becomes available for plant uptake.

So far, the exact processes involved in S and N mineralisation are not yet fully understood, but presumably microorganisms can use their enzyme systems to cleave S and N from substrates such as amino acids, esters, and other organic compounds such as thiols, thioester, steroid sulphates, lipid sulphate and glyco proteins (Dodgson *et al.*, 1982; Huxtable, 1986).

Detailed descriptions of the biochemistry of N mineralisation are given by Ladd and Jackson (1982) and Haynes (1986). The major nitrogenous compounds in soils which may be mineralised to release N include plant and animal residues (proteins, peptides, amides, amino acids nucleic acids, purines and pyrimidines), as well as soil microbial biomass and soil humic compounds. Both of these compounds contain amino acids and amino sugars.

Mineralisation of N and S in soils can be measured by laboratory or field incubation methods. Two basic types of incubation are used in the laboratory- 'closed' incubation and 'open' incubation. Both systems have some advantages and limitations. The most common method is to measure the net changes in the inorganic S and N during incubation of soil in a container, where mineralised S and N are allowed to accumulate in the system and measured at the end of the mineralisation experiment. The amounts of extractable sulphate and mineral N are measured before and after the incubation to determine the net mineralisation. Results from closed incubation systems have often produced very low levels of mineralisation (Barrow, 1961a, b; Williams, 1967; Kowalenko and Lowe, 1975b; Maynard *et al.*, 1985). In some cases, an initial flush of mineralisation has been recorded (Williams, 1967), but thereafter very slow mineralisation or even some immobilisation has been observed. In other studies, the pattern of sulphate release was entirely different, where an immobilisation of sulphate was followed by slow mineralisation of sulphate (Barrow, 1961a; Kowalenko and Lowe, 1975b). Some studies have shown a rapid mineralisation in the first two weeks followed by a plateau (Swift, 1983). The relatively low net S and N mineralisation in closed incubation systems has been attributed mainly to the reversible nature of S and N transformations where mineralised S and N are continuously incorporated back to organic matter. Therefore, it is difficult to measure total potentially mineralisable S and N in a closed incubation system. However, the use of radio-isotopic labeling in closed incubation systems has been helpful in the understanding of sulphate and mineral N immobilisation into organic forms (Frenay *et al.*, 1971; McLaren *et al.*, 1985).

The open incubation was initially developed for N mineralisation studies (Legg *et al.*, 1971). Tabatabai and Al-Khafaji (1980) were the first to use open incubation for S mineralisation studies. In this system, mineralised S and N are leached with an appropriate leaching solution from time to time thereby removing the mineralised S and N at regular intervals. Mineralisation of S and N in soils may vary depending on the incubation system used. The open incubation system gives a different pattern of S mineralisation from soils compared with closed incubation (Ghani, 1989; Tan, 1993; Tan *et al.*, 1994) and is assumed to simulate the crop removal of S and N, and provide a better measure of S and N mineralisation in soils. Significantly higher levels of S mineralisation in the open system of incubation have been reported previously (Tabatabai and Al-Khafaji, 1980; Maynard *et al.*, 1983). However, Maynard *et al.* (1983) found N mineralisation to be independent of the incubation systems used in their study.



### ***Comparative Aspects of Soil Sulphur and Nitrogen Mineralisation***

Because of the perceived similarity between microbial conversion of S and N, it has been generally assumed previously that the relative rates of mineralisation of these two elements from soil organic matter would be similar (Walker, 1957; White, 1959; Tabatabai and Al-Khafaji, 1980) i.e. S and N will be mineralised in approximately the same ratio as they occur in soil organic matter. In many cases, however, this assumption has been proved to be incorrect. In some studies the ratio of N to S mineralised was much higher than that of the soil organic matter (Williams, 1967; Tabatabai and Bremner, 1972b; Haque and Walmsley, 1972). Considerably smaller ratios of mineralised N to S than that of soil organic matter have also been observed (Nelson, 1964).

A dichotomous system proposed by McGill and Cole (1981) best explains the patterns of cycling of C, N, S and P through soil humus. In this system, two types of processes are involved in the mineralisation of organic matter, biological and biochemical mineralisation. A classical biological mineralisation process is that nutrients, which have direct association with C, are mineralised as a result of C oxidation to provide energy. As a result, inorganic forms of nutrients such as S and N are released from the organic matter. A part of the mineralised S and N may be reused by the soil microbes and the remaining would be available for plant uptake and may be lost due to leaching. In contrast, biochemical mineralisation is considered to be the release of inorganic sulphate from organic matter through enzymatic catalysis external to the cell membrane. This process is strongly controlled by the supply of and need for the S released rather than the need for energy. When the concentration of available sulphate in the soil is too low to meet the microbial demand, sulphate esters are hydrolysed by sulphatase enzymes. Nitrogen mineralisation in soil is described solely as a biological mineralisation, whereas, sulphate esters are mineralised through biochemical mineralisation. Carbon bonded sulphur is, however, thought to be mineralised by the biological mineralisation mechanism. The biochemical processes of mineralisation of some organic S compounds have been discussed by Freney (1967). Many authors, such as Dodgson et al. (1982), Freney (1986), Germida et al. (1992) have discussed the types and occurrence of sulphatases and their role in S mineralisation. In some soils S is reported to be more resistant to mineralisation than C and N (Bettany et al., 1980), and even a net immobilisation of S may occur concurrently with a net mineralisation of N (Saggar et al., 1981b).

Mineralisation of S from decomposing organic materials depends on the S content of the decomposing materials in much the same way as mineralisation of N depends on the N content (Barrow, 1960). Research on S mineralisation by many workers has revealed that during incubation inorganic S may be primarily derived from the C-bonded S fraction (Freney et al., 1975; Ghani et al., 1991; Tan, 1993), or from HI-reducible forms (Tsuji and Goh, 1979), or from both of the fractions. It has been suggested that of the two forms of organic sulphur, HI-reducible S (ester S) has a more transitory nature and is of greater importance in the short-term mineralisation of S (McLaren and Swift, 1977). Therefore, biochemical mineralisation is likely to be the predominant process for S mineralisation.

Studies of transformations of S and N under field conditions show that mineralisation patterns for S are sometimes different from those of N, with sulphate levels in uncropped soil undergoing much greater seasonal variation than levels of mineral N (Simon-Sylvestre, 1965 quoted in Tabatabai and Al-Khafaji, 1980). The manner in which S and N are mineralised during incubation follows one of following patterns (Tabatabai and Al Khafaji, 1980; Tan, 1993):

- i) immobilisation of S and N during the initial period of incubation, followed by mineralisation of S and N in the later period (Barrow, 1961a Nelson, 1964; Haque and Walmsley, 1972; Tabatabai and Bremner, 1972b; Nor, 1981),
- ii) a steady, linear release with time over the whole period of incubation (Williams, 1967; Tabatabai and Al Khafaji, 1980),
- iii) a rapid release of S and N during the first few days, followed by a slower linear release (Williams, 1967; Stanford and Smith, 1972; Feigin et al., 1974; Nor, 1981),
- iv) a rate of release which decreases with time, or
- v) a rapid release of sulphate during the first few days followed by irregular rate of sulphur release (Ghani, 1989).

Typical mineralisation curves for S are shown in Figure 3a together with a curve for N which indicates considerable difference in the mineralisation behavior of these two elements. Figure 3b, however, shows similar mineralisation behaviour for S and N in an open incubation system.

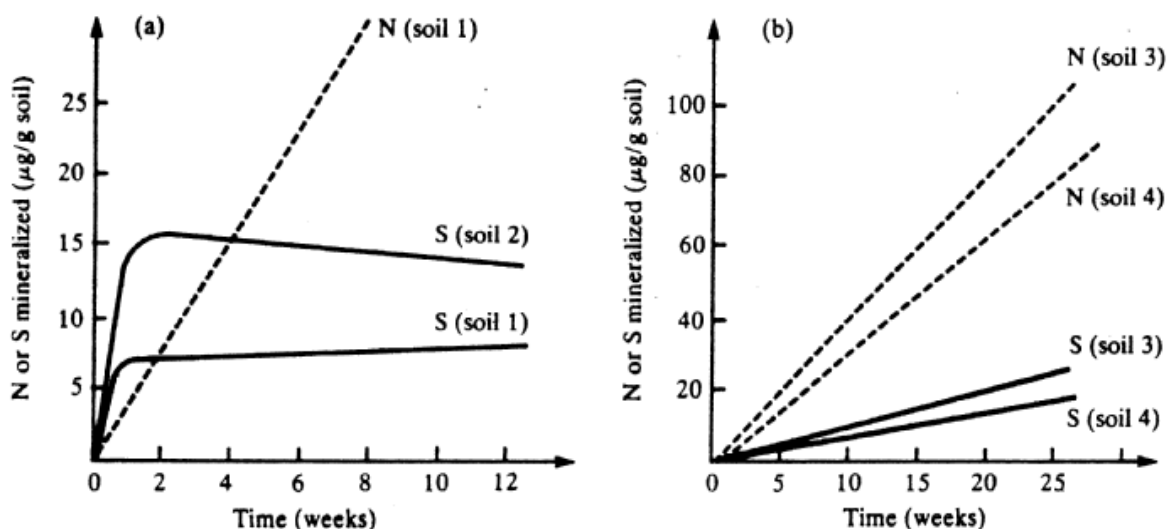


Figure 3. Mineralisation pattern of S and N during incubation studies; a) closed incubation, b) open incubation (Swift, 1985).

#### **Factors Affecting Mineralisation of Soil Sulphur and Nitrogen**

Since mineralisation is primarily involved with soil microorganisms, any factor which affects microbial growth and activity will also affect mineralisation (Williams, 1967). The rate of mineralisation is affected by environmental parameters including temperature, moisture, pH, plants grown, C, N and S Ratios, wetting and drying etc. Among these, temperature and pH are the two most important factors influencing the release of mineral S and N in soils of the temperate region (Tabatabai and Al-Khafaji, 1980).

#### **SUMMARY**

The information summarised in the review indicates that S and N exist in soil in various forms and undergo various transformations depending of the soil conditions and climatic variations. The forms in which S and N exist in soil are very important in terms of their availability to plants. Although organic forms of S and N are not directly available to plant uptake, they play an important role in plant nutrition through mineralisation-immobilisation processes. Because of the importance of S and N as plant nutrients, a considerable amount of work regarding the transformations of S and N in the soil plant ecosystem has been done in the past. Laboratory analyses and glasshouse experiments were the major tools for these studies of S and N transformations but in many cases the results obtained from these studies did not reflect the actual transformations that took place in the entire growing season in the field.

Accumulation and mineralisation of S and N, two very important and complex processes, have been studied extensively over the last few decades. Most organic matter build-up studies have been confined to permanent pastures and forestlands and their transformation into cultivated land over a long period of time. Soil organic matter accumulation and its subsequent mineralisation are dependent on a number of factors such as soil and climatic conditions, vegetation and management. Despite a significant number of studies on the accumulation and mineralisation of organic S and N in soils under various conditions, there is still considerable uncertainty regarding the biological turnover of organic S and N in soil plant ecosystems. In particular, there is a wide scope for research into the aspects of organic S and N cycling in short-term pasture-arable cropping rotations.

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