



Nutrient reviews

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For the purposes of *The Fertilisers Regulations*, nutrients are in three categories:

Major nutrients: nitrogen, phosphate, potash

Secondary nutrients: magnesium, sodium, sulphur, calcium

Trace elements (micronutrients): boron, cobalt, copper, iron, manganese, molybdenum, zinc

Chlorine is an essential nutrient for plants but is not covered by the regulations. Similarly, nickel is known to be essential for the formation of the enzyme urease which breaks down urea but is not covered by the regulations. The amounts of chlorine and nickel required by plants are small and deficiencies do not occur in field crops in the UK.

Selenium is an essential nutrient for animals and possibly for plants but is not covered by the regulations. Concentrations of selenium in crops and herbage are sometimes inadequate for livestock or human diets and supplementation by addition to fertilizers is a feasible treatment.



Boron

Boron in plants

Boron is an essential micronutrient for both plants and animals. The role or roles of boron in plant metabolism are not fully understood but include maintenance of cell membranes and transport of other nutrients through them (Shorrocks 1990). Where boron is deficient, cell division does not proceed normally so there are effects in growing points where tissues become distorted and eventually die. This can lead to loss of apical dominance, development of side shoots and a bushy appearance to the plant. Deficiency also affects pollination and seed set. A large proportion of hollow hulls in sunflower is a typical symptom of boron deficiency. Damage to cell walls is responsible for the brown flecks, stripes and zones associated with boron deficiency in sugar beet ('heartrot'), swedes ('brown rot'), carrots ('five o'clock shadow') and celery (stripes along stems). Photographs showing deficiency can be seen at www.luminet.net/~wenonah/min-def/list.htm.

Most boron is taken up by the plant passively as boric acid (H_3BO_3). Once taken up into leaves, boron tends to be immobile in most plant species and is not translocated from older to younger leaves to any great extent. Deficiency symptoms therefore appear first in younger tissues.

Typical concentration of boron in plant tissue is 20 – 200 mg B/kg dry-matter depending on crop species. For most broad-leaved crops, a concentration less than 20 mgB/kg dry-matter indicates probable deficiency. The concentration indicating deficiency is lower in grasses and cereals:

Boron concentration in leaf tissue (mg B/kg dry-matter) (Borax 2001).

:

| | Deficient | Normal |
|------------------|------------------|---------------|
| Wheat | <5 | 5 - 20 |
| Barley | <5 | 5 - 20 |
| Oats | <5 | 5 - 20 |
| Maize | <5 | 5 - 25 |
| Oilseed rape | <20 | 30 - 50 |
| Sunflower | <30 | 50 – 150 |
| Potato | <5 | 40 – 70 |
| Carrots | <18 | 30 – 200 |
| Sugar beet | <20 | 25 - 50 |
| Red beet | <15 | 27 – 83 |
| Turnip, swede | <15 | 45 – 50 |
| Beans | <10 | |
| Pea | <18 | 170 |
| Brussels sprouts | <19 | 70 |
| Cabbage | <18 | 22 – 38 |
| Cauliflower | <23 | 36 |
| Celery | <15 | 15 - 48 |



| | | |
|----------|-----|----------|
| Cucumber | <5 | 30 – 60 |
| Lettuce | | 27 – 43 |
| Tomato | <10 | 30 – 100 |
| Apple | <20 | 28 - 50 |
| Pear | <20 | 30 - 50 |
| Lucerne | <20 | 30 – 80 |

For top fruit, boron concentration in the fruit may be a more reliable guide. Optimum levels are 1.5 – 4.5 mg B/kg fresh weight. Less than 1.5 mg B/kg indicates probable deficiency (MAFF 2000).

Removal in arable crops usually is less than around 0.3 kg B/ha (Shorrocks 1991).

Crops vary in their susceptibility to boron deficiency:

| Susceptible | Moderately susceptible | More tolerant |
|--------------------|-------------------------------|----------------------|
| Apple | Brussels sprout | Barley |
| Broccoli | Cabbage | Beans |
| Cauliflower | Chinese cabbage | Grasses |
| Carrot | Flax | Oats |
| Celery | Maize | Peas |
| Oilseed rape | Potato | Rye |
| Red beet | Tomato | Strawberry |
| Sugar beet | | Wheat |
| Sunflower | | |
| Swede | | |
| Turnip | | |

Fertilizer declarations

Boron is a micronutrient and is declared in elemental form (B). The limit of variation on the declared content is 0.4%. Boron that occurs naturally in the fertilizer may be declared provided the content is at least 0.01% by weight for fertilizers applied to the soil or as leaf sprays. The following instruction should appear with the declaration: ‘To be used only where there is a recognised need. Do not exceed the appropriate application rates’.

Boron in the soil

Boron may be a component of silicate minerals, adsorbed on clay particles or in organic matter (Shorrocks 1990). The adsorbed boron probably is the main source for plant uptake and the amount will vary with the clay content of the soil. Light sandy soils will contain less adsorbed boron than will heavier textured soils. The degree of adsorption is affected by soil pH, being greatest at high pH. Boron is lost quite readily by leaching from light soils with low adsorption capacity. Deficiency therefore tends to occur on light soils with high pH. Liming will tend to reduce the availability of boron.



Plant available boron in soil is measured by the hot water extraction method (Berger and Truog 1944) and results are expressed usually as mg B/kg dry soil (ppm). A concentration of extractable boron in soil of less than 1 ppm often is taken to indicate possible deficiency. However, concentrations at which deficiency symptoms could appear can vary with soil texture. On heavy clay soils, deficiency is probable at less than 0.8 ppm, on medium texture soils at less than 0.5 ppm and on light sandy soils at less than 0.3 ppm (Borax 2001)

Sources of boron

Most soil-applied boron in the UK is in the form of sodium borate. The ratio of boron to sodium and the degree of hydration vary. Fertilizer grades of disodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$) are available for soil application. The readily soluble disodium octaborate ($\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$, 'solubor') also can be used as a spray for soil application or as a coating on granular fertilizers. A granular material (mixture of disodium tetraborate and disodium octaborate containing 14 - 15% B) is available for blending. Elsewhere, the less soluble calcium borate, for example as colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) is sometimes used for soil application.

Disodium octaborate may also be used in solution as a foliar spray usually at a concentration of 0.2 – 0.5% w/v. Chelated boron, typically 15% B w/v, is available for foliar application. As boron is relatively immobile in the plant, several foliar applications may be necessary to correct deficiency in the developing crop.

Sodium octaborate is used for nutrient feeds in protected crops and boric acid (H_3BO_3) is used in hydroponic systems.

Crop responses to boron

Amongst field crops, deficiencies are most likely in sugar beet, swedes and carrots (MAFF 1981, Reith 1977) but occur in brassica crops, celery, red beet and lettuce (Shorrocks 1991a). Frequent deficiencies have been reported in field grown courgettes. Deficiencies also have been reported in apples, raspberries, chrysanthemums and carnations (Shorrocks 1991a). Yield responses of 13 – 20% in oilseed rape have been recorded in the UK (Shorrocks 1991b).

Typical applications of boron are 2.0 - 2.5 kg B/ha for soil application or a 0.2 – 0.5% w/v concentration for foliar sprays. A foliar spray will apply around 0.6 kgB/ha and may need to be repeated during crop growth.

Excess boron sometimes can be a problem. Application of pulverised fly ash has been found to damage barley due to boron toxicity (Walker 1979), composted municipal waste can contain high concentrations (Lumis and Johnson 1982) as can irrigation water (Markus 1988). Critical tissue concentrations above which damage occurs vary among crops but in spring barley (a relatively sensitive crop), a critical value of 80 mg B/kg dry-matter at the 5 leaf stage has been reported (Davis *et al.* 1978).



Boron in manures and biosolids

Typical total boron concentration has been given as 20 mg B/kg dry-matter in FYM, 2 – 3 g B/m³ in pig slurry and 1.5 – 3.0 g B/m³ in cattle slurry (Bergmann 1984).

Some data for biosolids and manures have been presented by Eriksson (2001):

| Source | No. of samples | Mean | Minimum | Maximum |
|------------------|----------------|------|---------|---------|
| mg/kg dry-matter | | | | |
| Sewage sludge | 48 | 61 | 2 | 390 |
| Pig slurry | 4 | 84 | 65 | 91 |
| Pig FYM | 4 | 28 | 16 | 38 |
| Cattle slurry | 4 | 52 | 25 | 88 |

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Chlorine

Chlorine in plants

Chlorine was first established as an essential plant nutrient in 1954 (Broyer *et al.* 1954) although crop responses to salt had been recognised since the 19th century. It is a component or activator of enzymes involved in photosynthesis and cell division, acts as an osmo-regulator and plays a role in disease suppression.

Plants take up chlorine actively as the chloride ion Cl⁻. For some reason, there is often confusion over elemental chlorine (which is a toxic gas) and the chloride ion which is in solution. The same confusion is not apparent over elemental potassium or phosphorus (which are metals that spontaneously combust when exposed to air) and the ionic forms in solution. A minimum concentration in plant tissue of around 100 mg Cl/kg dry-matter is necessary for biochemical functions (Fixen 1993) but usually the concentration is much higher, around 0.2 to 2.0%. Concentrations as high as 10% can occur in some plants. Unlike other micronutrients, chlorine is not toxic to plants at high concentrations. Some of the non-biochemical roles of chlorine in osmo-regulation may require these high concentrations. Typical removal in crops is 20 – 80 kg Cl/ha.

Photographs of chlorine deficiency in wheat can be seen at www.back-to-basics.net/nds/Chloride.html

Chlorine deficiency symptoms usually include wilting, often beginning at leaf tips and progressing to bronzing or chlorosis. Roots may branch extensively. Details for individual crops are given in Fixen (1993).

Chlorine is highly mobile within the plant and easily translocated.

Critical concentrations (mg Cl/kg dry-matter) for chlorine in plant tissues have been reported as 1300 for potatoes (mature shoot) (Corbett and Gausman 1960) and 1200 – 4000 for wheat and barley (heading shoot) (Fixen 1993). As chlorine is mobile in the soil, sampling to 60 or 90cm is necessary (Halstead *et al.* 1991). In 36 sites in the USA sampled to 60cm, a critical value of 48 kg Cl/ha separated sites into responsive and non-responsive for spring wheat (Fixen 1993).

Toxic effects of high concentrations of chlorine are associated with osmotic effects in saline soils. In the UK, high soil salinity may be found in coastal areas or in soils irrigated with water containing high salt concentrations.

With a daily requirement of around 40 g Cl for a high yielding dairy cow (ARC 1965), dietary concentration should be at least 0.025% Cl in the dry-matter.

Fertilizer declarations

Chlorine is not covered by EU directives or by *The Fertilisers Regulations*.



Chlorine in the soil

Chloride (Cl^-) is the only form of chlorine found naturally; all other forms are unstable in the environment and convert to chloride. Owing to its high solubility, most chlorine in the soil is in solution. However, some acid clays may hold chlorine at anion exchange sites (Halstead *et al.* 1991, von Uexkull 1990).

Atmospheric deposition is a significant natural source of soil chlorine (Halstead *et al.* 1991). Close to coasts, annual deposition can be 100 kg Cl/ha whilst 200 km inland, this can drop to 20 kg Cl/ha (Fixen 1993).

The chloride ion is highly mobile in soils and easily leached. (Schumacher and Fixen 1989).

Chlorine (as chloride) affects some soil processes involving other nutrients. In acid soils (pH lower than around 6.1), chlorine inhibits nitrification of ammonium to nitrate-N (Roseberg *et al.* 1986). This effect appears not to occur in neutral or alkaline soils. Application of chloride-containing fertilizers has been reported to increase the availability of soil manganese (Fixen 1993).

Chloride concentration in the soil is measured by extraction with calcium sulphate (MAFF 1986)

Irrigation water can contribute to soil chlorine and, where concentrations are high, can cause foliar scorch. To prevent scorch, water chloride concentration should not exceed 300 mg Cl/litre for sensitive crops (peas, dwarf beans, strawberries, blackberries, gooseberries and plums), 400 mg Cl/litre for moderately sensitive species (broad beans, lettuce, radish, onion, celery, maize, apples, pears, raspberries and red currants) or 700 mg Cl/litre for slightly sensitive crops (potatoes, cabbage, carrots, cauliflower, wheat, oats, blackcurrants and vines) (MAFF 1981). Least sensitive crops (sugar beet, mangolds, red beet, spinach, asparagus, rape, kale and barley can tolerate up to 900 mg Cl/litre . These values relate to an annual irrigation need of 25mm. Lower concentration limits apply where irrigation need is greater.

Sources of chlorine

The main source of applied chlorine is potassium chloride (muriate of potash, KCl) which is the main form of fertilizer potash worldwide. This contains 47% Cl , all in the chloride form (there is no elemental chlorine in potassium chloride). Salt applied to sugar beet and some other crops contains around 56% Cl .

Calcium chloride, used to correct calcium deficiency in top fruit, is another source of chlorine. Again, all the chlorine is in the chloride form.

Crop responses to chlorine

Chlorine deficiencies are recognised in several tropical crops such as kiwifruit and have been reported in cereals in Europe (Russell 1978), the USA and Canada (Fixen 1993). In cereals, yield responses to chlorine have been associated with improved resistance to disease.



Much of the research on the disease suppressing effects of chloride-containing fertilizers has been done in the USA, often involving comparisons of ammonium sulphate and ammonium chloride as nitrogen sources. Another approach has been to measure effects of potassium chloride applied to soils high in available potassium. Suppressing effects of chloride have been reported for take-all, yellow rust, *Septoria*, *Fusarium* and downy mildew. Reviews of these disease-suppressing effects are in Halstead *et al.* (1991) and in Fixen (1993).

The role of the chloride ion in water relations within plants may be involved in some crop effects. There is evidence that the dry-matter content of potato tubers is somewhat lower where potash is applied in the chloride form (muriate of potash) than where it is applied in the sulphate form (Dickins *et al.* 1962, Gething 1968).

Chlorine in manures and biosolids

No representative UK analytical data found. However, estimates can be made from the sodium concentration in manures, assuming a Cl/Na ratio of 1.5:

| | <u>kg Cl</u> |
|-------------------------------------|------------------------|
| Farmland manure, stored under cover | 9 per 10 tonnes |
| Poultry manure, deep litter | 55 per 10 tonnes |
| Cow slurry, 10% DM content | 4.5 per m ³ |
| Poultry slurry, fresh undiluted | 1.2 per m ³ |
| Pig slurry, 10% DM content | 4 per m ³ |

Mean concentrations of 0.61% Cl in dry-matter of cattle dung and 2.38 g Cl/litre urine have been reported for seven farms in the USA (Whitehead 2000).

The mean concentration in 16 samples of sewage sludge in the USA was 0.4% Cl in dry-matter with a minimum 0.05% and maximum 1.02% (quoted in Whitehead 2000).

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Cobalt

Cobalt in plants

Cobalt is an essential nutrient for animals but not for higher plants. However, cobalt is required by the *Rhizobia* bacteria involved in nitrogen fixation in legumes. In animals, cobalt is necessary for the formation of vitamin B₁₂ (which contains around 4% cobalt) in the rumen. Animals can utilise cobalt only when it is in the form of vitamin B₁₂ also called cobalamin. This vitamin does not occur in the ruminant diet and livestock are dependent on its formation by micro-organisms in the rumen.

Cobalt is taken up by plants mainly as the ion Co²⁺ though there may be some uptake of intact chelates. Typical removal in crops is around 0.4 – 4.0 g Co/ha.

In the UK, cobalt deficiency occurs in the north and west of Scotland, the Cheviot Hills, Wales, Herefordshire, Worcestershire, Devon and Cornwall. In these areas, deficiency is responsible for ‘pine’ or ‘Moor Cling’ (Dartmoor) in livestock, especially in sheep. Affected animals lose appetite and weight, becoming weak and lethargic (Worden *et al.* 1963).

Cobalt concentration tends to be greater in clover than in grass foliage and practices that reduce clover content in the sward, for example nitrogen application, may reduce overall herbage cobalt concentration (Paterson *et al.* 1989). On the other hand, application of nitrogen has been found to increase substantially cobalt concentration in perennial ryegrass (Klessa *et al.* 1989).

Soil and herbage analyses may not be reliable guides to the cobalt status of grazing animals (Paterson *et al.* 1991). Herbage concentrations vary seasonally and with herbage maturity so a sample taken at one time may not be representative for the grazing season. Concentrations tend to be lower in late spring and summer than in early spring.

Concentrations in clover foliage of > 0.08 mg Co/kg dry-matter indicate that supply for nitrogen fixation by *Rhizobia* is likely to be adequate (Whitehead 2000). For ruminant livestock, a requirement for an average 0.1 mg Co/kg dry-matter in the diet has been proposed (ARC 1965). However, deficiencies in livestock are unlikely where average herbage concentration is > 0.08 mg Co/kg dry-matter (Whitehead 2000).

Fertilizer declarations

Cobalt is treated as a micro-nutrient and is declared in elemental form (Co). The limit of variation on the declared content is 0.4%. Cobalt which occurs naturally in the fertilizer may be declared provided the content is at least 0.002% by weight for fertilizers applied to the soil for crops or grassland or as leaf sprays. The anion for cobalt salts and chelating agent for chelates should be identified. The following instruction should appear with the declaration: ‘To be used only where there is a recognised need. Do not exceed the appropriate application rates’.



Cobalt in the soil

Cobalt in soil derives from the parent material. During weathering, cobalt is precipitated in oxide, hydroxide and carbonate forms which are sparingly soluble in neutral or alkaline conditions. The typical concentration of total cobalt in soils is 8 ppm. Toxicity effects in plants may occur where the concentration exceeds 40 ppm. Soils formed from granite and sandstones or those very high in manganese are most prone to cobalt deficiency (Price 1989, Whitehead 2000). The effect of manganese is due to the adsorption of cobalt by manganese oxides (Evans 1985, Jarvis 1984). Some correlation between soil copper and soil cobalt has been reported (Goovaerts and Webster 1994) suggesting that deficiencies of both may be found.

Availability of soil cobalt is affected by pH and is greater in acidic soils (Barrow and Whelan 1998, Klessa *et al.* 1989). Availability also can be low on peaty soils.

Total soil cobalt is measured by digestion with nitric and perchloric acids followed by dissolution of the residue in hydrochloric acid. Extractable cobalt usually determined by extraction with 0.5M acetic acid (MAFF 1986).

Sources of cobalt

The usual inorganic source is cobalt sulphate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 21% Co). This may be applied to the soil in solid form or in aqueous solution. Chelated cobalt is available in liquid formulations (typically 5% Co w/v) for soil application.

Small amounts of cobalt are present in inorganic fertilizers, 22 mg Co/kg reported for muriate of potash, up to 9 mg Co/kg for ammonium nitrate and up to 77 mg Co/kg for superphosphate (Whitehead 2000).

Deposition from the atmosphere may add 2 – 8 g Co/ha annually (Whitehead 2000).

Crop responses to cobalt

The growth of plants other than legumes does not respond to cobalt application. In the UK, responses in legumes do not appear to be common even in areas where cobalt is deficient for animal health. Application of cobalt increases the cobalt concentration in herbage (Evans 1985, Whitehead 2000).

Typical application rate for in the UK is 2.5 kg cobalt sulphate/ha equivalent to 0.5 kg Co/ha, every four or five years. Larger amounts, up to 5 kg cobalt sulphate/ha every two years have been suggested for some soils (Klessa *et al.* 1989). The application may be in solid form or as a liquid to be sprayed on. Application usually is in early spring or when the herbage has been removed by grazing or cutting so as to maximise contact with the soil. As the objective is to increase overall cobalt intake by livestock, the whole pasture area may not need covering. Application of cobalt sulphate to pasture has been found to be at least as effective as vitamin B₁₂ injections or use of boluses in preventing cobalt deficiency in sheep (Paterson *et al.* 1991).

On calcareous soils, where cobalt sulphate loses availability quickly, the greater cost of chelated cobalt may be justified.



Cobalt in manures and biosolids

Some data for biosolids and manures have been presented by Eriksson (2001):

| Source | No. of samples | Mean | Minimum | Maximum |
|---------------|----------------|------|------------------|---------|
| | | | mg/kg dry-matter | |
| Sewage sludge | 48 | 6.20 | 1.50 | 32 |
| Pig slurry | 4 | 0.65 | 0.47 | 0.90 |
| Pig FYM | 4 | 1.10 | 0.47 | 1.70 |
| Cattle slurry | 4 | 0.85 | 0.63 | 1.10 |

The mean value for 555 samples of sewage sludge in the UK was 10 mg Co/kg dry-matter with a minimum of <2 and maximum of 600 mg Co/kg (quoted in Whitehead 2000).

About half of the cobalt excreted by livestock is in the urine (quoted in Whitehead 2000).

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Copper

Copper in plants

Copper is an essential component of various enzymes involved in photosynthesis, respiration, protein synthesis and regulation of plant hormones. Owing to these diverse roles, deficiency of copper can lead to a variety of problems in plant growth some of which may display no visible symptoms apart from a loss of yield (Jewell *et al.* 1986, Tills and Alloway 1981, 1983).

Copper is taken up by plants as the ion Cu^{2+} . Offtake in arable crops is around 80 g Cu/ha.

In grassland areas, copper deficiency may also occur in livestock. It has been estimated that symptoms of clinical copper deficiency may occur in 0.9% of the UK cattle population (Price 1989). However, symptoms may be detected in only one third of the livestock that suffer from the effects of copper deficiency. In animals as in plants, copper is essential for many metabolic processes including haemoglobin synthesis, pigmentation and hair texture, fertility and reproduction and bone development. There are differences among breeds as well as species of livestock in their efficiency of copper absorption from the rumen so copper content of the diet may not be adequate to define deficiency. A copper concentration in herbage that is adequate for plant growth may be inadequate for livestock unless supplemented.

Visible symptoms in plants generally are associated with severe copper deficiency. There is evidence that moderate deficiency does not result in symptoms other than yield reduction, particularly in cereals. Copper is relatively immobile in plant tissue (more mobile than calcium or boron but less than nitrogen, potassium or phosphorus). Deficiency symptoms therefore tend to appear initially in young tissues. Severely affected cereals show pale green young leaves which may become twisted and whitened. Ears may be malformed with full grains at the base, shrivelled grain in the middle and none at all towards the tip. In sugar beet, young leaves become darker, blue green while older leaves show white tips. Photographs showing deficiency can be seen at www.luminet.net/~wenonah/min-def/list.htm. Symptoms are rarely seen in grass but deficiency in livestock appears as browning of hair and growth retardation in cattle and swayback in sheep. Symptoms in livestock are not necessarily associated with low soil or herbage copper status and are usually dealt with by direct treatment of the animal.

Soil and plant tissue analysis may be used to predict or diagnose copper deficiency in plants. In a review for HGCA, a soil concentration for extractable copper of 1.6 mg/kg was proposed as an indication of probable deficiency (Sinclair and Withers 1995). The soil concentration at which deficiency may be expected is influenced by organic matter content. An index system developed by ADAS showed:

| Extractable copper mg Cu/litre | Soil organic matter % | Index |
|-----------------------------------|--------------------------|-------|
| 0 – 0.8 | >10 | 0 |
| 0.9 – 2.3 | >10 | 1 |



| | | |
|---------|--------|---|
| >2.3 | >10 | 2 |
| 0 – 2.4 | 6 - 10 | 1 |
| >2.4 | 6 - 10 | 2 |
| 0 – 1.0 | 0 - 5 | 1 |
| >1.0 | 0 - 5 | 2 |

Treatment would be advisable at index 0 and desirable, given a history of deficiency, at index 1. A level of less than 4 mg Cu/kg dry-matter in plant tissue indicates possible deficiency for the plant though plant tissue testing may be less reliable than soil testing.

Soil type is an indicator of possible copper deficiency. Calcareous or organic soils, acidic sandy soils and peats are most likely to be deficient. In England and Wales for example, the Icknield chalks of the south and the breckland and peat soils in East Anglia are most prone to deficiency. Where there is doubt, soil analysis should be used to help formulate recommendations.

Dietary concentrations of 5 mg Cu/kg dry-matter and 10 mg Cu/kg dry-matter are considered adequate for sheep and cattle respectively (ARC 1965). These concentrations are significantly greater than that needed for full growth of the herbage.

Fertilizer declarations

Copper is a micronutrient and is declared in elemental form (Cu). The limit of variation on the declared content is 0.4%. Copper which occurs naturally in the fertilizer may be declared provided the content is at least 0.01% for fertilizers applied to the soil for crops or grassland, 0.002% for fertilizers applied to the soil for horticultural crops or 0.002% for leaf sprays. The following instruction should appear with the declaration: ‘To be used only where there is a recognised need. Do not exceed the appropriate application rates’.

Copper in the soil

The total copper content of UK soils is typically around 20 ppm but varies with location from less than 10 to more than 100 ppm (Thornton and Sweb 1975). Concentrations in soils of England and Wales are given in the *Soil Geochemical Atlas of England and Wales* (McGrath and Loveland 1992) and are summarised in Appendix 2 of *The Soil Code* (MAFF 1998). Soil samples were taken on a 5km grid. The values given are for total copper (extracted with strong acid) and not for the extractable amounts often used in soil tests for deficiency. The median total zinc concentration was 18 mg Cu/kg dry soil. Concentration in 10% of samples was less than 9 mg Cu/kg and in 10% was greater than 37 mg Cu/kg.

Several fractions of this total copper have been recognised: (i) soil solution and exchangeable copper, (ii) copper weakly bound to inorganic compounds, (iii) organically bound copper, (iv) copper held in clay lattice structures. The bulk of the available copper reserves appear to be in the organically bound fraction (McLaren and Crawford 1973). In free draining soils, copper is usually fairly evenly distributed through the soil profile. However in Icknield chalks and Breckland soils, total copper can vary from 10 ppm near the surface to less than 3 ppm below 30cm.



Copper deficiency in crops can be due to low total copper in the soil or to low availability of the copper that is present. Low total copper occurs in sandy soils, that may be acidic, low in organic matter and derived from igneous rocks such as granites, pumice or gneiss. Such soils occur in the Breckland of East Anglia and sandstones in Scotland. Low total copper also is found in calcareous soils derived from chalk and limestone. Here deficiencies may be exacerbated by the high pH and free CaCO_3 which favour the formation of insoluble oxides. Low availability of copper usually is associated with organic soils (>10% organic matter) and peats where copper becomes strongly bound. Availability also tends to be lower where soils are relatively dry, for example in warm dry summers (Caldwell 1971).

Sources of copper

Deficiency can be treated by soil or foliar application of copper. Traditionally, copper sulphate (25% Cu) was used for soil application and, depending on the amount applied and soil texture, the correcting effect could last up to ten years. A typical application rate would be 10 – 14 kg Cu/ha.

Foliar applications are usually of copper oxychloride (52% Cu in powder, around 25% Cu in liquid formulation) or of chelated copper (typically around 9% Cu w/v). Application rate is usually around 200 g Cu/ha for copper oxychloride and 70 g Cu/ha for chelated copper.

Relatively small amounts of copper oxysulphate (a mixture of copper oxide and copper sulphate, typically 20% Cu in powder form) and fritted copper are used.

Crop responses to copper

The extent of crop response will depend on the degree of deficiency in relation to crop demand. For copper, as for other micronutrients, there is no meaningful typical or average yield response. In the UK, responses of various sizes have been found in wheat, barley and sugar beet among the arable crops.

Estimates of the extent of copper deficiency have indicated that around 15% of UK sugar beet (Allison *et al.* 1996) and 5% of cereals in England and Wales and 30% of cereals in Scotland (Sinclair and Withers 1995) could be at risk of copper deficiency.

Excessive sulphur concentrations in grass can reduce absorption of copper by livestock through formation of insoluble copper thiomolybdates in the rumen (Dick *et al.* 1975). The problem tends to occur when there is an incipient copper deficiency in livestock and the concentrations of sulphur and molybdenum in the herbage dry-matter are greater than 0.4% S and 3 mg/kg Mo respectively. Normal applications of sulphur should not significantly increase the risk of copper deficiency in livestock unless the grass is already well supplied with sulphur and there is an incipient copper deficiency. The antagonistic effect of soil molybdenum on copper uptake by livestock is well documented. High molybdenum concentrations tend to occur in soils derived from granites and shales. The availability of molybdenum is increased by liming and by the reducing conditions associated with poor drainage. A combination of these



factors can lead to a molybdenum-induced copper deficiency in livestock, as occurs for example on the ‘teart’ soils of Somerset.

Copper concentration tends to be higher in clover than in grass leaves and the depressing effect of nitrogen fertilizer on herbage copper content that is sometimes reported can be due to suppression of clover (Reith *et al.* 1984).

Copper deficiency can affect the quality of wheat grain for bread making. A survey, funded by the HGCA, of 400 samples of grain from the main cereals areas of Great Britain found copper contents in the range 1.49-7.34 µg Cu/g (McGrath *et al.* 1995). Application of copper to six bread-making varieties of wheat showed slight effects on loaf quality. The results of the bread making assessment showed only slight effects of adding Cu on loaf quality. Reasons for this could have been linked to site-to-site variations or other agronomic effects masking the effects of copper but the most likely reason was thought to have been the masking effect of the ascorbic acid, which was added during the bread making process. Ascorbic acid is a powerful oxidising agent that may swamp the effects that copper may have on bread making quality.

Copper deficiency has been found to increase the proportion of non-marketable lettuce and cucumber but to have no effect on tomato ripening in crops grown in peat (Adams *et al.* 1978)

Copper in manures and biosolids

Copper is added to the diet of fattening pigs and the slurry produced can contain up to 2 g Cu/kg dry-matter (Copper Development Association undated).

Some data for biosolids and manures have been presented by Eriksson (2001):

| Source | No. of samples | Mean | Minimum | Maximum |
|------------------|----------------|------|---------|---------|
| mg/kg dry-matter | | | | |
| Sewage sludge | 48 | 390 | 78 | 1800 |
| Pig slurry | 4 | 149 | 136 | 161 |
| Pig FYM | 4 | 113 | 50 | 161 |
| Cattle slurry | 4 | 24 | 23 | 25 |

The average copper concentration in UK sewage sludge applied to agricultural land was 625 mg Cu/kg dry solids in 1982/83 and 473 mg Cu/kg dry solids in 1990/91 (Department of the Environment 1993). The maximum permissible concentration of copper in soil (mg/kg dry solids) following application of sewage sludge is 80 (soil pH 5.0 – <5.5), 100 (soil pH 5.5 - <6.0), 135 (soil pH 6.0 – 7.0) and 200 (soil pH >7.0). The maximum permissible average annual rate of copper addition in sewage sludge over a ten-year period is 7.5 kg Cu/ha (Sludge (Use in Agriculture) Regulations 1989). These limits appear to include significant safety margins (Smith 1994).



Minimum concentrations in plant dry-matter that were associated with toxicity have been reported as 19, 21, 16 and 18 mg Cu/kg for spring barley, ryegrass, oilseed rape and wheat respectively (Davis and Beckett 1978).

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Iron

Iron in plants

Iron is an essential nutrient for both plants and animals. It is necessary for the formation of chlorophyll and so for the green colour of foliage. Iron also is involved in respiration.

Iron is taken up by plants as the ion Fe^{2+} but iron is transported to the root surfaces as organo-mineral complexes. Typical removal in crops is around 200 - 500 g Fe/ha. Iron tends to be immobile within the plant and does not translocate significantly from older to younger tissues. Deficiency symptoms therefore occur in the younger leaves.

Graminaceous plants such as cereals and maize, secrete molecules called phytosiderophores from the roots that form complexes with insoluble Fe^{3+} in the soil, making this iron available for uptake (Klair *et al.* 1996, Romheld and Marschner 1986). Broad-leaved plants do not appear to do this although the gene responsible for the mechanism has been found in *Arabidopsis* (Curie *et al.* 2001). However, broadleaved plants may adapt to low soil iron availability by increasing growth of root hairs and by excreting protons that reduce pH around the root (Brown 1976, Marschner *et al.* 1986).

Worldwide, iron deficiency is common in calcareous and semi-arid soils. It has been estimated that some 40% of world soils are prone to iron deficiency (Chen and Barak 1982, Vose 1982). Within Europe, deficiency is found mainly in the Mediterranean area. In the UK, iron deficiency is found in fruit and nursery plants but very rarely, if at all, in field crops.

Crop species, and varieties within species, vary in their susceptibility to iron deficiency (Chen and Barak 1982). The excretion of phytosiderophores by cereals and maize makes these species resistant to deficiency. In the UK, top fruit and nursery plants are the more susceptible crops.

In iron deficient plants, there is yellowing between the veins of the youngest leaves whilst older leaves remain dark green. In severe cases, youngest leaves become white and then die. Photographs showing iron deficiency can be seen at www.luminet.net/~wenonah/min-def/list.htm.

Soil and plant tissue analysis are not always regarded as reliable indicators of deficiency. However, 50 mg Fe/kg dry-matter has been proposed as a minimum satisfactory leaf concentration for ornamentals (Pasian 2001) and strawberries (<http://strawberry.ifas.ufl.edu/fertilizer.htm>) and concentrations of 300 – 2000 mg Fe/kg dry-matter have been associated with toxicity. Extraction with DTPA is used to indicate potential deficiency in soil available iron. The value below which deficiencies may occur has been given as 4.5 ppm or as 6 ppm for field soils and 5 ppm for glasshouse soils (Chen and Barak 1982).

For ruminant livestock, a requirement for an average 30 mg Fe/kg dry-matter in the diet has been proposed (ARC 1965).



Fertilizer declarations

Iron is a micronutrient and is declared in elemental form (Fe). The limit of variation on the declared content is 0.4%. Iron which occurs naturally in the fertilizer may be declared provided the content is at least 0.5% by weight for fertilizers applied to the soil for crops or grassland, or 0.02% by weight for fertilizers applied to the soil in horticulture or as leaf sprays. The anion for iron salts and chelating agent for chelates should be identified. The following instruction should appear with the declaration: ‘To be used only where there is a recognised need. Do not exceed the appropriate application rates’.

Iron in the soil

Iron is one of the most abundant elements in the earth's crust and concentration of total iron in soils often is around 3%. Where crop deficiencies occur, the problem usually is associated with low availability of iron rather than with the amount of iron present in the soil.

Availability of iron in the soil is affected by pH. Availability is low in soils of high pH (>7.0) and especially when free calcium carbonate is present. Liming can reduce the availability of iron, inducing ‘lime chlorosis’. This is due partly to uptake of bicarbonate (HCO_3^-) which immobilises iron within the plant and prevents its movement to young tissues (Alhendawi *et al.* 1997). In acid soils, waterlogging encourages anaerobic bacteria to reduce iron to the soluble Fe^{2+} form so increasing availability. However, in alkaline soils, waterlogging tends to increase bicarbonate formation and this can reduce availability of iron to young tissues in the plant.

High concentrations of manganese, zinc, copper, calcium, magnesium, phosphate and potassium in the soil or growing medium may interfere with iron uptake (for example, Raja-Harun 1998).

Iron toxicity may occur in waterlogged acid soils or where excessive amounts of soluble iron have been applied. Symptoms are bronzing or necrotic spots on the leaves.

Borehole water can contain significant concentrations of iron which oxidises to insoluble hydroxides when exposed to air. This can result in blockage of irrigation nozzles and spotting of leaves with iron deposits. For crops such as lettuce where spotting affects value, the iron concentration of irrigation water should be less than 1 mg Fe/litre (MAFF 1981). Iron can be removed through precipitation by aeration or by storage of irrigation water.

Sources of iron

The usual inorganic source is ferrous sulphate (usually heptahydrate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 20% Fe, sometimes monohydrate $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, 30% Fe). This may be applied to the soil or as a foliar spray (usually around 10% w/w). Chelated iron is available in liquid formulations (usually 10 – 12% Fe w/v) for soil application or, more usually, for foliar sprays. Some products, especially for turf, contain both inorganic and chelated iron in



liquid formulation. Iron oxysulphate (typically 20 - 40% Fe) can be used in solid form as a slower release soil treatment.

As iron is immobile in the plant, repeated foliar applications usually are needed as new leaves develop. Soil applications may be ineffective where iron deficiency is due to high soil pH.

Injections of liquid ferrous sulfate into tree trunks under pressure have been effective for one to two seasons. In the USA, encapsulated ferric ammonium citrate inserted into pin oak trees around the base of the trunk has been used to prevent iron chlorosis for up to three years (Pasion 2001).

Crop responses to iron

In the UK, iron deficiencies are most likely to be found in fruit and nursery stock. Species particularly susceptible to iron deficiency include ornamentals, shrubs, trees, apple, pear, plum, strawberry and turf. Iron is used to enhance the green colour of turf grass by promoting chlorophyll formation. When used on turf to green-up and to control moss, application rates may be 50 kg Fe/ha.

Typical application rate for chelated iron is 100 g Fe/ha as a foliar spray and up to 3 kg Fe/ha as a soil application. Several foliar applications may be needed. Iron should be applied only where a deficiency has been diagnosed.

Iron in manures and biosolids

The mean iron concentration in 555 samples of sewage sludge in the UK was 1.6% Fe in the dry-matter with a minimum of 1.2% and maximum of 10.7% (quoted in Whitehead 2000). In analyses of 48 sewage sludge samples in Sweden, Eriksson (2001) found an average concentration of 49 mg Fe/kg dry-matter with a maximum 94 mg/kg and minimum 4.4 mg/kg. The concentration is likely to vary with the use of iron salts to precipitate phosphorus during sludge treatment.

Around 95% of the iron excreted by livestock is in the dung. Concentrations in cattle dung of 1600 – 2000 mg Fe/kg dry-matter have been reported (Whitehead 2000). Iron returned to the soil by grazing animals may amount to 5 kg Fe/ha annually.

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Magnesium

Magnesium in plants

The main role of magnesium in plants is as the central atom in the chlorophyll molecule. Photosynthesis therefore is dependent on magnesium. However, only some 15 to 20% of the magnesium in a plant is in the chlorophyll. Another important role of magnesium is in enzyme activators which are essential for processes of protein formation and energy transfer.

Magnesium is taken up by plants as the ion Mg^{2+} .

Magnesium is mobile in the plant and may translocate from older to younger tissues. Deficiency often occurs first or more noticeably in older leaves and can be confused with potash deficiency.

Symptoms of magnesium deficiency in crops tend to occur when the concentration in the dry-matter of green material falls below 0.2% Mg (not MgO – the usual convention is to express nutrient concentrations in plant tissue and in soils in elemental form). Early symptoms of magnesium deficiency include the loss of healthy green colour between veins. This may be followed by yellowing (chlorosis), which starts at the leaf tips and margins and progresses inward until the entire leaf is chlorotic, curling of the leaf margins, death of these areas and premature defoliation. These symptoms can be confused with nitrogen or manganese deficiency. A mottling, dark green/light green, appearance is more typical of magnesium deficiency (I'm told this effect was known in the past as 'spotted dick' by some at Rothamsted). Some plants, for example strawberries, can develop orange or reddish colouring of leaves. In cereals, deficiency causes the distinctive green/pale green mottling of the leaves. Many crops develop transient magnesium deficiency symptoms in early spring but these are not always followed by any effect on yield. Photographs showing deficiency can be seen at www.luminet.net/~wenonah/min-def/list.htm.



Typical offtakes for magnesium are:

| | kg MgO/tonne fresh material |
|-------------------|-----------------------------|
| Cereal grain | 2.00 |
| Wheat straw | 1.35 |
| Barley straw | 1.15 |
| Oilseed rape seed | 3.50 |
| Potato tubers | 0.35 |
| Sugar beet roots | 0.50 |
| Sugar beet tops | 1.15 |
| Peas grain | 3.00 |
| Beans grain | 2.35 |
| Cabbage | 0.35 |
| Kale | 0.50 |
| Forage rape | 0.50 |
| Forage maize | 1.15 |
| Silage grass | 0.50 |
| Strawberries | 0.22 |
| Blackcurrants | 0.30 |
| Raspberries | 0.35 |
| Apples (desert) | 0.08 |
| Plums | 0.12 |
| Pears | 0.07 |
| Cherries | 0.15 |

Offtake can vary with magnesium supply and growing conditions so these values should be used as general guides only. However, it appears a 9t/ha wheat crop can remove 25 to 30kg MgO/ha in grain and straw. Bearing in mind that not all the available soil nutrient is removed in a crop, this probably is equivalent to a required supply from all sources in the soil of around 50kg MgO/ha.

Offtake values underestimate nutrient requirement by a crop as large proportions of crops (roots, stubble, straw, haulm which contain the nutrient) are left in the field.

Fertilizer declarations

In the UK, magnesium content of fertilizers is declared as % oxide (MgO) followed by % elemental (Mg) in parentheses. To convert oxide to elemental, multiply by 0.6. The minimum content required for declaration is 2% MgO (1.2% Mg).

Magnesium in the soil

The total magnesium concentration in soil is usually between 0.05 and 0.5% Mg but only a small proportion (typically around 5%) is in forms available for plant uptake. Most is found as relatively insoluble carbonates. The available fraction comprises magnesium in soil solution and that held on exchange sites of clays and organic matter (exchangeable magnesium). Unlike potassium, magnesium does not appear to move from non-exchangeable to exchangeable forms easily.



It has been reported in the USA that where exchangeable magnesium comprises a high proportion of the total cation exchange capacity (CEC) of the soil, workability can be reduced. However, there appears to be no evidence for this effect in European soils. High soil exchangeable magnesium concentrations may be associated with low available K and so a risk of K deficiency. There is some evidence that even where soil exchangeable potassium is not low, potassium deficiency can occur especially in dry summers if soil exchangeable magnesium is very high (index 5+).

In general, high soil exchangeable magnesium concentrations do not adversely affect crop growth. Where soil magnesium is felt to be excessively high, the first step should be to determine if this is due to magnesium applications, for example in magnesian limestone. If applications are responsible, there may be opportunities for their reduction or elimination. Crop offtake will then tend to reduce soil magnesium over time. If this is not possible, application of gypsum can induce leaching of magnesium (Oates and Caldwell 1985, Sumner 1993).

Available soil magnesium is measured in the UK by extraction with ammonium nitrate (essentially this is a measure of exchangeable magnesium). Indices bands are:

| Index | mgMg/l |
|-------|-------------|
| 0 | 0 – 25 |
| 1 | 26 – 50 |
| 2 | 51 – 100 |
| 3 | 101 – 175 |
| 4 | 176 – 250 |
| 5 | 251 – 350 |
| 6 | 351 – 600 |
| 7 | 601 – 1000 |
| 8 | 1001 – 1500 |
| 9 | >1500 |

Sources of magnesium

The main fertilizer sources are the various forms of magnesium sulphate, magnesium carbonate and magnesium oxide. Magnesium nitrate (typically 15.7% MgO, 10.8% N in solid form) is used for some higher value crops and magnesium ammonium phosphate ('struvite', typically 29% MgO, 10% N, 51% P₂O₅) and magnesium oxysulphate (typically 55% MgO) are sometimes used in both agriculture and horticulture. Some liquid formulation chelated magnesium products (for example containing 5% MgO w/v) have been produced for foliar application.

Epsom salts/Bittersalz (16% MgO, 33% SO₃) and kieserite (27% MgO, 36% SO₃) contain magnesium in the sulphate form. Magnesium sulphate is soluble in water and Epsom salts and Bittersalz are usually applied as foliar sprays. Kieserite, available in both powder and granular forms, is soil applied.

Kainit, a naturally occurring mixed salt, contains typically 5% MgO as magnesium sulphate.



Magnesium oxide is available as calcined magnesite (typically 80% MgO) for soil application. The magnesium is less water-soluble than is that in kieserite and this can affect availability. The temperature of calcination can affect availability of the magnesium in calcined magnesite to crops. (Draycott and Allison 1998). Whilst soil pH has little effect on availability of magnesium in kieserite, it can affect availability in calcined magnesite. Lower effectiveness of calcined magnesite at pH 7.6+ has been reported (Draycott and Durrant 1972, Draycott, Durrant and Bennett 1975). Fine grinding of calcined magnesite tends to improve availability (Heming and Hollis 1995). Magnesian or dolomitic limestone contains around 20% MgO and application as a liming agent will tend to raise soil magnesium levels. Prolonged use of magnesian limestone is a principal cause of the very high soil exchangeable magnesium levels found in some areas, often associated with low exchangeable potash.

Crop responses to magnesium

As all crops require magnesium, all are potentially responsive to application where the soil otherwise is deficient. However, in the UK, the crops most likely to show yield responses to applied magnesium are sugar beet and potatoes. Both crops tend to be grown on lighter soils where exchangeable magnesium concentrations are most likely to be low unless magnesian limestone has been used.

Deficiency symptoms that can lead to yield loss usually appear in sugar beet from July onwards. Deficiency can be confirmed by leaf tissue analysis, values of 0.10 – 0.15% Mg in dry-matter in August to October indicating deficient plants and 0.25 – 0.60% Mg indicating healthy plants (Draycott and Allison 1998). At soil magnesium index 0, an average yield response of 0.33 t sugar/ha to 100 kg Mg/ha as kieserite has been reported (Draycott and Allison 1998). In some crops, 2 t sugar/ha response was found at index 0. Magnesium is most commonly applied to sugar beet as a component of blended fertilizers that are ploughed down in autumn or late winter. The thorough mixing of fertilizer with the soil aids uptake. Some is applied after ploughing or in suspension fertilizers. The usual recommendation is 150 kg MgO/ha at soil magnesium index 0 and 75 kg MgO/ha at index 1 (MAFF 2000).

In potatoes, magnesium deficiency appears as yellowing of interveinal areas on the leaf and, in severe cases, stunting and premature senescence. At flowering, a concentration in the whole leaf of <0.15% Mg in dry-matter indicates deficiency and concentrations of >0.26% Mg indicate healthy plants (Draycott and Allison 1998). Varietal differences in susceptibility to magnesium deficiency have been reported. Determinate varieties, such as Estima, that produce relatively few leaves, may be most susceptible to magnesium deficiency. The application of potassium can reduce magnesium concentrations in plant tissues and may induce magnesium deficiency where soil exchangeable magnesium concentration is low.

Foliar applications of magnesium, usually as Epsom salts or Bittersalz, are more common in potatoes than in sugar beet. These applications can be conveniently tank mixed with blight sprays. However, kieserite and blended fertilizers containing magnesium also are used. For soil applications, the usual recommendations are 150 kg MgO/ha at soil index 0 and 75 kg MgO/ha at index 1 (MAFF 2000).

Where sugar beet or potatoes feature in the rotation, the magnesium applied for these crops often will be adequate for the whole rotation. Where sugar beet or potatoes are not



grown and soil magnesium index is 0, forage maize and fodder root crops will benefit from 50 – 100 kg MgO/ha every four years. The usual recommendation for most vegetables and bulbs is 150 kg MgO/ha at index 0 and 100 kg MgO/ha at index 1 (MAFF 2000).

Low soil exchangeable magnesium should be corrected before establishment of fruit crops. For fruit, applications of 165, 125 and 85 kg MgO/ha would be recommended at soil indices 0, 1 and 2 respectively (MAFF 2000). Subsequent applications may be needed to keep the soil exchangeable K/exchangeable Mg ratio lower than 3/1. If deficiency symptoms occur, a spray of Epsom salts or Bittersalz will be most rapidly effective. In most fruit crops, a leaf concentration of less than 0.20% Mg in dry-matter may indicate magnesium deficiency.

Herbage magnesium and animal diets

Magnesium is essential for animals and is found in all tissues. Around 70% of the magnesium in an animal body is in the skeleton, compared with 75 – 80% for phosphorus and 99% for calcium. Liveweight contains around 360 – 385 mg Mg/kg (Agricultural Research Council 1965). Milk contains typically 125 mg Mg/kg and lactating cattle are particularly prone to magnesium deficiency in the diet. A 500kg cow yielding 20 kg milk/day requires 22 g Mg/day in the diet. It has long been recognised that acute hypomagnesaemia ('grass tetany' or 'staggers') in livestock is related to a deficiency of magnesium in the diet (Wolton 1963). The dietary concentration below which acute hypomagnesaemia may occur has been given as 0.2%Mg (Wolton 1963) or 0.25% Mg (Whitaker 1983) in the dry-matter. As the concentration in grass frequently is lower than these values (Hemingway and Parkins 2001), that in other dietary components must be higher. However, if these concentrations can be achieved in grass (whether grazed or ensiled), there may be little or no need for magnesium supplementation. Supplementation may be needed, even if herbage magnesium concentration appears adequate, if dry-matter intake is restricted – for example when livestock graze wet, lush grass. Calcined magnesite and suspensions of finely divided magnesium hydroxide have been used to increase magnesium intake by adhering to herbage (rather than being taken up through the roots) (Hemingway and Parkins 2001). In addition to acute hypomagnesaemia, a chronic form may occur where the disease results in reduced production rather than death. Stress and other dietary components as well as low magnesium concentration are implicated in chronic hypomagnesaemia (Whitaker 1983).



Magnesium in manures and biosolids

Manures and biosolids can provide significant amounts of magnesium. Typical concentrations are:

| | | |
|----------------|-----------------------------|---------------------------|
| Solid manures: | Cattle FYM | 0.7 kg MgO/t |
| | Pig FYM | 0.7 kg MgO/t |
| | Layer manure | 2.2 kg MgO/t |
| | Broiler/turkey litter | 4.2 kg MgO/t |
| Slurries: | Cattle slurry (6% DM) | 0.7 kg MgO/m ³ |
| | Pig slurry (4% DM) | 0.4 kg MgO/m ³ |
| Biosolids: | Digested liquid (4% DM) | 0.2 kg MgO/m ³ |
| | Digested dewatered (25% DM) | 0.8 kg MgO/t |

These are typical values and are subject to considerable variation depending on manure/biosolids treatment and storage methods. Chemical analysis before application may give a more accurate value for a particular manure. There appear to be no published data on the availability of the magnesium in manures and biosolids. The best estimate probably is 50% availability to the crop following application. The remaining magnesium would become available in later years.

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Manganese

Manganese in plants

Manganese deficiency is the most widespread micronutrient problem in the UK. Some 15 – 20% of the cropping area is treated with manganese annually.

The main role of manganese in plants is as a component of enzymes involved in photosynthesis and other processes. The major symptom of deficiency is a reduction in the efficiency of photosynthesis leading to a general decline in dry matter productivity and yield. Manganese also is involved in the reduction of nitrate within the plant.

Manganese is taken up by plant roots as the divalent ion Mn^{2+} . The amount of manganese needed is small and offtake usually is less than 1 kg Mn/ha in cereals and around 2 kg Mn/ha in sugar beet. However, the concentration of manganese in plant tissues can vary widely. Ranges of 6 – 1765 mg Mn/kg dry-matter for cereal straw, 5 – 75 mg/kg for grain and 10 – 2000 mg/kg for hay and pasture plants have been reported (Stahlberg and Sombatpanit 1974a). Once taken up, manganese is not mobile within the plant (Henkens and Jongman 1965).

Sugar beet, oats, barley, dwarf beans and peas are more susceptible than most other crop species to manganese deficiency. Differences in susceptibility can be found between varieties as well as between crop species (Nyborg 1970). Deficiency symptoms differ somewhat between species:

| | |
|-------------------|---|
| Cereals generally | Symptoms not often seen before 3-leaf stage. Field patches show as areas of pale, floppy growth. Symptoms usually seen on the middle third of the leaf, top remaining green even if the leaf breaks in the middle and hangs down. Effects on development may also occur leading to reduced tillering, smaller anthers and infertile pollen grain. |
| Wheat | Rows of interveinal white streaks. |
| Barley | More susceptible than wheat. Rows of interveinal brown spots in spring barley. Symptoms in winter barley more similar to those in wheat. |
| Oats | Interveinal yellowing with grey/buff streaks ('grey speck') which turn necrotic in severe cases. |
| Sugar beet | May show symptoms at 2-leaf stage. Interveinal yellow mottle on older leaves with leaf margins curled inwards to give a triangular erect leaf ('speckled yellows'). |
| Potatoes | Initial paleness in younger leaves followed by blackish/brown spots along the veins in some varieties (best seen on underside of leaf). |
| Oilseed rape | Interveinal yellowing in older leaves, particularly near margins. Easily confused with magnesium deficiency though this usually shows some reddening. |



| | |
|-------------|--|
| Peas | Interveinal yellowing of older leaves. Dried peas show brown discolouration of the centre of the pea, visible when split ('marsh spot'). |
| Red beet | Loss of green colour results in dull red leaves. Leaf margins curl inwards. Field patches have dull red colour. |
| Carrots | Light green patches in the field, easily confused with other nutrient deficiencies. |
| Dwarf beans | Strong interveinal yellow mottle in older leaves. Veins remain green. |
| Onions | Pale green leaves. Older leaves show yellow mottling in severe cases. |
| Celery | Interveinal yellowing especially near margins. |
| Fruit | Interveinal yellowing beginning near the margins and extending towards the midrib. Bands of green left along the veins. |

Photographs showing deficiency can be seen at www.luminet.net/~wenonah/min-def/list.htm.

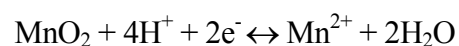
Plant tissue analysis is often used as a diagnostic test for manganese deficiency. Usually, 20 mg Mn/kg dry-matter is considered borderline for deficiency. However, sugar beet can be deficient where leaf concentration is 30 mg Mn/kg (Farley and Draycott 1973).

Fertilizer declarations

Manganese is a micronutrient and is declared in elemental form (Mn). The limit of variation on the declared content is 0.4%. Manganese which occurs naturally in the fertilizer may be declared provided the content is at least 0.1% for fertilizers applied to the soil for crops or grassland, 0.01% for fertilizers applied to the soil for horticultural crops or 0.01% for leaf sprays. The following instruction should appear with the declaration: 'To be used only where there is a recognised need. Do not exceed the appropriate application rates'.

Manganese in the soil

Soils usually contain far more manganese than is needed by crops but most is in unavailable forms. Manganese moves from unavailable to an available form and vice versa at rates controlled largely by soil acidity and reduction-oxidation potential. The equilibrium reaction can be summarised by the following redox equation:



(unavailable Mn ↔ available Mn)

As the H⁺ ion concentration increases (that is as pH falls), the equilibrium is driven to the right and the concentration of available manganese increases. A reduction in H⁺



concentration (that is an increase in pH) drives the equilibrium to the left and results in a reduction in available manganese.

Agricultural practices that affect soil pH will therefore also affect the availability of manganese. Liming will reduce availability and can cause manganese deficiency. Application of lime-stabilised sewage sludge has been reported to induce manganese deficiency in wheat (Brown *et al.* 1997). Some NPK fertilizers can generate soil acidity close to the granule after application. Combine drilling NPK products or placement close to the seed has been found to increase the amount of manganese available to seedlings (Erjala 1986, Goldberg *et al.* 1983, Holmes *et al.* 1983).

The growing plant can affect soil conditions immediately around the root so as to increase the availability of manganese. The roots exude organic compounds that can increase acidity and act as chelating agents. As a result, the concentration of available manganese close to the root can vary through the season, usually being highest in mid-summer (Linehan *et al.* 1989, Sinclair *et al.* 1990, Stahlberg and Sombatpanit 1974a). This and increasing soil temperatures have been proposed as reasons why deficiency symptoms can appear in early growth, but can disappear (without treatment) later in the season. There also is evidence that formation of available Mn^{2+} increases as soil dries (Stahlberg and Sombatpanit 1974a) which could cause seasonal changes in availability of manganese.

Manganese can become adsorbed to the cation exchange complex of organic matter resulting in a decrease in available Mn^{2+} (Stahlberg and Sombatpanit 1974b). Manganese deficiency often is associated with soils high in organic matter (Chalmers 1995). Addition of chloride to some soils (which will occur where muriate of potash is applied) has been reported to increase manganese availability (Fixen 1993). Heavy applications of superphosphate have been found to increase manganese availability in neutral or alkaline soils, probably due to formation of soluble manganese-phosphate complexes (Larsen 1964). Soil application of elemental sulphur has been found to improve uptake of manganese from applied manganese sulphate, probably due to a pH effect (Soliman 1987). However, this beneficial effect of sulphur may not be found in all soils (Reuter *et al.* 1973).

Good contact between root and soil is important for manganese uptake and poor consolidation can result in crop deficiency (Goldberg *et al.* 1983, Holmes *et al.* 1983). This can sometimes be seen as stripes of green crop along and beside wheelings within a generally pale and deficient crop. Rolling has been found to limit manganese deficiency on puffy organic soils.

Soil analysis (usually measuring exchangeable divalent manganese or easily reducible manganese) as an advisory aid for plant available manganese is used in North America (Nielsen *et al.* 1990, Warden and Reisenauer 1991) and elsewhere (Stahlberg and Sombatpanit 1974a) but is generally regarded as unreliable in the UK.

Sources of manganese

There are three main sources of manganese in manufactured fertilizers: manganese sulphate, manganous oxide and chelated manganese. Manganese sulphate and chelated manganese usually are foliar applied and manganous oxide is always soil applied.



Manganese sulphate (MnSO_4 , around 24% Mn in solid form but concentration varies with degree of hydration) can be purchased for making up into solution but can be difficult to dissolve. It is usually supplied as a ready made flowable suspension with stickers and wetters in a tank mix formulation (typically around 15% Mn). A typical application would be 1.5 – 3.0 kg Mn/ha.

Chelates are usually based on EDTA but sometimes lignosulphate or phenolics as the chelating agent (typically 6 – 7% Mn in liquid form as supplied for subsequent dilution). They are more compatible with other chemicals and will not cause scorch but are more expensive per unit than manganese sulphate.

Manganous oxide (MnO , usually around 60% Mn but can be as low as 40%) is used for soil application in various parts of the world. It is less soluble than manganese sulphate and reportedly less susceptible to loss of availability after application. Manganous oxide is sometimes supplied in mixture with manganese sulphate as manganese oxysulphate (typically 27 – 40% Mn depending on the ratio of oxide to sulphate forms) for soil application.

Crop responses to manganese

Crop deficiencies of manganese tend to occur most on alkaline soils, particularly those with high organic matter content. Low soil clay content has been associated with deficiency. Much of the trial work in the UK has been done on sugar beet. In ten field trials, Draycott and Farley (1973) found yield responses to foliar-applied manganese sulphate of around 5% where 21 to 60% of plants showed deficiency symptoms and of around 17% where more than 60% of plants showed symptoms. Where 20% or less of plants showed symptoms, there was little response to manganese application. In these trials, there was no response to soil applied manganous oxide. However, in earlier trials, also reported by Draycott and Farley (1973), soil applications of 14 or 42 kg Mn/ha as manganese sulphate increased sugar beet yields.

Increases of up to 50% in yield of deficient barley crops have been achieved by treatment with manganese (Macaulay Institute 1982).

Foliar application of manganese sulphate has reduced the incidence of marsh spot in peas without any increase in yield (Knott 1996).

There are situations where spray applications may not be effective or efficient. For example, sugar beet seedlings can be deficient but their leaf area is small and only a small fraction of the spray is intercepted. Spraying may be done after symptoms appear which can be too late for small seedlings.

As there is little transfer of manganese between leaves, spraying may have to be done repeatedly (this applies generally to all deficient crops). There is incentive therefore for development of effective soil or seed treatments. Manganese treatment of seed is an effective way of controlling early deficiency (Macaulay Institute 1982).

Manganese in manures and biosolids

Limited data are available but some have been presented by Eriksson (2001):



| Source | No. of samples | Mean | Minimum | Maximum |
|------------------|----------------|------|---------|---------|
| mg/kg dry-matter | | | | |
| Sewage sludge | 48 | 280 | 46 | 1100 |
| Pig slurry | 4 | 313 | 259 | 406 |
| Pig FYM | 4 | 250 | 139 | 362 |
| Cattle slurry | 4 | 234 | 152 | 413 |

If a concentration of 250 mg Mn/kg dry-matter is assumed, an application of 40m³ of cattle slurry at 6% dry-matter would add 0.6 kg Mn/ha to the soil. Assuming the same concentration for cattle or pig FYM at 25% dry-matter, an application of 30 t/ha would supply 1.9 kg Mn/ha. Manures therefore are significant potential sources of manganese but not all the manganese may be in an available form.

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Molybdenum

Molybdenum in plants

Molybdenum has been known as an essential nutrient for plants only since 1939 (Arnon and Stout 1939). Soon after, yield responses to molybdenum were found in subterranean clover in Australia (Anderson 1942). Deficiency was then identified as the cause of ‘whiptail’ in cauliflower where the leaf lamina is restricted. Molybdenum is known to be involved in the enzymes nitrogenase and nitrate reductase and is essential for protein formation. For a comprehensive review of the roles of molybdenum, see Mitchell (2002).

Plants take up molybdenum as the molybdate ion MoO_4^{2-} . Typical concentration in green tissue dry-matter is 0.03 – 5.0 mg Mo/kg and removal in crops is around 4 – 5 g Mo/ha.

A photograph of molybdenum deficiency in cauliflower, can be seen at www.luminet.net/~wenonah/min-def/cauliflr.htm

Molybdenum deficiency can occur in pot plants. Symptoms are similar to those of nitrogen or iron deficiency and ammonium toxicity. Plants tend to be stunted, leaves are small and chlorotic, and leaf margins may become scorched. Leaves tend to curl upward.

Soil or plant tissue analyses may be used to diagnose molybdenum deficiency. For soil analysis, extraction usually is with acid ammonium oxalate (‘Tamms reagent’). Leaf and curd concentrations are around 2.0 mg Mo/kg in normal plants and around 0.35 mg Mo/kg in deficient plants. Typical concentrations (mg Mo/kg dry-matter) in healthy plants are 0.20 – 0.65 in wheat grain, 0.7 – 8.4 in peas, 0.20 – 0.80 in forage maize and 0.10 – 0.20 in sugar beet tops (Shorrocks 1991). The uppermost mature leaves of woody ornamentals normally contain 0.1 – 1.0 mg Mo/kg dry-matter.

Molybdenum toxicity in crops is extremely rare and occurs at much higher concentrations than those that cause livestock health problems in forages. Concentrations in dry-matter at which yield reduction begins to occur have been given as 600 – 1000 ppm in wheat, 100 – 200 ppm in sugar beet 150 – 300 ppm in potatoes and 70 – 120 ppm in lettuce (Kluge 1983).

Fertilizer declarations

Molybdenum is a micronutrient and is declared in elemental form (Mo). The limit of variation on the declared content is 0.4% for sodium or ammonium molybdate, molybdenum-based fertilizers or molybdenum fertilizer in solution. Boron which occurs naturally in the fertilizer may be declared provided the content is at least 0.001% by weight for fertilizers applied to the soil or as leaf sprays. The following instruction should appear with the declaration: ‘To be used only where there is a recognised need. Do not exceed the appropriate application rates’.



Molybdenum in the soil

Molybdenum occurs in silicates in feldspars and micas or as the sulphide molybdenite MoS_2 . Other minerals containing molybdenum in association with calcium (powellite, CaMoO_4), iron (ferromolybdite, $\text{Fe}(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$) and lead (wulfenite, PbMoO_4) are hardly soluble (Shivashankar and Hagstrom 1991). High molybdenum concentrations tend to occur in soils derived from granites and shales

Typical total molybdenum concentration in soil is 1 – 2ppm and is greatest in clays. Sandy soils have low total molybdenum concentrations. The availability of molybdenum (unlike that of other micronutrients) tends to increase with soil pH. Under acidic conditions, molybdenum combines with iron oxides into insoluble forms (Smith *et al.* 1997). Anaerobic conditions, for example where drainage is poor, also can increase molybdenum availability.

Molybdenum also occurs in organic forms so the total concentration and the availability are affected by soil parent material, texture, pH and mineralisation of organic matter (Gupta 1997).

Sources of molybdenum

In the UK, ammonium molybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 54% Mo) and sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 39% Mo) are the usual sources (Mortvedt 1997). Both are made up into solution for application as a soil or foliar spray or in hydroponics. Elsewhere, molybdenum trioxide MoO_3 , 66% Mo), molybdenum sulphide (MoS_2 , 60% Mo), ammonium phosphomolybdate ($(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$, 61% Mo) and molybdic acid (H_2MoO_4 , typically 57% Mo) are sometimes used. Sodium molybdate can be used as a seed treatment.

Crop responses to molybdenum

Crop species differ in susceptibility to molybdenum deficiency. Cauliflower, broccoli, lettuce, peas, clovers and spinach are more susceptible than most other crops (Shorrocks 1991). In the UK, deficiency is reported most often in cauliflower growing on soils with a pH less than 6.0. Typical foliar application rates for cauliflower are 10 g Mo/ha at the two-leaf stage followed by 15 g Mo/ha before flowering. Soil application usually is in the range 0.25 – 1.00 kg Mo/ha as sodium molybdate. However, deficiencies are unlikely if the soil is limed uniformly to pH 6.5.

Omission of molybdenum from peat beds used for growing cucumbers depressed yield by 50 – 84% (Adams 1985). Raising pH from 5.1 to 6.7 without addition of molybdenum doubled yield.

High molybdenum concentration in herbage (>3mg Mo/kg dry-matter), especially if associated with high sulphur (>0.4%S in dry-matter), can reduce the uptake of copper by livestock and lead to copper deficiency. This is well documented for the 'teart' pastures of Somerset, parts of Gloucestershire, the Edale shales of Derbyshire and the Thames marshes where molybdenum concentration in herbage can exceed 15 mg Mo/kg dry-matter. At these very high herbage molybdenum concentrations, it may not be clear if livestock are suffering from molybdenum-induced copper deficiency or



copper-alleviated molybdenum toxicity. Soils derived from black marine shales are at particular risk.

Molybdenum in manures and biosolids

FYM typically contains 1 – 2 ppm in fresh material (Shivashankar and Hagstrom 1991). An application of 35 t/ha would therefore supply 35 – 70 g Mo/ha.

Some data for biosolids and manures have been presented by Eriksson (2001):

| Source | No. of samples | Mean | Minimum | Maximum |
|---------------|----------------|------|-------------------------|---------|
| | | | mg/kg dry-matter | |
| Sewage sludge | 48 | 6.7 | 2.4 | 20.0 |
| Pig slurry | 4 | 4.9 | 4.0 | 5.4 |
| Pig FYM | 4 | 6.8 | 2.5 | 17.0 |
| Cattle slurry | 4 | 4.5 | 2.4 | 8.2 |

Molybdenum is not covered by EC Directive 86/278/EEC on use of sewage sludge in agriculture and so is not included in the *Sludge (Use in Agriculture) Regulations 1989*. However, the *Code of Practice for the Agricultural Use of Sewage Sludge* introduced by the DoE in 1989 set an accepted safe concentration in soil of 4 mg Mo/kg after sludge application. This value relates to extraction with strong acid. The maximum acceptable average rate of application in sludge over a ten-year period was set at 0.2 kg Mo/ha. In some parts of the UK, soil molybdenum concentration naturally exceeds 4 mg/kg. In these areas, sewage sludge may still be applied) provided other requirements are met) but expert advice will be needed. This advice would take account of potential effects on copper nutrition of livestock (MAFF 1998).

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Selenium

Selenium in plants

Selenium is an essential nutrient for animals, necessary for the formation of glutathione peroxidase, an anti-oxidant, but is not widely recognised as a plant nutrient. However, there is evidence that selenium is either essential or beneficial for the American vetch *Astragalus* (Broyer et al. 1972) and may be beneficial in other species (Hartikainen and Ekholm 2001). Beneficial effects of selenium also have been reported for ryegrass and lettuce (Hartikainen and Ekholm 2001). For many years after the discovery of selenium in 1817 (in a Swedish sulphuric acid plant), interest concentrated on its toxic effects. Only later were the essential biochemical roles of selenium identified. Today, deficiency is recognised as a serious problem in many regions, notably the cool temperate parts of New Zealand, USA, China and northern Europe (Gissel-Nielsen *et al.* 1984).

A study in England and Wales (Anderson *et al.* 1979) found 40% of sheep flocks fell into 'low/marginal' or 'deficient' categories. Analyses of cereal grain and herbage samples found 60% of grain samples and 39% of herbage samples contained < 0.03 mg Se/kg (Heys and Hill 1984). Survey data collected at the Rowett research Institute indicated an average of 0.027 mg Se/kg (range 0.003 to 0.233 mg Se/kg) for herbage in the north of Scotland (Price 1989).

Daily human requirement is around 0.04 mg Se for an adult. Survey data indicated typical daily intakes of 0.043 and 0.029 – 0.039 mg Se in 1994 and 1995 respectively (MAFF 1997). Part of the reason for an apparent fall in selenium intake since 1985 has been the substitution of North American wheat (relatively high in selenium) by UK wheat for bread making.

Plants take up selenium as the selenate (SeO_4^{2-}) or selenite (SeO_3^{2-}) ions. Selenate is the form more easily taken up and the chemical similarity of this ion and the sulphate ion (SO_4^{2-}) suggests that the active uptake mechanisms are similar, accounting for antagonism between sulphur and selenium uptake. Although selenium does not appear to be an essential nutrient for most plants, it is incorporated into amino acids and proteins after uptake. In these forms, the selenium is available to livestock and humans. Some plant species can accumulate large amounts of selenium in the form of amino acids. It appears that these amino acids are not incorporated in protein and that this prevents toxicity to the plant. Excess selenium may be lost by volatilisation from the plant as dimethylselenide.

Selenium concentration in herbage tends to be lower in summer than in spring.

The extractants used to assess soil available selenium (hot water, calcium chloride, calcium nitrate, potassium sulphate or ammonium bicarbonate-DTPA) may be more useful in identifying potentially toxic concentrations than deficiencies (Gissel-Nielsen *et al.* 1984).

A dietary concentration of < 0.1 mg Se/kg dry-matter could be deficient for livestock and one of > 2 mg Se/kg could be toxic. Most cases of acute deficiency have been



associated with dietary concentrations < 0.03 mg Se/kg dry-matter (Price 1989). Symptoms of deficiency in livestock include ‘white muscle disease’, a form of muscular dystrophy in which animals eventually collapse. Lambs and calves are especially prone to deficiency. There can be damage to the immuno-suppression system, increased susceptibility to infections and loss of weight. Non-acute symptoms may be difficult to diagnose.

Fertilizer declarations

Selenium is not covered by EU directives or by *The Fertilisers Regulations*.

Selenium in the soil

Selenium occurs in igneous rocks mainly as selenides which on weathering are oxidised to selenite and, to a lesser extent, selenate. Selenite is then retained in the soil by adsorption onto organic matter or iron oxides. Selenate is less firmly retained and is more available for both plant uptake and loss by leaching. Selenium occurs in both organic and inorganic forms in the soil. Temperate soils typically contain 0.01 – 2.0 mg total Se/kg dry soil and usually 0.2 – 0.3 mg Se/kg (Whitehead 2000). The concentration tends to be greater in clay than in sandy, chalk or limestone soils (Thornton *et al.* 1983). In some soil, for example those derived from black marine shales, concentrations can be as high as 30 mg Se/kg.

Several soil conditions affect the availability of selenium. The availability of selenium often increases with soil pH (van Dorst and Peterson 1983). At pH > 6.5, selenite becomes oxidised to selenate which is less strongly held by clays and organic matter and so is more available for plant uptake. Liming therefore tends to increase selenium availability. Selenium uptake by plants tends to decrease with increasing soil sulphate concentration. Depressing effects of sulphur application on selenium uptake by herbage have been reported (Whitehead 2000).

Atmospheric deposition is a significant natural source of soil chlorine (Halstead *et al.* 1991). Close to coasts, annual deposition can be 100 kg Cl/ha whilst 200 km inland, this can drop to 20 kg Cl/ha (Fixen 1993).

Some selenium can be lost from soils to the atmosphere as dimethylselenide, produced by plants and micro-organisms. As the residence time in the atmosphere could be several days, the selenium could travel far from the point of volatilisation (Whitehead 2000).

Sources of selenium

The main sources of applied selenium are sodium selenate (Na_2SeO_4 , %Se) and sodium selenite (Na_2SeO_3 , 45% Se). These salts may be incorporated in fertilizers or sprayed onto a carrier. In New Zealand, superphosphate and pumice (graded to 1mm) have been used as carriers.

Small amounts of selenium occur naturally in phosphate fertilizers. Concentrations of 4 – 8 mg Se/kg have been reported for superphosphate (Whitehead 2000). Deposition from the atmosphere may amount to 2 – 7 g Se/ha annually in the UK (Haygarth *et al.* 1995).



Some waste materials, notably fly ash, contain significant amounts of selenium.

Crop responses to selenium

As selenium is not an essential plant nutrient, crop growth does not show a response to applied selenium. However, application can beneficially increase the selenium concentration in the crop and so in livestock or human diets. Selenium can be applied incorporated in solid fertilizers or in an aqueous spray to the soil or to foliage. Selenium appears to be taken up through leaves when applied as a foliar spray (Gissel-Nielsen 1984).

Applied selenate usually is more effective than selenite in increasing the selenium concentration in crops and herbage (Archer 1983, Sima and Gissel-Nielsen 1985, Gissel-Nielsen *et al.* 1984, Shand *et al.* 1992)

Application of 4 g Se/ha as sodium selenite incorporated in CAN five times or a single spray of 10 g Se/ha as sodium selenite in spring have been reported to increase herbage selenium concentration from around 0.04 mg Se/kg to 0.06 – 0.10 mg Se/kg (Gissel-Nielsen 1984). Application of 5 g Se/ha as selenate or selenite increased the selenium concentration in barley grain from deficient to adequate (Gissel-Nielsen 1984, Sima and Gissel-Nielsen 1985).

In Finland in 1985, as a measure to improve the selenium content of human and livestock diets, all NPK fertilizers were supplemented with selenium as selenate. Between 1985 and 1990, the inclusion rates were 16 and 6 mg Se/kg fertilizer for cereal crops and grassland respectively. After 1990, the inclusion rate was 6 mg Se/kg for all crops (Ekholm 1997, Hartikainen and Ekholm 2001). This operation effectively increased the selenium concentrations in all Finnish foods, and as a result the average daily intake increased to an adequate level. The fertilisation practice was found to be safe, because the plants acted as effective buffers against too high selenium concentrations.

Selenium in manures and biosolids

Selenium excreted by livestock seems to be largely unavailable for plant uptake. Most is excreted in the dung where it is mainly in insoluble elemental or selenide forms. A concentration of 0.2 mg Se/kg dry-matter in cattle slurry has been reported (Whitehead 2000).

Some data for biosolids and manures have been presented by Eriksson (2001):

| Source | No. of samples | Mean | Minimum | Maximum |
|------------------|----------------|------|---------|---------|
| mg/kg dry-matter | | | | |
| Sewage sludge | 48 | 1.3 | 0.50 | 2.8 |
| Pig slurry | 4 | 1.4 | 1.4 | 1.5 |
| Pig FYM | 4 | 0.89 | 0.19 | 1.30 |
| Cattle slurry | 4 | 0.56 | 0.40 | 0.77 |



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Sodium

Sodium in plants

Sodium is not generally regarded as an essential nutrient for all higher plants. However, sodium can substitute for potassium to a greater or lesser extent in different plant species (Wybenga 1957). Some crops will show a yield response to sodium even in the presence of adequate amounts of potassium. For some species, including sugar beet, red beet, fodder beet, mangolds and spinach, sodium is essential and cannot be substituted completely by potassium (Chiy and Phillips 1995). The amounts of sodium removed by crops are highly variable but are usually around 95 kg Na₂O/ha in sugar beet (of which about 75 kg Na₂O/ha is in the tops, the remainder in the roots). Other crops remove somewhat less sodium.

Sodium is essential for animals and herbivores depend on the content in plants to supply their needs. There is, therefore, a role for sodium in herbage species additional to that of plant nutrient.

Much of the agronomic research on sodium requirements of arable and horticultural crops was done before 1980. More recently, research on the role of sodium in grassland systems has been done at Bangor and Cambridge (refs Wybenga 1957, Chiy and Phillips 1993 - 2000, Phillips and Chiy 1994). Members of the HDC can obtain a review of sodium use in horticulture 'Review of the value of salt as a fertilizer and herbicide for vegetables' by George Wadsworth (code FV51). For copies, tel HDC at 01732 848383 or visit the HDC web site www.hdc.org.uk.

Role of sodium in plants

Like potassium, sodium is involved in the osmotic regulatory function in plants and occurs mainly as the Na⁺ ion in plant tissue. Uptake from the soil is almost entirely in the form of the cation and mass flow is the main route for sodium into the roots.

Fertilizer declarations

The Fertilisers Regulations 1991 specify that the sodium content of fertilizers should be expressed in oxide form (Na₂O) followed by the elemental content in parentheses. General usage within the industry is the oxide form. The conversion factor for elemental to oxide form is x 1.348 and for oxide to elemental is x 0.742.

Despite this usage, soil and plant tissue analyses are expressed usually in elemental form (as is the case with potassium and phosphorus). Care needs to be taken when interpreting soil analysis results.

Sodium in the soil

Most of the sodium in soils is held in the exchangeable form on clay particles or is in solution. The amounts are less than those of potassium. Typical exchangeable levels are (Archer 1985):



Typical exchangeable Na levels (mg Na/l)

| | |
|-------------|----|
| Sand | 15 |
| Light loam | 18 |
| Medium loam | 24 |
| Silt | 30 |
| Clay | 30 |
| Organic | 50 |

A survey of 800 soils in the UK (Draycott and Bugg 1982) confirmed these differences among soil types and the higher levels of exchangeable sodium in organic soils. Two thirds of the sandy and silty soils contained less than 20 mg Na/l while half the organic soil contained more than 40 mg Na/l.

Sodium is highly susceptible to leaching and available soil sodium can be lost over winter. Deeper-rooted crops such as sugar beet will be able to access sodium that has moved below the plough layer. It is not possible to build up reserves of sodium in the soil by repeated applications over years.

High levels of exchangeable sodium can disperse clay particles resulting in a loss of soil structure. This is often seen where arable land has been flooded by seawater. Such effects are not significant where sodium is applied to land at rates generally associated with salt or fertilizer use.

Sources of sodium

The main source of sodium is rainfall which, over a year, can introduce 12-27 kg Na₂O/ha in inland areas and 70-135 kg Na₂O/ha near coasts. Most of the exchangeable and dissolved sodium in soil derives from recent rainfall.

Irrigation water can be a significant source of sodium, typical contents being 50-1000 mg Na/l. At a seasonal application rate of 200 mm, irrigation could provide 135-2700 kg Na₂O/ha. Relative to these sources, mineralisation of soil organic matter is a minor source of sodium.

Animal manures contain some available sodium:

| | <u>kg Na₂O</u> |
|-------------------------------------|---------------------------|
| Farmyard manure, stored under cover | 8 per 10 tonnes |
| Poultry manure, deep litter | 50 per 10 tonnes |
| Cow slurry, 10% DM content | 4 per m ³ |
| Poultry slurry, fresh undiluted | 1 per m ³ |
| Pig slurry, 10% DM content | 4 per m ³ |



The main sodium-containing fertilizer materials are salt (sodium chloride, 50% Na₂O), kainit (mixture of potassium and sodium salts, 10-27% Na₂O) and sylvinit (26% Na₂O). Small amounts of sodium nitrate (35% Na₂O) are used mainly in horticulture.

Salt and kainit may be applied as straights, alternatively, salt can be incorporated in blended fertilizers. Blends for sugar beet, usually applied in autumn, generally do not contain nitrogen and their particle size distribution can be very wide. Such products are intended for application by contractor.

Crop responses to sodium

Some crops can show yield responses to applied sodium even where soil potassium levels appear adequate. Other crops can respond where potassium is yield limiting (Truog *et al.* 1953, Cope *et al.* 1953, Larson and Pierre 1953, Costigan and Mead 1987).

Responsive where K is adequate

Sugar beet
Beetroot (red beet)
Fodder beet
Mangolds
Turnips
Celery Kale
Carrots

Responsive where K is deficient

Barley
Wheat
Oats
Peas
Cabbage

Field research on sodium as a nutrient in Europe has concentrated on sugar beet where yield responses are common. For instance, a series of 36 trials over 5 years (1975-79) in the UK compared sodium applications of 0, 50, 100, 200, 400 kg Na₂O/ha, either in autumn or in spring on contrasting soil types (Draycott and Bugg 1982). On the mineral soils, 200 kg Na₂O/ha increased sugar yield by an average 0.2 t/ha. There were no responses on organic soils. Most of the responses occurred where exchangeable sodium level was less than 20 mg Na/l and a few occurred in the range 20-40 mg Na/l.

Responses to applied sodium have been assessed in many other crop species, much of this work being done in the period 1910-1960. In most crops tested, sodium could substitute for potassium to some extent. Deficiencies of potassium were partially alleviated by application of sodium.

Produce quality

Application of sodium has been reported to improve taste in carrots and turnips and to reduce stringiness in celery and turnips (HDC 1990).

Herbage sodium and animal diets

Deficiencies of sodium in grazing livestock have been reported in many countries. In Europe, such deficiencies are often associated with spring grass (Kemp and Gevriink 1978, Morris 1980). Sodium deficiency has also been proposed as a contributing



cause of hypomagnesaemia in ruminants (Maretens *et al.* 1987). Deficiencies are most likely to occur in milking cows and some form of supplementation (eg. salt licks) is often needed. The appendix shows dietary sodium requirements for cattle and sheep.

Dry matter intake (DMI) by grazing cattle can be estimated from live weight (LW in kg) by:

$$\text{DMI (kg/day)} = 0.0234 \text{ LW} + 0.32 \quad (\text{Baker 1964})$$

A 500 kg cow is, therefore, likely to consume around 12 kg grass DM/day. To satisfy a sodium requirement of 27 g Na/day at a milk yield of 30 kg/day, the grass would need a minimum sodium content of 0.23% Na in DM. This is likely to be somewhat greater than the mean content of herbage in practice

A considerable amount of recent research on the effects of applied sodium on herbage and livestock performance has been carried out at the Universities of Bangor and Cambridge. The work at both centres has been directed by Dr C J C Phillips (Chiy and Phillips 1993 – 2000). One comparison, (Phillips and Chiy 1994) shows the effects of applied sodium. It should be emphasised that the effects of applied sodium will depend on the levels of soil exchangeable sodium and potassium:



Table 1 Effect of Applying 43 kg Na₂O/ha/year to grassland reported by Phillips and Chiy (1994)

| | <u>No sodium applied</u> | <u>Sodium applied</u> |
|---|--------------------------|-----------------------|
| Herbage composition (g/kg DM) | | |
| Na | 3.5 | 4.2 |
| K | 16.2 | 14.5 |
| Mg | 1.8 | 2.0 |
| Ca | 4.5 | 4.9 |
| DM digestibility | 71.6 | 71.9 |
| Water-soluble carbohydrates | 190 | 319 |
| Rumen characteristics | | |
| Fluid turnover/hr | 0.065 | 0.078 |
| DM degradation in rumen (g/kg consumed) | 677 | 731 |
| pH | 6.6 | 7.3 |
| Cow production | | |
| Milk yield (kg/d) | 18.1 | 20.0 |
| Fat content (g/kg) | 37.3 | 38.8 |
| Protein content (g/kg) | 33.6 | 33.3 |
| Lactose content (g/kg) | 43.7 | 45.6 |
| Weight gain (kg/d) | 0.02 | 0.21 |

This comparison shows benefits in several measured characteristics resulting from sodium applications. It has also been claimed that sodium application can reduce the somatic cell count in milk.

Increases in herbage intake by grazing cattle have been reported (Chiy and Phillips 1993 – 2000, Phillips and Chiy 1994) which may be due to improved palatability and more rapid digestion in the rumen.

Deficiency diagnosis and prediction

There are no visible plant symptoms specific to sodium deficiency. Soil analysis has proved useful for predicting requirement for responsive crops, particularly where soil type is taken into account.

A general recommendation for sugar beet is (MAFF 2000):



Silt and fen peat: - apply no sodium.

| Other soils: | <u>Exchangeable soil Na</u> (mg/l) | <u>Sodium Application</u> (kg Na ₂ O/ha) |
|--------------|---------------------------------------|--|
| | < 20 | 200 |
| | 20 - 40 | 100 |
| | >40 | 0 |

The minimum sodium content in herbage relates to animal dietary requirement but a level of 0.2% Na in DM seems reasonable as a threshold below which animals could be deficient. Much depends on the extent and effectiveness of access by the animals to other sources of sodium such as supplements and salt licks.

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Appendix Dietary Requirements for Sodium of Cattle and Sheep
(g Na/day)

a) Cattle

| Liveweight (kg) | 0.33 | Liveweight gain (kg/day) | 0.5 | 1.0 |
|-----------------|------|--------------------------|-----|-----|
| 50 | 1.4 | 1.6 | 2.3 | |
| 200 | 3.9 | 4.1 | 4.8 | |
| 400 | 7.3 | 7.5 | 8.2 | |

b) Sheep

| Liveweight (kg) | 0.1 | Liveweight gain (kg/day) | 0.2 | 0.4 |
|-----------------|------|--------------------------|------|-----|
| 10 | 0.31 | 0.45 | 0.73 | |
| 30 | 0.65 | 0.79 | 1.07 | |
| 50 | 0.99 | 1.13 | 1.41 | |



c) Milking cows

| <u>Milk yield (kg/day)</u> | <u>Sodium requirement (gNa/day)</u> |
|--------------------------------|---|
| 5 | 12 |
| 10 | 15 |
| 20 | 21 |
| 30 | 27 |



Zinc

Zinc in plants

Zinc is an essential nutrient for both plants and animals. It is a component of enzymes involved in several biochemical processes including photosynthesis, sugar formation and protein synthesis. Deficiency of zinc affects fertility and seed production, growth regulation and defense against disease.

Zinc is taken up by plants as the ion Zn^{2+} . Typical removal in crops is around 200 g Zn/ha.

Zinc deficiency is a serious problem in many parts of the world, mainly in areas of calcareous and semi-arid soils. Australia, the USA, India and parts of Africa and South America are particularly affected. Within Europe, zinc deficiency is found mainly in the Mediterranean area. However, deficiencies have been recorded in the UK.

Crop species vary in their susceptibility to zinc deficiency. The susceptibility of rice adds to the importance of zinc deficiency worldwide. In the UK, top fruit and maize are the more susceptible crops. Cherries and apples are more susceptible than plums and pears. Zinc deficiency has been reported in cereals and potatoes in the Romney Marsh. Deficiency in wheat and barley growing on shale-derived soil has been reported in Ireland (Macneidhe *et al.* 1986).

Symptoms of zinc deficiency are distinctive. In apples, buds along shoots fail to develop, leaves are small and narrow and tend to form rosettes at tips of shoots ('little leaf'). A photograph of zinc deficiency can be seen at www.luminet.net/~wemonah/min-def/apple.htm. In maize, there may be light streaking of the leaf followed by a broad whitish band, starting slightly in from the leaf edge and extending to the midrib (copper deficiency also can cause striping but without the broader chlorotic areas). The leaf edges, midrib and tip remain green. Plants are stunted with short internodes. A photograph of deficiency in maize is at www.iza.com/zwo_org/Publications/ZincProtects/ZP1108/110803.htm.

Soil and plant tissue analyses may be used to diagnose zinc deficiency. Soil analysis usually is by EDTA extraction when values less than 0.5 mg Zn/kg indicate probable deficiency in susceptible crops, less than 1.50 mg Zn/kg indicate possible deficiency in susceptible crops. In plant tissues, concentrations less than 16 mg Zn/kg dry-matter indicate probable deficiency and less than 20 mg Zn/kg dry-matter indicate possible deficiency (Alloway 2002)

For livestock, a requirement for an average 50 mg Zn/kg dry-matter in the diet has been proposed (ARC 1965).

Fertilizer declarations

Zinc is a micronutrient and is declared in elemental form (Zn). The limit of variation on the declared content is 0.4%. Zinc which occurs naturally in the fertilizer may be



declared provided the content is at least 0.01% by weight for fertilizers applied to the soil for crops or grassland, or 0.002% by weight for fertilizers applied to the soil in horticulture or as leaf sprays. The following instruction should appear with the declaration: ‘To be used only where there is a recognised need. Do not exceed the appropriate application rates’.

Zinc in the soil

Total soil zinc content usually ranges from 10 to 300 ppm depending on the parent soil material. Soils originating from basic igneous rocks have a high zinc content whereas siliceous parent materials have a low Zn content.

Concentrations in soils of England and Wales are given in the *Soil Geochemical Atlas of England and Wales* (McGrath and Loveland 1992) and are summarised in Appendix 2 of *The Soil Code* (MAFF 1998). Soil samples were taken on a 5km grid. The values given are for total zinc (extracted with strong acid) and not for the extractable amounts often used in soil tests for deficiency. The median total zinc concentration was 82 mg Zn/kg dry soil. Concentration in 10% of samples was less than 38 mg Zn/kg and in 10% was greater than 147 mg/kg.

The availability of zinc in the soil is affected by pH. Availability is low in soils of high pH (>7.0) and especially when free calcium carbonate is present. Liming can reduce the availability of zinc. High soil phosphate can be associated with reduced availability of zinc through the formation of insoluble zinc phosphate complexes (Agbenin 1998). The concentration of soil phosphate must be high for this effect to be significant but could occur where fertilizer phosphate is placed next to the seed.

Zinc toxicity is a potential problem though not common. Toxicity was found in re-seeded grass flooded by the river Trent in the 1970s due to industrial discharges. Such a problem is unlikely to be encountered today.

Sources of zinc

The usual inorganic source is zinc sulphate (monohydrate $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ 35% Zn or septahydrate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ 22% Zn). This may be applied to the soil or as a foliar spray (usually around 10% w/w). Zinc oxide (ZnO 67 – 80% Zn) and zinc chloride (ZnCl_2 45% Zn) are sometimes used. Zinc frits and zinc oxysulphate can be used as slower release soil treatments. Chelated zinc is available in liquid formulations for foliar sprays. Zinc occurs in phosphate rock and some is carried through into processed fertilizers. Concentration in fertilizer is related to phosphate content (and to source of rock) but in a 1:1:1 grade is typically 150 – 250 mg/kg product. An application of 400 kg fertilizer would, in this case, supply 60 – 100 g Zn.

Crop responses to zinc

Deficiency, and so potential yield responses, are rare in field crops in the UK, even in susceptible species like maize. Deficiencies are more likely to be found in top fruit, especially in apples but remain uncommon.

Typical application rate is 300 – 500 g Zn/ha. For apples, several applications may be needed. Zinc should be applied only where a deficiency has been diagnosed. Application



during bloom or after petal fall has been found to increase the incidence of bitter pit in Bramley (Hipps *et al.* 2000)

Zinc in manures and biosolids

The average zinc concentration in sewage sludge applied to agricultural land was 1205 mg Zn/kg dry solids in 1982/83 and 889 mg Zn/kg dry solids in 1990/91 (Department of the Environment 1993). The *Sludge (Use in Agriculture) Regulations 1989* set a limit of 15 kg Zn/ha/year over a ten-year period where sewage sludge is applied. The *Regulations* also state that, following sludge application, soil zinc (extracted with strong acid) should not exceed 200 ppm (soil pH 5.0 < 5.5), 250 ppm (soil pH 5.5 < 6.0), 300 ppm (soil pH 6.0 – 7.0) or 450 ppm (soil pH >7.0).

Some data for biosolids and manures have been presented by Eriksson (2001):

| Source | No. of samples | Mean | Minimum | Maximum |
|------------------|----------------|------|---------|---------|
| mg/kg dry-matter | | | | |
| Sewage sludge | 48 | 550 | 230 | 2300 |
| Pig slurry | 4 | 582 | 394 | 680 |
| Pig FYM | 4 | 680 | 347 | 821 |
| Cattle slurry | 4 | 154 | 128 | 170 |

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