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A review of the non-NPKS nutrient requirements of UK cereals and oilseed rape

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1. Abstract

This review investigates the importance of non-NPKS nutrients within cereal and oilseed rape production systems. The review considers crop requirements, sources of nutrients, occurrence and diagnosis of deficiencies, strategies for avoiding/rectifying deficiencies, and knowledge gaps.

Crop requirements. The function of each nutrient for the plant is summarised and, where possible, data on crop uptake and offtake amounts quantified. Up to date information for maximum crop uptake and crop offtake could not be found for all nutrients (e.g. Molybdenum) and further work is required to rectify these knowledge gaps.

Sources of nutrients. The concentration range of each nutrient in agricultural soils is summarised. Factors and soil processes which affect the availability of nutrients for plant uptake are described. Sources of each nutrient are summarised, and where possible quantified, including from additions such as manures, organic residues and atmospheric deposition. Information about the nutrients that could be supplied in manures could not be found for all nutrients (e.g. boron and manganese). Without additions of manures, organic residues or fertiliser sources, crop offtake may exceed inputs for copper, zinc and magnesium, and possibly manganese.

Incidence of deficiency. More than 400 crop response experiments were analysed. These included information in published literature and unpublished data for soils and climates which were either UK or relevant to UK conditions. All experiments had replicated treatments and were statistically analysed. Statistically significant yield responses were found for five out of 48 boron experiments on oilseed rape (three out of 19 in the UK), none out of 33 boron experiments on cereals (13 of which were in the UK), 93 out of 197 copper experiments on cereals (61 out of 114 in the UK), 33 out of 111 manganese experiments on cereals (28 out of 80 in the UK), two out of 14 magnesium experiments (two out of 13 in the UK), four out of eight molybdenum experiments on oilseed rape in the UK, and 11 out of 72 cereal experiments on zinc (six out of 36 in the UK). A survey of agronomists indicated that the most prevalent deficiencies were, for cereals: magnesium, manganese, copper and zinc; and for oilseed rape: magnesium, boron, manganese and molybdenum.

Diagnostic methods. Details and guidance for soil and tissue tests from different laboratories and organisations were compared. This indicated reasonable, but not complete, agreement between the analytical methods used and guidance on thresholds. Confidence in soil testing for non-NPKS nutrients could be improved by standardisation of testing methods. Research is also required to clarify the effects of factors such as soil type and pH on nutrient availability and the thresholds.

Treatment strategies. The most effective treatments for correcting deficiencies are summarised.

Economic evaluation. The yield response required to cover the cost of non-NPKS fertilisers was generally less than 0.1 t/ha which is less than the smallest statistically significant difference that can be detected using conventional experimental designs (0.3 to 0.5 t/ha). It is therefore important that experimental methods are developed that will allow smaller differences in crop response to be reliably detected.

2. Introduction

There is uncertainty within the UK arable industry regarding the importance of, and crop requirement for, non-NPKS nutrient fertilisers. The RB209 Fertiliser Manual 8th edition (Defra, 2010) includes updated advice about target soil magnesium indices, but limited guidance for other minor nutrients such as boron, copper, manganese, molybdenum, zinc. The most recent government-sponsored advice was published in the 1980s (MAFF, 1983) and HGCA advice is only available for cereals (HGCA, 2001). The main areas of uncertainty include the diagnosis of nutrient deficiency, the thresholds for soil and tissue tests, the most appropriate remedial treatments and the likely crop response to treatment. Correct fertilisation of non-NPKS nutrients may be becoming more important, e.g. Lombnæs & Singh (2003) predicted that the incidence of minor nutrient deficiencies in cropping systems may have increased as a result of fertility depletion through intensive cultivation of high-yielding varieties, decreased recycling of plant residues, the use of micronutrient-free fertilisers and limited use of animal manures.

Conventional advice has been to apply non-NPKS products only when visual symptoms in crops are apparent or when leaf and/or soil analysis indicates a risk of deficiency. On this basis, prevalence of non-NPKS deficiencies in the UK is generally low. It has been suggested that crops which show no deficiency symptoms may still respond to micronutrient applications due to a 'hidden hunger' in the crop (e.g. Allen-Stevens, 2011). This claim is related to Liebig's 'law of the minimum,' the idea that crop yields can only be improved by increasing the supply of whichever factor is limiting, such that 'the availability of the most abundant nutrient in the soil is only as good as the availability of the least abundant nutrient in the soil.' A further argument for the greater use of minor nutrient fertilisers is that soils with expected deficiencies of, for example, manganese, copper or zinc (e.g. sandy or organic) tend to be low yielding, yet crops with greatest demands for micronutrients must be those with high potential yields, so conventional experiments have not always targeted appropriate soil types.

A further source of uncertainty about when non-NPKS fertiliser applications are justified results from the limited statistical strength of conventional field experiments. The 'least significant differences (LSD)' from conventional plot experiments are typically 0.3 to 0.5 t/ha, but most non-NPKS fertiliser applications can be paid for by a yield response of less than 0.1 t/ha. Consequently, experiments may fail to detect economic yield responses to treatments.

This project will review the importance of non-NPKS fertilisers within present day cereal and oilseed rape production systems. The review will consider crop requirements, taking account of increased yields, other sources of these elements and recent data on soil fertility. Occurrence and diagnosis of nutrient deficiencies and strategies for avoiding/rectifying deficiencies will be

considered, with the aim of identifying knowledge gaps requiring further research and updating recommendations to growers and consultants. This review will build on the review on non-NPK nutrient use in cereal crops that was carried out by Chalmers *et al*. in 1999 (HGCA RR41). To our knowledge there has been no review of non-NPKS nutrients for oilseed rape. This review also offers the opportunity to better understand the properties and functions of phosphite which is often marketed in conjunction with non-NPKS nutrients.

Specific objectives include:

1. Crop requirement: Quantify the cereal and oilseed rape crop requirement for non-NPKS nutrients and the amounts removed from the field in grain and straw.
2. Soil supply: Review factors which affect crop deficiency and the supply of non-NPKS nutrients from the soil.
3. Incidence of deficiency: Review evidence for effects of non-NPKS nutrients on the yield and quality of cereals and oilseed rape.
4. Diagnosis methods: Review of visual symptoms, soil and tissue tests. Recommendations to optimise diagnostic methods.
5. Treatment strategies to prevent or rectify deficiencies.
6. Economic evaluation: Analysis of approaches for avoiding/rectifying deficiencies.
7. Recommendations for further research.

3. Crop requirements

An understanding of micronutrient offtake by crops is a useful starting point when examining the requirement of crops for micronutrient applications. Nutrients removed in a harvested crop do not necessarily need to be replaced by fertiliser applications, as they may be supplied from other sources such as atmospheric deposition or be in very large supply in the soil; but if soil supplies are low and are not replenished from other sources, offtake values provide a guide to potential crop requirements. Typical offtake values of non-NPKS nutrients are shown in Table 1 for cereals and oilseed rape. It is notable that maximum crop uptake and crop offtake information could not be found for all nutrients and further work is required to rectify these knowledge gaps.

Table 1. Micronutrients offtake. Data from Van Paemel *et al*., (2010), Chalmers *et al*., (1999), Shorrocks (1997) and MAFF (1980).

Source	Boron (g/t)	Calcium (g/t)	Copper (g/t)	Iron (g/t)	Magnesium (g/t)	Manganese (g/t)	Molybdenum (g/t)	Zinc (g/t)
Barley (grain)	-	500	9	158	1300	16	0.44	30
Oats (grain)	-	900	3	106	-	40	0.83	23
Oilseed rape (seed)	20	-	3	216	5600	34	-	40
Wheat (grain)	-	300	6	59	1200	42	0.46	21
Wheat (straw)	-	2000	3	171	800	42	1.2	19

- denotes no information

3.1. Boron

3.1.1. Boron function in plants

Boron (B) is an essential micronutrient for plants, involved in controlling metabolic processes via the regulation of cell membranes. Additionally, boron is an important structural component of cell walls, where it controls porosity (Fleischer *et al*., 1999) and tensile strength (Ryden *et al*., 2003). Boron has secondary roles in sugar translocation, protein synthesis and auxin metabolism. Boron deficiency leads to abnormal cell division, which affects growing points causing tissues to become distorted and eventually die (Gupta, 1979; Shorrocks, 1991). Symptoms of B deficiency include dieback of the apical growing point on the main stem, followed by subsequent growth and dieback of side shoots (Bould *et al*., 1983). Other symptoms may include brittle leaves, stunting and poor seed set.

3.1.2. Boron uptake and offtake

Boron is taken up by the plant passively as boric acid ($H_2BO_3^-$). Cereals do not have a high requirement for B; deficiencies have not been detected in wheat, barley or oats in the UK (Shorrocks, 1997). Leaves are the main site for B accumulation in wheat and boron uptake decreases after anthesis (Subedi *et al*., 1999). Boron is thought to be immobile in cereals.

Oilseed rape has a much higher requirement for B than cereals, and B deficiencies occur worldwide. A 4 t/ha oilseed rape crop requires approximately 320 g/ha B for growth and removes approximately 80 g/ha B (Shorrocks, 1997) (Table 1). In oilseed rape, B has limited mobility.

3.2. Calcium

3.2.1. Calcium function in plants

Calcium (Ca) has a major role in the formation, structure and stability of cell membranes as well as being an important signalling molecule (Hepler, 2005). Through its function as a signalling

molecule, Ca is involved in nutrient uptake, the heat stress response and disease mitigation. Calcium deficiency can lead to the deterioration of cell membranes and consequently cell and tissue death.

3.2.2. Calcium uptake and offtake

Calcium is taken up by the plant as the ion Ca^{2+}. Although Ca is an essential micronutrient, Ca deficiency is rarely observed in cereals since in most cases the Ca concentration in the soil is sufficient for the demand of the crop. The Ca demand for growth is higher in dicotyledons than monocotyledons, but again Ca deficiency symptoms are rarely observed in oilseed rape crops (Orlovius, 2003).

3.3. Chlorine

3.3.1. Chlorine function in plants

Chlorine (Cl) is an essential plant nutrient with functions in both photosynthetic and protective activities within the plant (Bould *et al*., 1983). Chlorine also has a role in the movement of water and other solutes into and out of cells. Additionally Cl has important roles in the regulation of the opening and closing of stomata and cell division.

3.3.2. Chlorine uptake and offtake

Chlorine is taken up by the plant as Cl^-. Chlorine deficiency is not often seen in crops grown in field conditions, however leaf spotting, which is a symptom of Cl deficiency has been described in winter wheat grown in Montana, USA (Engel *et al*., 1997, 2001).

3.4. Copper

3.4.1. Copper function in plants

Although the fungicidal properties of copper (Cu) were known as early as 1761, it was not until 1931 that Cu was identified as an essential nutrient for plant growth. Copper is required for a range of different functions in plants, including production of viable pollen for grain production (Graham, 1975) and maintenance of the cell wall structure (Graham, 1976; Brussler 1981). Additionally, Cu is an essential component of many proteins which are required for oxidation and reduction reactions within metabolic pathways such as photosynthesis, respiration and the regulation of plant hormones (Bould *et al*., 1983). Copper is also involved in processes related to the reduction of nitrate nitrogen (NO_3-N) to ammonium nitrogen (NH_4-N) in plants, hence plants which are deficient in Cu can have large accumulations of carbohydrate, NO_3-N and polyphenols in vegetative tissue (MAFF, 1976). Due to the numerous functions of Cu within a plant, deficiency can lead to a variety

of plant growth problems, although not all of these display visual symptoms (Jewell *et al*., 1985; Tills and Alloway, 1981, 1983).

3.4.2. Copper uptake and offtake

Copper is taken up by crops as the ion Cu^{2+}. Copper deficiency was first identified in the UK on wheat on a deep fen peat soil in Norfolk and, thereafter, on a restricted range of soils in many countries around the world (Caldwell, 1976). The relative susceptibility of cereal crops to Cu deficiency is in the order: barley > oats > wheat (McAndrew *et al*., 1984). It has been suggested that the reproductive phase of the plant lifecycle may have a higher requirement for Cu than vegetative growth (Bell & Dell, 2008). Winter cereals are less susceptible than spring cereals to drought-induced copper deficiencies as their root structure is better developed, allowing them to exploit micronutrients which sit lower in the soil.

Oilseed rape is more tolerant of low levels of Cu supply than cereals and so deficiencies are rarely observed (McAndrew *et al*., 1984; Orlovius, 2003). The offtake of Cu in seed by oilseed rape is approximately a third of that of barley and a half of that of wheat (Table 1) and this could partly explain why oilseed rape is more tolerant of Cu deficiency.

3.5. Iron

3.5.1. Iron function in plants

The importance of iron (Fe) as a plant nutrient has been described in a recent review by Conte & Walker (2011). Iron acts as an essential cofactor for a range of cellular redox reactions involved in photosynthesis and respiration. Chloroplasts require Fe for metabolic reactions including photosynthetic electron transport and chlorophyll biosynthesis. In mitochondria, Fe is required for the synthesis of iron–sulphur clusters and for proper function of the respiratory electron transport chain. Iron deficiency can lead to chlorosis of younger leaves, which may in part be due to reduced chlorophyll synthesis.

3.5.2. Iron uptake and offtake

Iron is taken up by crops in the form of Fe^{3+}. Although there is no doubt that Fe is an essential micronutrient, there is currently little information with regard to the iron requirement of oilseed rape plants. Iron deficiency in cereals has not been recorded in the UK (Chalmers *et al*., 1999). Iron offtake in cereal grains ranges from 59 to 158 g/t and for oilseed rape offtake is approximately 216 g/t (Table 1).

3.6. Magnesium

3.6.1. Magnesium function in plants

Magnesium (Mg) is not considered a micronutrient, being found in soils in large concentrations and at g/kg levels within plants. The principal role for Mg in plants is as an essential component of chlorophyll. However, only approximately 15 to 20% of the plant Mg content is present in chlorophyll with the remainder in either the ionic state or bound in complexes with organic constituents. Additionally, Mg has a role in a range of enzyme-regulated physiological processes including phosphorylation, assimilation of carbon dioxide and protein synthesis.

3.6.2. Magnesium uptake and offtake

Magnesium is taken up by the plant as the ion Mg^{2+}. Ripe cereal grain contains about 0.12% Mg, while straw Mg content can be as low as 0.05% (Chalmers *et al*., 1999). In cereals, typically 1.2 kg/t and 0.8 kg/t are removed in the grain and straw respectively (fresh material) (Chalmers *et al*., 1999; Table 1). In the majority of soil types, soil Mg reserves are gradually depleted unless Mg is applied at some stage in the crop rotation. Higher yielding, modern oilseed rape varieties are thought to have an increasing requirement for Mg (Billericay Fertiliser Services, date unknown), although there is a lack of empirical evidence for this trend. Oilseed rape seed removes approximately 5.6 kg/t Mg. Although deficiency symptoms may be apparent in cereal crops, particularly in the spring in response to cold, dry conditions, the effect on plant growth and yield is minimal (Chalmers *et al*., 1999).

3.7. Manganese

3.7.1. Manganese function in plants

The main role for manganese (Mn) in plants is as a constituent and activator of enzymes involved in protein synthesis, lipid metabolism and photosynthesis. Manganese regulates the activity of nitrate reductase, so Mn deficiency leads to an accumulation of NO_3-N in plant tissue. Given the role of Mn in regulating photosynthetic enzymes, Mn deficiency leads to a reduction in photosynthetic efficiency which causes a progressive decline in dry matter productivity and yield.

3.7.2. Manganese uptake and offtake

Manganese is taken up by the plant roots as the divalent ion Mn^{2+}. Manganese deficiency is widely acknowledged to be the most widespread micronutrient problem in arable crops in the UK. Mn deficiency occurs most commonly in cereals, with approximately 15 to 20% of crop area being treated with Mn annually (Sinclair & Edwards, 2008). The relative susceptibility of cereal crops to Mn deficiency is in the order: oats > wheat > barley (Chalmers *et al*., 1999). The requirement for Mn throughout the plant lifecycle is largely continuous as little Mn remobilisation occurs within the

plant. Winter cereals are less susceptible than spring cereals to drought-induced Mn deficiencies as their root structure is better developed, allowing them to better exploit micronutrients from within the soil profile. Maximum uptake of Mn in a winter wheat crop yielding 8 t/ha is approximately 400 to 500 g/ha, with 150 to 200 g/ha Mn removed in the grain at harvest (Chalmers *et al*., 1999).

Oilseed rape is less sensitive to Mn deficiency than cereals. The level of Mn required by oilseed rape during the reproductive phase of the lifecycle is considerably higher than during the vegetative phase (Merrien, 1992). Oilseed rape Mn offtake as seeds is approximately 34 g/t (Table 1).

3.8. Molybdenum

3.8.1. Molybdenum function in plants

Arnon & Stout (1939) first demonstrated that molybdenum (Mo) was required for plant growth using hydroponically grown tomatoes. Molybdenum is required for the function of enzymes involved in redox processes (Mendel & Haensch 2002; Sauer & Frebort, 2003). For example, Mo is an essential component of primary nitrogen assimilation and nitrogen reduction enzymes, responsible for the utilisation of NO_3-N within the plant. Molybdenum-containing enzymes are also involved in purine catabolism, ABA and IAA metabolism and sulphur metabolism (Kaiser *et al*., 2005).

3.8.2. Molybdenum uptake and offtake

Molybdenum is taken up by crops as the molybdate ion MoO_4^{2-}. In the UK, cases of Mo deficiency in cereal crops have not been identified. Mo deficiency has been reported in wheat in New Zealand (Chalmers *et al*., 1999).The demand for Mo by oilseed rape is classed as medium (Bergmann, 1992). Information on the offtake of Mo is shown in Table 1 for cereals; offtake data for oilseed rape was not available.

3.9. Zinc

3.9.1. Zinc function in plants

The essential plant requirement for zinc (Zn) was first demonstrated in maize (Mazé, 1915) and then in barley and dwarf sunflower (Sommer & Lipman, 1926). Zn is a component of enzymes involved in photosynthesis, sugar formation and protein synthesis. Proteins which are stabilised by an ionic form of Zn, known as Zn finger proteins, have an important role in DNA synthesis and gene regulation. Plants grown in Zn deficient conditions display defects in fertility, seed production, growth regulation and ability to defend against disease.

3.9.2. Zinc uptake and offtake

Zinc is taken up by crops as the ion Zn^{2+}. Oilseed rape tends to be less sensitive than cereals to Zn deficiency; it is unusual for symptoms of Zn deficiency to be observed (Orlovius, 2003). Information on the offtake of Zn is shown in Table 1 for cereals and oilseed rape.

4. Soil supply

In the initial stages of soil formation, the micronutrient contents of the soil will be that of the geological parent material and are usually lowest in soils derived from acid igneous rocks and sands. However, with time, the composition will change under the influence of pedogenic processes, which themselves are impacted by vegetation, topography and, especially, climate. The soil can also gain nutrients through natural, wet (rainfall) and dry (dust) deposition and by pollution from human activity. Soil concentrations vary from a few parts per million (ppm), for Cu, Zn, Mo and B, to very high values, for Mg and Fe (Table 2). The 'availability' of most of micronutrients is primarily determined by the ease of weathering of the primary minerals of which they are a part but are subsequently modified by a number of soil and crop factors such as soil pH, organic matter, surface absorption, drainage and leaching, microbial activity, crop rooting density, nutrient uptake and release of organic substances from plant roots. In general, micronutrient deficiencies are more common on the 'sandy and light,' 'chalk and limestone' and 'peaty' soil types shown in Figure 1 than on medium or heavy soils.

Table 2. Concentration range of elements in soils from the literature

Element	Soil content Range (mg/kg)	Archer & Hodgson, 1987[1] Range, mg/kg (n)	Notes
Mn	20 – 3000*	n.a.	* Knezek and Ellis, 1980
Fe	1.0 – 10.0%*ǂ	n.a.	ǂ 10,000 – 100,000 mg/kg
Cu	10 – 80*	1.8 – 215 (1468)	* Knezek and Ellis, 1980
Zn	10 – 300*	3.9 – 975 (1520)	* Knezek and Ellis, 1980
B	2 – 100**	7 – 119 (396)	** Swaine, 1955
Mo	0.6 – 3.5**	0.03 – 13 (646)	** Swaine, 1955
Cl	18 – 806[+]	n.a.	[+] Wild, 1988
Mg	0.05 – 0.5%***	n.a.	*** Schroeder & Zahiroleslam, 1963

[1] Based on stratified sample of agricultural fields in England & Wales;

n.a. analyses for these elements not included;

(n) sample numbers.

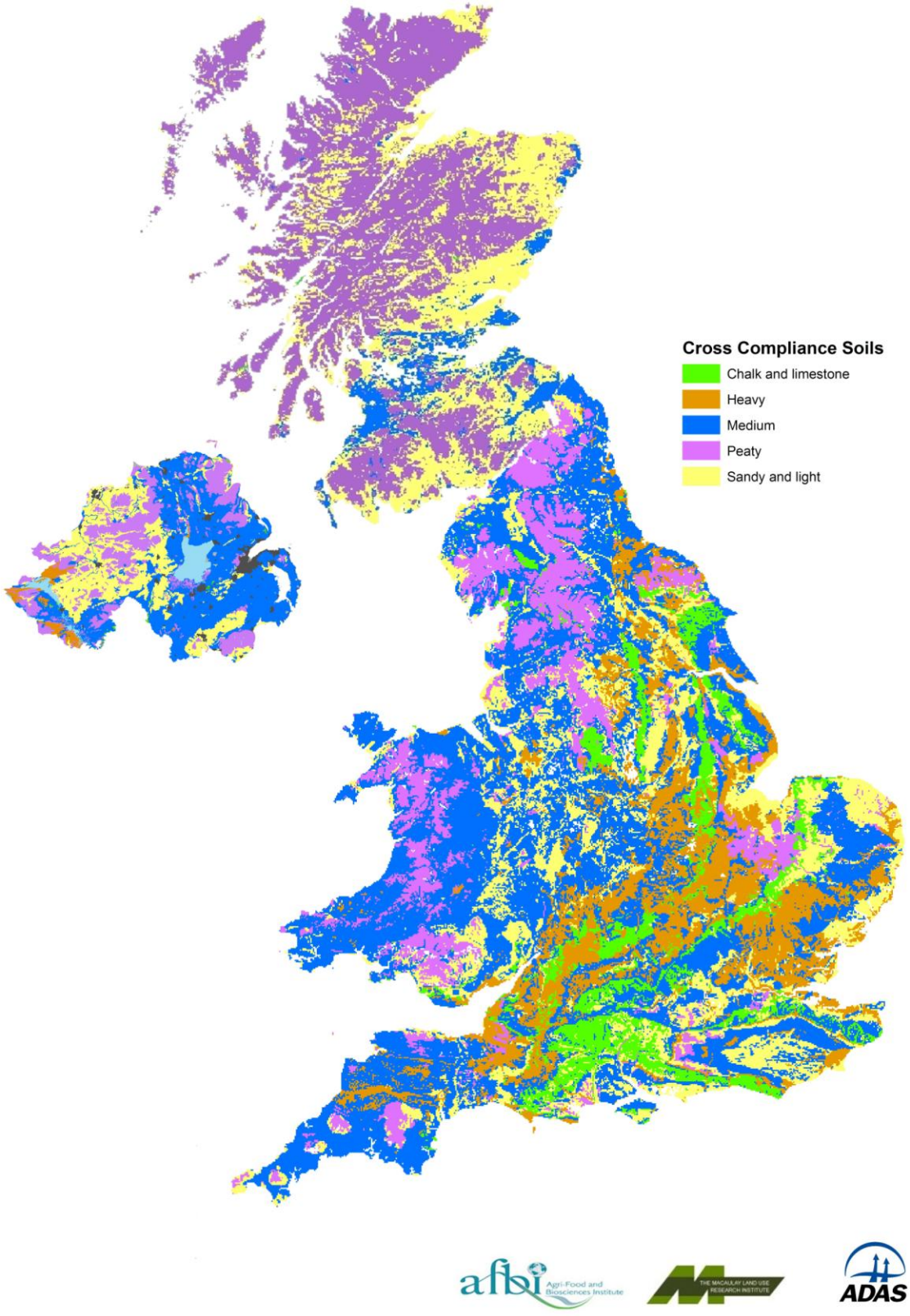

Figure 1. Map of basic soil types in the UK.

The soil chemical processes involved in the release and transfer of micronutrients between primary minerals, the various forms and phases of the elements within the soil and in soil solution, are extremely complex and, in some cases, are not fully understood. Such detail is therefore largely excluded from the current review, with only the key factors and their impacts considered in relation

to soil supply, crop requirements and potential nutrient deficiency. In general, the availability of most micronutrients decreases at higher soil pH levels (Figure 2). Low temperatures and other factors that affect root growth and activity, such as waterlogging or soil compaction, will also reduce micronutrient and other nutrient uptake. The impact of important factors will be considered further, as appropriate, for specific elements, but it is important to stress that the following factors can override the presence of micronutrients and limit their availability or uptake, thereby giving rise to temporary or more permanent deficiency:

- Low pH (for most micronutrients) or high pH (for Molybdenum),
- Dry or waterlogged soils,
- Impeded drainage,
- Low temperature,
- Soil compaction (reduced porosity),
- Root damage due to pest attack,
- Disease infection.

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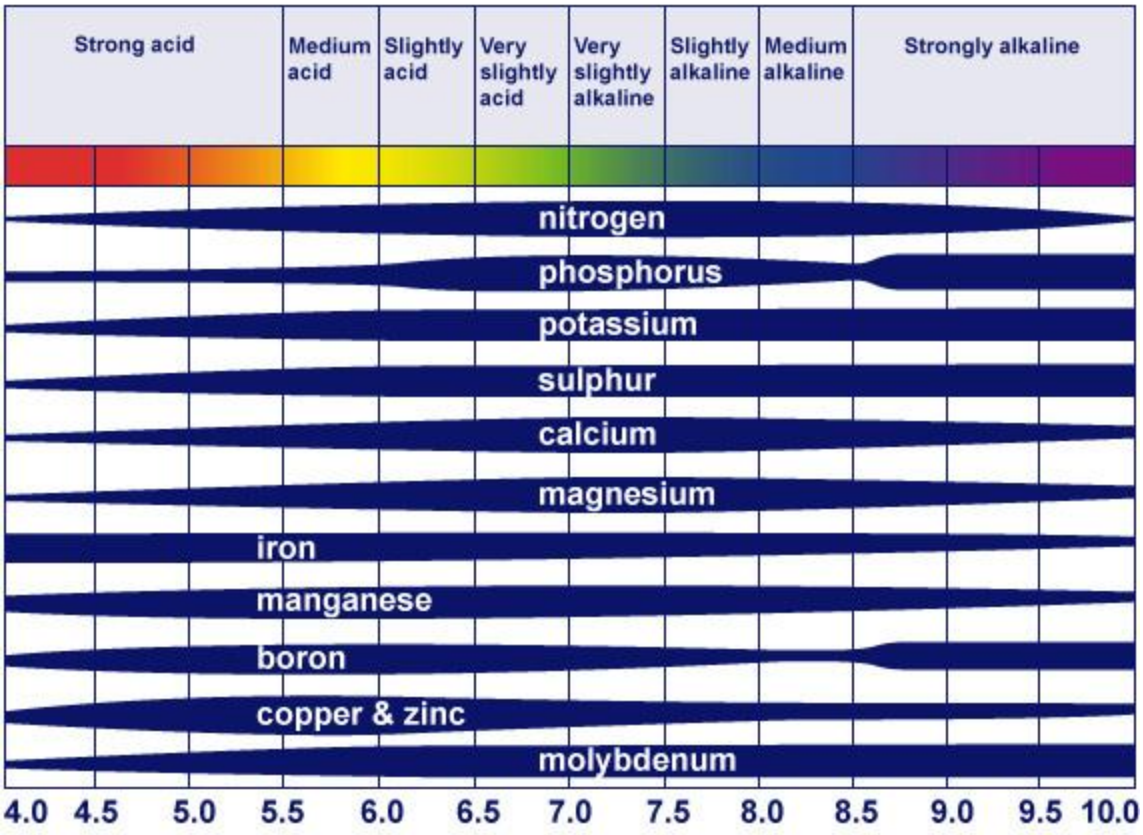

Figure 2. The effect of soil pH on nutrient availability.

4.1. Boron

The B content of soils varies from 2 to 100 mg/kg, with a mean value of 10 mg/kg (Swaine, 1955). Some examples of the B content of rocks are as follows: igneous rocks – 10 mg/kg; shales – 100 mg/kg; sandstones – 35 mg/kg; limestones – 20 mg/kg. Boron occurs as boric acid or borates within minerals. The most important mineral is tourmaline (3 to 4% B), and aschevite in marine sediments.

Boron can substitute for silicon (Si) in tetrahedral mineral structures. Most of the B is not available to plants and availability is usually measured by extraction with hot water (Anon, 1980a), which extracts boric acid, $B(OH)_3$. Water soluble B levels have been recorded for a number of soils, with values ranging 0.3 to 2.0 ppm in shale and sandstone soils and 0.3 to 0.9 ppm in limestone soils (Fleming, 1980). In contrast to other essential micronutrients in soils within the normal pH range, $B(OH)_3$ does not dissociate into its constituent ions, so B is mainly present in a non-ionised form which is, therefore, vulnerable to leaching loss from the soil when there is through-drainage. Sea water contains about 4.6 mg/l B, whereas fresh waters contain much lower levels. Boron is thus most abundant in saline soils and in both clays and hydrous oxides from marine sediments.

Boric acid can convert to the anion, $B(OH)_4^-$, at high soil pH and this can be adsorbed by sesquioxides and clay minerals by ligand exchange, OH^- being replaced by $B(OH)_4^-$. This may explain why B adsorption increases with soil pH and why B availability decreases as soil pH increases (high rate lime application can induce B deficiency). There is evidence of a strong association between B and soil organic matter, with B availability reducing with increasing organic matter. However, the associated compounds represent a significant reserve of B in slightly acid/neutral agricultural soils.

Boron is of interest in crop production because of potentially adverse effects arising both from deficiency and toxicity, when present in excess. Deficiency is most likely to occur on soils derived from acid igneous rocks and, especially sandy soils which inherently contain little B. Boron availability varies seasonally; deficiency is observed more frequently in a dry summer following a cool, wet spring, especially if growing conditions improve rapidly after a dry period (Batey, 1971). Boron is also toxic to some plants, including cereals and oilseed rape, at levels only a little above those required for optimum growth. Thus care must be taken to ensure that excessive amounts of B applied to correct potential deficiency in one crop do not present a potential toxicity risk to a following crop, particularly where this may be cereals, potatoes or french beans. Hot water extractable soil B levels of 5mg/kg or more are associated with B toxicity (Ahmad *et al*., 2012).

4.1.1 Boron sources

Annual atmospheric (total wet and dry) deposition was reported to range from 47 to 260 g/ha B over the years 1973 to 74 (Cawse, 1980), for non-urban sites. The highest deposition levels, 260 and 240 g/ha were recorded at Leiston, Suffolk and Collafirth, Shetland, respectively; these both being coastal sites and, hence, under strong maritime influence. Rainfall inputs from six sites sampled across England and Wales from 1968 to 1972 were estimated at 0.1 to 0.32 kg/ha B, with the highest (0.32 kg/ha) recorded at Efford Experimental Horticulture Station, also under maritime influence, being close to the south coast in Hampshire (Wadsworth & Webber, 1980). These amounts from atmospheric deposition are generally greater than the estimated oilseed rape crop offtakes for B of 60 to 80 g/ha (Table 1).

Although B analysis of organic residues is rarely undertaken, some of these materials are known to be significant sources of B, including composts, biosolids and some effluents (Purves & MacKenzie, 1973). The residue arising from the combustion of coal, pulverized fly ash (PFA) also contains high concentrations of B (Severson & Gouch, 1983) and can be significant where PFA is either applied to land or when PFA deposition sites have been reclaimed (e.g. clay pits in E. England near Peterborough).

4.2 Chlorine

In crops and soils chlorine exists as the chloride anion, Cl^-. Chloride is widely distributed in the environment and is rapidly recycled. The chloride ion is one of the most mobile because it is not adsorbed by soil minerals or organic matter and is thus, rapidly leached in soil drainage water. Chloride is involved in a number of important processes within the plant and deficiency can occur, but has never been recorded in the UK.

Crop demand for Cl ranges from 4 to 10 kg/ha and only soils with very low Cl content (<2 ppm) are likely to give rise to deficiency (Johnson, 2004). Annual atmospheric inputs are high in the UK, ranging from 21 kg/ha, up to 720 kg/ha (Shetland) in total deposition (Cawse, 1980) and from 23 kg/ha up to 141 kg/ha in rainfall (Wadsworth & Webber, 1980). Therefore, inputs are adequate for crop requirements even without the considerable inputs from fertilizers (muriate of potash) and animal manures (especially pig slurry).

4.3 Copper

Copper occurs most commonly in the form of sulphides, oxides and also as neutral and basic salts in minerals containing copper carbonates, sulphates and chlorides. The usual source of Cu in soils is from the weathering of rocks containing Cu compounds associated with the primary minerals.

Copper is widely distributed in igneous rocks, with granite containing much greater Cu content than basalt. In igneous rocks Cu content is typically 10 to 100 µg/g and in sedimentary rocks, 4 to 4.5 µg/g Cu. Deficiency is much more common in soils derived from silica and carbonate-rich sediments, though shales have markedly more Cu than limestone or sandstone. Based on data summarized by Sinclair & Withers (1995) the total Cu content in mineral and organic agricultural soils in GB ranges from 1 to about 100 mg/kg, with a similar range (10 to 80 mg/kg) reported by Knezek & Ellis (1980) (Table 2). Much larger concentrations can be found near Cu mining areas or where there has been long term, frequent use of Cu-containing foliar sprays or of waste products with high Cu content. Normal ranges of total Cu content are 1 to 15 mg/kg in very sandy soils, with *ca.* 25 and 60 mg/kg in loamy and clayey soils, respectively (Caldwell, 1976).

Copper deficiency has been recorded on only a few specific soil types in the UK: organic and peaty soils, reclaimed heathland sands, and shallow, organic chalk soils (with 6 to 12% organic matter) in S. England (Archer, 1985). The most extensive areas of Cu deficient soils are on the shallow chalks in SW and SE England and, in East Anglia, on peats and heathland soils. On account of the common occurrence of Cu deficiency on reclaimed peat soils, the deficiency has been referred to as 'reclamation disease' (Mengel & Kirkby, 1987). In the peaty fenlands, as the underlying clay and silt have become increasingly mixed with the soil, by wastage of the peat, or by the process of 'claying', Cu deficiency has become much less common or absent. In Scotland, Cu deficiency occurs in soils derived from acid schists and granitic rocks, as well as peaty soils (Chalmers *et al*., 1999).

Copper occurs predominantly as the divalent cation Cu^{2+}, either on clay exchange sites or complexed with organic matter. Copper is held strongly by exchange surfaces in clay minerals and by soil organic fractions which play a major role in regulating the mobility of Cu in soils and availability for plant uptake. Some soil Cu is also immobilized by micro-organisms. A relatively small part of the total Cu present in soils is, therefore, readily available for plant uptake. Soil analysis data for England and Wales (Archer & Hodgson, 1987) indicated that EDTA-extractable Cu, as a measure of 'available' Cu to plants, is about 20% of the total Cu concentration in soils. The restricted availability means that Cu does not leach easily through the soil, although mobility is slightly greater in sandy than in peaty or clayey soils, which leads to more severe deficiency in dry seasons. Mobility is, however, increased considerably in poorly drained soils. Most of the applied Cu remains in the cultivated topsoil layer of well drained agricultural soils, often resulting in a sharp decrease in Cu content in the subsoil.

Chalmers *et al*., (1999) reported that 31% of soils tested in the North of Scotland and a similar percentage for the whole of Scotland, but less than 5% of soils in England and Wales, had low extractable soil Cu concentrations likely to require routine Cu treatment for cereal cropping,

because of the risk of Cu deficiency (Sinclair & Withers, 1995). A local survey of soil Cu levels in shallow chalk soils in West Berkshire in 1987 suggested that 44% of the fifty fields tested were slightly deficient, requiring Cu treatment when cropped with cereals (Wadsworth, ADAS, unpublished). The results of the micronutrients survey of soils in England and Wales (Archer & Hodgson, 1987), showed a median EDTA extractable soil Cu content of 4.8 mg/l indicating the soils were generally well supplied with Cu (Table 2). In a small number of soils (106 samples, 7% of the total and similar to the findings of Sinclair & Withers, 1995), EDTA Cu was below 2 mg/l Cu, where deficiency would be expected in susceptible crops.

4.3.1 Copper sources

Chalmers *et al*., (1999) suggested that the incidence of Cu deficiency in cereal crops is greater in Scotland than in the rest of the UK. At that time, foliar Cu sprays were typically applied to about 5% of the cereal area in England and Wales, and to 10% of cereals grown in Scotland (Chalmers *et al*., 1999).

In the Agricultural Soils Metals Inventory (Nicholson *et al*., 2010), atmospheric deposition, livestock manures and biosolids were shown to be the major sources of Cu inputs onto agricultural land, each representing >25% of total annual inputs (Table 3). Livestock manures and biosolids represent the most significant inputs at the field level, at typical application rates, with 2.3 kg/ha Cu from biosolids (applied at 250 kg total N/ha/yr; *ca.* 6.5 t dry solids/ha/yr) and Cu addition rates from pig manures, at *ca.* 0.6 to 1.3 kg/ha Cu (applied at 250 kg total N/ha/yr). This compares with wheat crop offtake rates of up to 60 g/ha (Table 1).

4.4 Iron

Iron is invariably present in all soils, occurring in many primary and secondary minerals and, as a result of the weathering of ferromagnesian minerals, Fe occurs in illitic clay minerals. The average concentration of Fe in the earth's crust is estimated at 50,000 ppm, but Fe can be concentrated or depleted during soil development, giving rise to concentrations varying from 3,000 to 500,000 ppm total Fe in the soil (Knezek & Ellis, 1980) (also varying within the soil profile according to development processes). Iron is capable of forming stable species with oxides, carbonates, silicates and sulphides, the oxidation status of the environment primarily impacting on the compounds formed.

Soluble Fe occurs in soils as Fe^{3+}, $Fe(OH)_2^+$, $Fe(OH)^{2+}$ and Fe^{2+}, but all at very low levels, relative to the total Fe content of the soil. Iron solubility is largely controlled by the solubility of hydrous Fe(III) oxides that release Fe^{3+} via hydrolysis (Lindsay, 1972):

$$Fe^{3+} + 3OH^- \leftrightarrows Fe(OH)_3 \text{ (solid)}$$

The equilibrium is highly pH dependent and favours the precipitation of $Fe(OH)_3$ with the activity of Fe^{3+} decreasing with increasing pH. Thus the concentration of soluble inorganic Fe is very low in calcareous soils, which explains the incidence of Fe deficiency in susceptible crops (not arable crops) on these soils.

From the high Fe content of soils it is clear that any problems of Fe deficiency in crops must be due to Fe availability. Within the normal pH range of agricultural soils, it has been shown that the likely plant-available Fe levels in soils are far below those required by plants (Lindsay, 1974). It is therefore apparent that soluble organic complexes, mainly chelates, can play an important role in supplying Fe to most crops. The mechanism involves absorption of Fe from the organic molecule at the root surface and it appears that soil-root contact is important for the process. It follows that soil conditions likely to inhibit root development and branching, such as waterlogging and soil compaction, will limit Fe uptake and increase the risk of Fe deficiency.

Atmospheric deposition of Fe has been reported at a moderate level of 1.5 to 7.7 kg/ha Fe across the UK (Cawse, 1980). Whilst such rates of deposition appear to be significantly above crop offtakes, they are of little significance to crops, given that Fe availability is limited by soil factors rather than the Fe content of soils, and that Fe deficiency occurs only in fruit and nursery stock in the UK.

4.5 Magnesium

Soil Mg content ranges from *ca.* 5000 mg/kg in sandy soils to 50,000 mg/kg in clays (Table 2); Mg is present in relatively easily weatherable ferromagnesian minerals such as biotite, serpentine, hornblende and olivine and is present in secondary clay minerals, such as illite and montmorillonite. Soils may also contain substantial amounts of Mg as $MgCO_3$ or dolomite ($CaCO_3.MgCO_3$) as in Magnesian limestone (3 to 12% Mg).

4.5.1 Factors affecting magnesium availability in soils

The distribution of Mg in soils is similar to that of potassium (K), with non-exchangeable, exchangeable and water soluble forms. The greatest part of Mg is present in non-exchangeable form, with about 5% as exchangeable, this usually comprising about 5 to 20% of the cation exchange capacity (with Ca approx. 80% and K approx. 4%). Magnesium in association with organic matter is usually small, at <1% total soil Mg. The exchangeable fraction, along with the water soluble Mg is of greatest significance for plant uptake. Magnesium (Mg^{2+}) ions, like Ca ions, may be present in high concentrations in soil solution (often between 2 to 5 mM). Magnesium, therefore, is relatively easily leached from the soil, with rates depending on mineralogy and weathering, as well as leaching intensity and plant uptake.

The level of Mg in soils depends substantially on soil type. Highly leached and weathered soils such as podzols are generally low in Mg and, on the other hand alluvial and gleyed soils, developed on sites of nutrient enrichment, tend to be high in Mg; podzols and marsh soils representing the extreme range of soil Mg content in soils (Table 2) (Schroeder & Zahiroleslam, 1963).

From the above, it can be seen that only a small proportion for the total soil content of Mg is available for plant uptake, availability being dictated by the amount of exchangeable Mg held on soil particles, with very little release of Mg from soil organic matter. An absolute shortage of Mg is most likely to occur on sandy soils with low cation exchange capacity, especially where the latter is dominated by other cations (as in very acid or alkaline soils) and Mg is subject to leaching loss. On heavier soils, weathering of soil minerals can be expected to be sufficient to maintain a satisfactory level of exchangeable Mg and solution concentrations are relatively high.

Chalmers *et al*, (1999) reported results from the early Representative Soil Sampling Scheme (Skinner *et al*., 1992), which showed that only 3% of arable fields in England and Wales were deficient (Index 0, <26 mg/l Mg) in Mg. Results from the National Soil Inventory for England and Wales showed a median value of 98 mg/l (Index 2) for extractable magnesium concentration in topsoils (McGrath & Loveland, 1992). Very recent data published by the Professional Agricultural Analysis Group (PAAG) covering commercial and research laboratories in the UK (Anon, 2012), from a total of >175,000 samples, showed 0% of soil samples were in index 0, with 13% of arable samples and only 2% of grass samples in index 1 for Mg. These results indicate that soils generally have adequate Mg status for arable cropping.

4.5.2 Factors affecting magnesium uptake

Cereals and oilseed rape have relatively low Mg concentrations, typically ranging from 0.1 to 0.2% in expanded cereal leaves and 0.2 to 0.5%, mid season in OSR (ADAS, unpublished data), tending to decrease as the season progresses. This variation reflects both the ability of different soils to supply Mg and the large influence that plant rooting density and seasonal weather patterns exert on Mg uptake by the plant. The uptake of Mg is also highly dependent on concentrations of other cations (Ca^{2+}, K^{+} and NH_4^{+}) in the soil solution and an excess of other cations, especially of K^{+} and NH_4^{+}, can inhibit uptake of Mg^{2+} (Mengel & Kirkby, 1987). On the other hand, Mg uptake is enhanced by some anions such as nitrate and phosphate.

Chalmers *et al*, (1999) noted the absence of widespread magnesium deficiency on chalk soils, despite often low extractable soil Mg levels, suggesting that the Ca/Mg interaction is less important than the K/Mg interaction. A high K/Mg ratio is likely to inhibit Mg uptake in fruit crops, though

rarely is there a concern in arable crops. Similarly, an application of NH_4-N to crops suffering from Mg deficiency can temporarily intensify the symptoms, but when the NH_4-N has been nitrified, the plant is then better able to use the available Mg. Magnesium deficiency symptoms are often associated with nitrogen deficiency, but a crop response to applied N is more likely than to Mg (Archer, 1985). On soils of adequate Mg status, transient deficiency symptoms may often occur, coincident with periods of rapid growth as Mg is transported from older leaves to younger, expanding leaves, or may be induced by drought. Under such conditions, crop response to Mg fertilisation via foliar sprays is unlikely (Archer, 1985).

Symptoms of Mg deficiency, where they occur in arable crops, including cereals and oilseed rape, are much more likely to have been induced by poor soil conditions or other factors which restrict root development and Mg uptake, rather than an absolute shortage in the soil. Soil compaction, drainage impedance and surface waterlogging, surface capping, also root damage due to pest attack e.g. cereal cyst eelworm or disease infection e.g. take-all, may all induce symptoms of Mg deficiency.

4.5.3 Magnesium sources

Biosolids and livestock manures generally contain small to moderate amounts of Mg and are a useful source of this nutrient, relative to most crop requirements when applied at agronomically sensible rates (rates varying from 34 to 75 kg/ha MgO from different manures and biosolids). Some Mg, on average about 4 kg/ha/year (Anon, 1998), is supplied from atmospheric deposition, including rainfall, but this input can be as high as 10 kg/ha/year near to coastlines (Archer, 1985). This compares with crop offtakes of 18 to 22 kg/ha Mg for oilseed rape (Table 1).

4.6 Manganese

Manganese is tenth in order of abundance of the elements in the earth's crust, having an average content of *ca*. 900 mg/kg. It occurs very widely in minerals and almost as frequently as iron as a constituent of rocks (MAFF, 1976). During soil forming processes the Mn released by weathering of primary minerals such as olivine, hornblende, biotite and augite may be absorbed into or adsorbed onto clay minerals, form complexes with organic matter or oxides such as pyrolusite (MnO_2), manganite (MnOOH), or hausmannite Mn_3O_4. A series of manganese oxides as well as other manganese compounds can form in the soil, ranging from soluble manganous, to highly oxidized, manganic forms of low solubility.

The total Mn content of soils varies widely from a trace to >7000 mg/kg, but is most commonly within the range 20 to 3000 mg/kg (Knezek & Ellis, 1980) (Table 2). The small fraction of Mn present in soil solution is readily available for plant uptake. Manganese in soil solution is replaced

by exchangeable Mn held in the colloidal complex of the soil. Neither total, nor exchangeable Mn shows much correlation with the composition of the soil parent material. Like other micronutrients, including Cu, Fe and Zn, Mn may undergo a number of transformations within the soil including precipitation reactions (forming, e.g. oxides, hydroxides, carbonates and sulphides), oxidation-reduction reactions, or complex formation with organic ligands. In practice, available Mn content is strongly influenced by the soil pH, the degree of aeration of the soil and the level of soil microbial activity. A fraction termed the 'easily-reducible' Mn has been determined by soil analysis as an indicator of Mn availability for plants; however, this fraction is impacted by a number of factors including soil temperature, water content, level of microbial activity and oxidation conditions. Soil analysis to determine the amount of Mn available to crops under a range of soil conditions has been very difficult and to date has been largely unsuccessful.

Chalmers *et al.* (1999) reported that the incidence of Mn deficiency in cereal crops appears to have been substantial in Scotland for at least 15 years and was thought to have increased in the late 70s and early 80s (Sinclair, 1982). A similar trend also seems likely over this period in England, at least in cereals if not in OSR. Chalmers *et al.* (1999) suggested that this increased incidence of deficiency may have arisen as a result of an increased susceptibility in crop cultivars or, even that some change in soil chemistry may have adversely affected the availability of Mn to the plant or potential for plant uptake.

The capacity of soil surfaces to absorb and retain transition element ions (including Mn^{2+}) at a particular pH is known to be enhanced by the adsorption of phosphate onto oxide surfaces (Diaz-Barrientos *et al*., 1990). The increasing and continued use of phosphate fertilisers in arable agriculture over the 70s and early 80s resulted in a build-up of phosphate in some Scottish soils (Sinclair *et al*., 1989). It is possible that this resulted in increasing adsorption of Mn by oxide surfaces in these soils, thus causing depressed soil solution Mn^{2+} concentrations and enhanced Mn deficiency. Trends in fertiliser use, however, appear to have changed since the early 1980s, with a progressive reduction in phosphate use. Thus, the British Survey of Fertiliser Practice (BSFP) recorded 70 and 56 kg/ha P_2O_5 use on tillage land in Scotland and England and Wales, respectively in 1985, and 50 and 27 kg/ha P_2O_5 in Scotland and England and Wales, in 2011 (BSFP, 1985; 2011).

Batey (1971) commented that Mn deficiency had been observed in all parts of the UK, though often occurring only in patches in fields; however, incidence of the deficiency could be associated with and, therefore, anticipated on a number of geological formations and soil types. Moderate to severe Mn deficiency in arable crops usually only occurs on:

- Organic, peaty and marshland soils with soil pH over 6.0, especially over 6.5;
- Sandy soils (sand, loamy sand) with soil pH over 6.5, especially over 7.0.

Transient deficiency may be seen in field crops grown on a wide range of soil types, including poorly structured fine-textured soils (e.g. clays or clay loams) with a soil pH over 7.0. Very sandy soils low in organic matter and (acidic) podzolic soils are particularly low in Mn, but in most other soils Mn content is adequate. Consequently, Mn deficiency is usually induced by low availability of soil Mn for crop uptake, rather than being due to an absolute shortage of soil Mn. Field conditions most often associated with Mn deficiency in the UK are: high soil pH; high organic matter content; poor root development; poor root-soil contact in under-consolidated (fluffy) seedbeds; low soil temperatures; and below average rainfall. The overall combination of these factors will dictate the severity of the deficiency in crops when it occurs. The higher the organic matter content, the lower the soil pH needs to be to prevent deficiency occurring. A temporary shortage of Mn is also often induced under poor soil physical conditions, especially after periods of cold, dry weather which put a poorly rooted crop under stress. Bright, sunny weather conditions promoting rapid growth can accentuate Mn deficiency, compared with dull, humid conditions. It is apparent from advisory experience that once deficiency has been observed on a particular field, recurrence of the problem can be expected in susceptible crops, under the conditions outlined above.

4.6.1 Manganese uptake

Manganese is taken up by plant roots from the soil solution as the divalent cation Mn^{2+}. The divalent Mn^{2+} is also adsorbed on clay minerals and organic matter and the equilibrium between the various forms of Mn (solution, adsorbed and Mn oxides) is governed by oxidation- reduction processes. Factors impacting on these processes include soil pH, organic matter content, microbial activity and soil moisture status. Divalent Mn^{2+} is fairly mobile in the soil and can easily be leached, as occurs in acid podzolic soils. Microbial oxidation of Mn, to oxides of very low solubility, occurs relatively slowly at between pH 5 and 6 but increases markedly as the pH is raised to 7.5 (Wild, 1988). Manganese availability depends on the chemical reduction of Mn oxides by organic matter, also on biological processes involving root exudates and the rate of reduction increases at more acid pHs. Lindsay (1972) has shown that soluble Mn decreases 100 fold for each unit increase in soil pH. Nutrient interactions can produce large differences in both crop growth and elemental uptake (Reisenauer, 1988). Competitive effects between macronutrient cations (K^{+}, Mg^{2+}, Ca^{2+}) and Zn^{2+} on Mn^{2+} uptake are considered to be significant, while those from copper and boron are less important. Applications of acidifying fertilisers such as ammonium sulphate have been shown to increase Mn uptake by crops, particularly in poorly buffered acidic and non-calcareous soils (Schung & Finck, 1982).

Although Mn is more available under conditions of poor drainage, these conditions are also likely to result in shallow/restricted rooting which may reduce Mn uptake, especially as shallow rooted crops are then more susceptible to subsequent dry soil conditions during the summer. Crops require a continuous supply of Mn, since Mn is relatively immobile within the plant (Wittwer &

Teubner, 1959). Thus, transient deficiency may readily occur, due to changing weather and soil conditions. The Mn content of plants varies greatly, usually from a trace, up to 500 mg/kg in dry weather and depending on soil Mn availability. Much larger, toxic concentrations can occur in plants growing on very acid soils.

4.6.2 Manganese sources

Annual atmospheric (total wet and dry) Mn deposition was reported to range from 68 to 320 g/ha Mn over the years 1972 to 1975 (Cawse, 1980), for non-urban sites. Crop offtakes were estimated to represent *ca*. 45%, 34% and 38% of the Mn inputs (320 g/ha Mn), respectively, for grass (hay), kale and wheat at typical yield levels (Cawse, 1980). Rainfall inputs from six sites sampled across England and Wales from 1968 to 1972, were similarly estimated at 63 to 297 g/ha Mn, with estimates at ≤100 g/ha, at five of the sites and the highest, 297 g/ha recorded at Great House Experimental Husbandry Farm, in the Lancashire Pennines (Wadsworth & Webber, 1980). Crop offtakes for a 10 t/ha wheat crop may be estimated at 400 g/ha (Table 1) which indicates that crop offtake may be greater than atmospheric deposition, in contrast to Cawse (1980).

Other sources include agrochemicals such as the broad spectrum fungicide mancozeb (also containing Zn), although no information is available on extent and rates of use to enable calculation of total Mn inputs. Manures and biosolids are also likely to be significant sources (Smith & Unwin, 1983), although there are few analytical data including the Mn content of these materials.

4.7 Molybdenum

Total Mo content of most agricultural soils ranges from 0.6 to 3.5 ppm (Swaine, 1955) (Table 2), with an average total Mo at 2.0 ppm and available at 0.2 ppm (Johnson, 2004). Unlike most of the other micronutrients, Mo occurs in soils mainly as an oxycomplex, molybdate (MoO_4^{2-}) and, as a result, its behaviour in soil is similar to that of phosphate, being adsorbed by sesquioxides and clay minerals. The molybdate anion is strongly bound by ligand exchange, most strongly at pH 4.0 and decreasing with increasing soil pH (Figure 2). Liming is well known to increase Mo availability and is the most effective treatment to correct/prevent the deficiency. Mo deficiency has been reported in brassica crops on a wide range of acid soils derived from granite, Devonian Shale, Old Red Sandstone, Keuper and Lower Greensand (Williams, 1971). However parent material had little effect on the deficiency, soil acidity being the most important factor.

Molybdenum is important for legumes, due to the requirement within the nitrogen-fixation process and Mo accumulates within the root nodules. Although liming of acid soils is an effective treatment for prevention of Mo deficiency, it may sometimes be better to apply Mo salts if an increase in soil pH is likely to have other unwanted effects. However, consideration should also be given to crop

use, as for example, high Mo concentrations in animal feed can be toxic to animals, especially ruminants.

4.7.1 Molybdenum sources

Annual atmospheric (total wet and dry) deposition was consistently very low, with <10 g/ha Mo over the years 1973 to 1974, across all the monitoring sites reported by Cawse (1980). Rainfall inputs from six sites sampled across England and Wales from 1968 to 1972, were similarly estimated at low levels of 1 to 13 g/ha Mo, except at Great House Farm in the Lancashire Pennines, with the higher inputs of 36 g/ha Mo possibly being influenced by industrial pollution (Wadsworth & Webber, 1980). This compares with wheat crop offtakes of about 4 g/ha (Table 1). No data could be found for oilseed rape crop offtakes.

4.8 Zinc

Zinc content of soils varies between 10 to 300 mg/kg (Swaine, 1955). Soils originating from basic igneous rocks are reasonably well supplied with Zn, whereas much less is found in soils developed from the weathering of granite, gneiss or quartzite. Sedimentary rocks vary more widely, with shales containing *ca*. 100 mg/kg, while limestones and sandstones are much lower, with 20 mg/kg and 16 mg/kg Zn, respectively (Lindsay, 1972).

Soil solution Zn concentrations are little influenced by Zn containing minerals and, instead, Zn^{2+} is held largely on exchange sites on clays, hydrous oxides and organic matter. The amount of Zn^{2+} adsorbed by a soil often relates to its cation exchange capacity, with most of the extractable zinc present in the clay fraction of the soil. Some clay minerals are able to fix additional Zn, the extent of which varies according to the dominant clay species present. Iron, aluminium and manganese hydrous oxides are also involved in Zn exchange and fixation processes. Organic matter can form soluble complexes with Zn, increasing plant uptake, but can also immobilise or 'fix' zinc via other binding mechanisms. Much of the soil solution Zn is complexed with soluble organic matter arising from the breakdown of plant residues and from root exudates. These organic ligands maintain Zn availability at pH values where Zn would otherwise be 'fixed' in immobile forms. Zinc availability and, hence, crop uptake varies considerably, depending on a number of factors (Lloyd, 1981).

- *Soil pH*. The solubility of Zn decreases with increasing pH and deficiency is most prevalent on calcareous soils at pH ≥7.4. Similar to soil manganese, Zn solubility has been estimated to decrease 100-fold per unit increase in pH (Lindsay, 1972), possibly as a result of increasing adsorption on OH^- on Al and Fe oxides, increasing adsorption on clay minerals, or due to increasing stability of organic complexes.

- *Soil phosphorus.* There is sometimes conflicting evidence of a potential antagonistic effect of P applications on Zn uptake, not least because P fertilizers can themselves supply Zn as a contaminant.
- *Nitrogen.* There is some evidence of increasing N supply being associated with Zn deficiency but this may simply be the result of increased crop growth and, therefore, requirement for Zn.
- *Other ions.* Evidence of a potential antagonistic effects of other ions such as Fe, Cu and Mg is sparse and, again, conflicting.
- *Soil organic matter*. Zinc deficiency has often been reported on restored sites where surface soil has been substantially removed/reduced. Research has often shown a strong relationship between organic matter and extractable Zn.
- *Soil conditions*. Soil compaction, waterlogging and low soil temperatures, all factors impacting negatively on root growth, are therefore also likely to depress Zn uptake. Moreover, low soil temperatures can reduce soil microbial activity and, hence, release of Zn from organically bound Zn.

Despite being a common deficiency around the world, Zn deficiency is extremely rare in the UK and appears very unlikely to occur in UK crops, even on very sandy soils. The results of the early micronutrients survey of soils in England and Wales, showed a median EDTA extractable soil Zn content of 5.4 mg/l indicating a satisfactory soil Zn status, with no soil samples of <1 mg/l and only 25 samples (3% of total of 782) of 1 to 5 mg/l, in the range indicating only slight risk of deficiency (Archer & Hodgson, 1987).

4.8.1 Zinc sources

Foliar Zn sprays are the most likely remedial treatment for deficiency. As for Cu, atmospheric deposition, livestock manures and biosolids are shown to be the major sources of Zn inputs onto agricultural land, atmospheric deposition and manures representing 30% of total annual inputs and biosolids 20% (Table 3). Livestock manures and biosolids are the most significant inputs at the field level, with 4.3 kg/ha Zn from biosolids, at typical application rates (applied at 250 kg N/ha/yr; *ca.* 6.5 t dry solids/ha/yr) and additions from pig manures at *ca.* 2.0 to 3.5 kg/ha Zn (applied at 250 kg total N/ha/yr). This compares with 200 g/ha crop offtake for wheat (Table 1).

4.9 Sources of micronutrients for agricultural soils

Of significance to soil supply of micronutrients are a number of sources other than specific micronutrient fertilisers, including atmospheric deposition, other fertilisers, supplies from organic materials including livestock manures, biosolids, composts, digestates etc., some of which are

likely to have changed significantly over recent years. Table 3 summarises inputs of elements including Cu and Zn to agricultural soils from these sources.

Table 3. Estimated total annual metal inputs (t/yr) to agricultural soils in England and Wales in 2008, from different sources (SP0569) (Nicholson *et al.*, 2010)

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Atmospheric deposition	1009	333	72	99	6.3	20	8.1	9.0
Livestock manures	998	364	21	34	1.7	23	9.5	0.1
Biosolids	701	364	42	167	1.9	101	6.6	1.5
Industrial 'wastes'[1]	80	41	32	10	1.2	10	0.2	0.2
Dredgings	63	17	8	19	0.3	9	2	0.2
Compost[2]	116	34	9	64	0.4	14	<0.1	0.1
Digestate	1	<1	<1	<1	<0.1	<1	nd	nd
Footbaths[3]	28	17	-	-	-	-	-	-
Fertilisers and lime	150	32	25	12	6.7	71	4.5	<0.1
Ash[4]	145	43	<1	<1	<0.1	<1	<0.1	<0.1
Plant protection products	16	2	nd	nd	nd	nd	nd	nd
Irrigation water	1	<1	<1	<1	<0.1	<1	0.1	<0.1
Corrosion	28	nd	nd	nd	nd	nd	nd	nd
Lead shot	nd	nd	nd	3250[5]	nd	nd	nd	nd
Total (2008)	3336	1248	210	406	18.5	248	31	11

nd: no data

[1] Including paper crumble, food 'wastes', water treatment cake

[2] Including green compost and green/food compost

[3] Only includes the proportion of footbaths disposed directly to land. Metals in footbaths emptied to slurry/manure stores are assumed to be included in the contribution from livestock manures

[4] Ash from the incineration of poultry litter (not including paper sludge ash)

[5] Pb not included in total due to the uncertainty of the estimate from lead shot

In the absence of additions of organic residues or fertiliser sources, crop offtake may be less than inputs for B and Mo (for cereals), but crop offtake may exceed inputs for Cu, Zn and Mg, and possibly Mn. However, these conclusions are in some cases uncertain where atmospheric deposition data are from the 1970s and nutrient leaching must also be adequately accounted for.

5. Incidence of deficiency

5.1. Yield responses

A literature search was conducted for cereal and oilseed rape yield response experiments to non-NPKS nutrients. The search was confined to studies conducted in the UK and sites thought to have

reasonable similar climates and yield potential to the UK, namely northern Europe, Canada and New Zealand. ADAS archives were also searched for relevant unpublished experimental reports.

Producers and distributors of non-NPKS nutrient products were also invited to submit data to the review, on commercially-funded yield response experiments. Frontier provided a large number of reports on experiments undertaken in Cambridgeshire, Yorkshire and Lincolnshire from 2000 to 2012 to investigate the effects of micronutrient sprays and seed treatments on yield. Experimental reports and data were also provided by NIAB-TAG and Micromix Plant Health. These commercial experiments are included with independent published and unpublished experiments in the summary tables below.

Where appropriate, meta-analyses have been done on experiments from different sources: paired t-tests have been used to examine whether firm conclusions may be drawn on nutrients for which most experiments have given non-significant yield responses, and regressions have been fitted to test the correlations between soil or tissue test results and yield responses.

5.1.1. Boron

Evidence for statistically significant oilseed rape yield responses to applied B are limited; results from a total of 48 experiments carried out between 1981 and 2008 in the UK and Canada show a significant improvement in yield in response to applied B at only five of the sites tested (Table 5). A single significant yield response was obtained from a series of 22 experiments carried out in Western Canada (Table 5, Karamanos *et al*., 2003a), which occurred in response to foliar application of Micro Plus B (0.55 kg B/ha). However at the same site, foliar application of a different B product, Solubor, (0.55 kg B/ha) led to a significant decrease in yield. A study investigating the ability of autumn and spring foliar applications of B to rectify B deficiency showed that single applications out-yielded split applications for both seed and oil yield (Table 4; Prince & Johnson, 1982).

Across all the experiments, the average treated yield was only 100.3% of the untreated yield, and a paired t-test of untreated control and mean treated yields confirmed no significant yield response. For the experiments with several B treatments, the treated yield was an average across all the B treatments. There was also no correlation between the yield response to B and soil B status (Figure 3) or tissue B level (Figure 4), although relatively few reports included tissue B data.

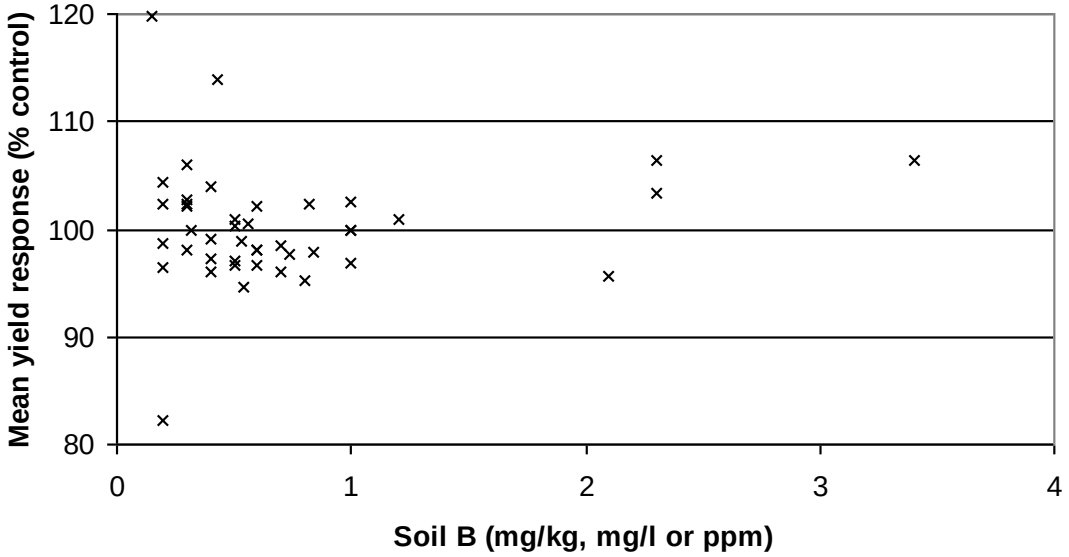

Figure 3. Relationship between hot water soluble soil boron and mean yield response to boron applications, for the 43 experiments listed in Table 5 for which sufficient data were available.

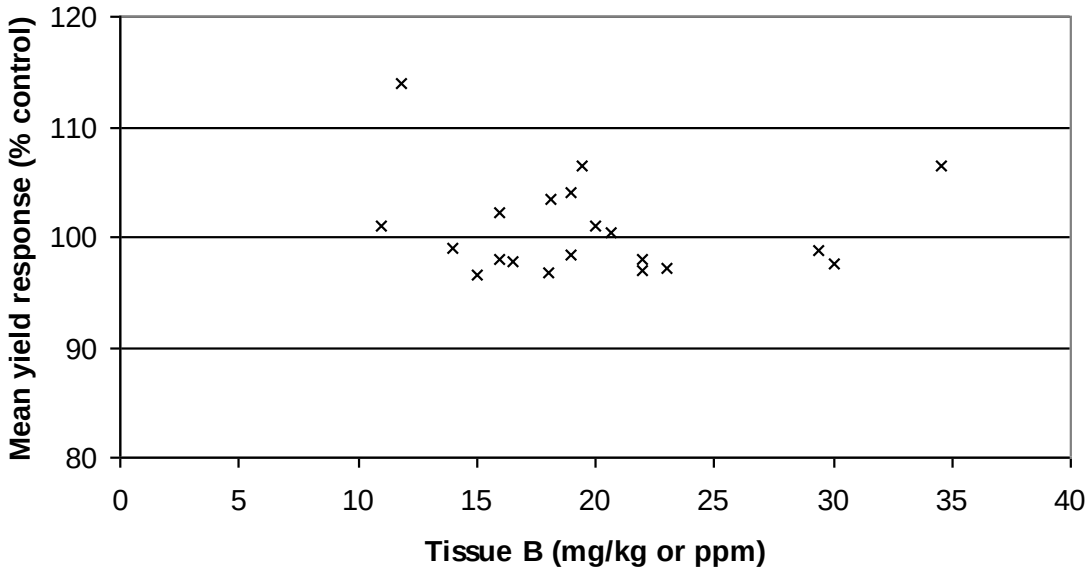

Figure 4. Relationship between tissue boron levels in spring and mean yield response to boron applications, for the 20 experiments listed in Table 5 for which sufficient data were available.

An alternative analysis was done of the highest yielding B treatment at each site, to remove the effects of ineffective treatments, timings or rates. The average yield of the best treatments was 104.7% control yield, and the paired t-test showed a significant effect of B treatment ($P<0.001$), but there was still no correlation of yield response with soil B status. This result should be interpreted with caution, as use of the best treatment from each experiment introduces a positive bias: most experiments include only one control treatment but several B treatments, such that even if there is

no effect of B, it is likely through random yield variation that with several treatments to 'choose' from, the highest treated yield will be greater than the control yield.

Thirty-three experiments were found which tested cereal yield responses to B; none of these showed a significant yield response (Table 6). A paired t-test comparing untreated and mean treated yields across all these experiments confirmed no significant effect of B on yield, and the average treated yield was 99.4% of untreated yield. For the experiments for which soils analysis data was available, there was no correlation between soil status and yield response. Most experiments included only a single B treatment, so there was no need to analyse best treated yield separately from mean treated yield.

Table 4. Yield response of oilseed rape to autumn and spring single and split applications of boron (Prince & Johnson, 1982). Different letters indicate significantly different yields at P<0.05.

Treatment	Seed yield (t/ha @ 90% DM)	Oil yield (t/ha)
Control	2.86[a]	0.94[a]
10 kg/ha Solubor Foliar spray in Autumn	3.33[b]	1.12[b]
10 kg/ha Solubor Foliar spray in Spring	3.42[b]	1.14[b]
5 kg/ha Solubor Foliar spray in Autumn & Spring	3.04[c]	0.99[c]
SED	0.092	0.041
CV %	3.57	4.76

Table 5 Oilseed rape yield responses to foliar-applied boron for field experiments carried out in the UK and Canada.

Year	Soil type & boron content (hot water soluble, unless otherwise stated)	Responsive sites/ total number of sites[†]	Yield response range (% control;. includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
1981	Loam; 0.50-0.53 mg/l B	0/2	94-104%	2.55	Nottinghamshire, UK	Anon, 1981
1981	0.74-0.84 mg/l B	0/2	97-99%	2.96	Suffolk, UK	Anon, 1981
1982	Loamy sand; 0.43 mg/l B	1/1	106-119%	2.86	Lincolnshire, UK	Prince & Johnson, 1982
1985-1988	Various; 0.3-1.2 mg/l B (analysis method not stated)	1/9	96-104%	2.90	Cumbria, Kent, Lincolnshire, Powys, Yorkshire	Withers, 1988
1991-2003	0.1-1.0 mg/kg B	1/22	87-120%	2.71	Western Canada	Karamanos *et al*., 2003a
1997-2000	Loam, sandy loam, loam sand; 0.11-0.82 mg/kg B	1/7	82-134%	1.19	Northeastern Saskatchewan, Canada	Malhi *et al*., 2003
2006	Flinty clay loam; 2.3 ppm B	0/1	103%	2.68	Yorkshire	Frontier, 2006a
2006	2.1 mg/l B	0/1	93-101%	3.19	Cirencester	NIAB TAG
2007		0/1	104%	4.12	East Yorkshire	NIAB TAG
2008	Flinty clay loam, limestone brash; 2.3-3.4 ppm B	1/2	100-111%	3.51	Lincolnshire, Yorkshire	Frontier, 2008a

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

Table 6. Yield responses to boron for field experiments carried out in the UK and New Zealand for cereals. Bold treatments are those which led to significant yield responses.

Crop	Year	Soil type & boron content (hot water soluble, unless otherwise stated)	Responsive sites/ total number of sites[†]	Treatment type	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat	2005-2007	Silt loam, sandy loam, sand; 0.5-1.2 mg/kg B	0/20	Broadcast	92-103%	9.4	Canterbury, New Zealand	Curtin *et al*., 2008
Winter wheat	2001	Chalky till; 1.2 ppm B	0/1	Foliar	-	9.72	Lincolnshire	Frontier, 2001
Winter wheat	2002	Flinty clay loam; 1.0 ppm B	0/1	Foliar	101%	11.83	Yorkshire	Frontier, 2002
Winter wheat	2003	Flinty clay loam; 2.3 ppm B	0/1	Foliar	-	11.99	Yorkshire	Frontier, 2003
Spring barley	1972-1973	Various	0/9	Broadcast	94-106%	5.1	North-east Scotland	Chalmers *et al*., 1999
Spring barley	1976	Sandy loam; 0.5 mg/l B (analysis method not stated)	0/1	Foliar	102%	2.08	Bristol area	Wadsworth, 1977

- denotes insufficient information available

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

5.1.2. Copper

Yield responses to Cu must be interpreted with caution, due to the fungicidal effects of Cu oxychloride, Cu sulphate, and other Cu compounds used as foliar nutrients. To separate the nutrient and fungicidal effects of Cu sprays, Cu response experiments should include a robust programme of non-Cu fungicides, and disease assessments to confirm effective disease control. Unfortunately, most reports on Cu response experiments do not contain sufficient detail to check whether this was the case.

Yield responses to applied Cu are variable, as shown by the cereal experiments summarised in Table 7. Of the replicated experiments in the UK, 63 out of 119 showed significant yield responses to Cu treatments (Table 7). However, many of these sites were chosen for their responsive status (e.g. Caldwell, 1971; Davies *et al*., 1971), so it cannot be assumed that this frequency of yield response would occur in UK crops as a whole. In a further series of unreplicated trials carried out in the UK, 19 out of 52 sites gave yield responses >0.38 t/ha, deemed by the authors to be 'significant' (Davies *et al*., 1971). Significant yield responses to Cu also occurred in 27 out of 54 replicated experiments in Canada, and 1 out of 23 experiments in New Zealand (Table 7). Across all the experiments, yield responses to Cu were more common in spring crops than in winter crops.

Across 30 field experiments in north-east Scotland, Reith (1968) found a significant negative correlation between EDTA-extractable soil Cu levels and the grain yield response to Cu treatment, with 18 out of 20 sites with soil Cu <0.7 ppm showing significant yield responses, but none of the sites with soil Cu >1.0 ppm (Table 7).

To further investigate the relationship between soil Cu status and cereal yield response to Cu treatment, an analysis was done of all the experiments from Table 7 for which soil analyses were available. The average yield of the Cu treatments in each experiment, as a percentage of the untreated control yield, was plotted against the EDTA-extractable or DTPA-extractable soil Cu status in mg/kg, mg/l or ppm, which are all equivalent units. Exponential curves were fitted to the data. For the unpublished ADAS reports in which analysis method was not stated (Wadsworth 1977, 1989) it was assumed that EDTA extraction was the method used, since this was the predominant method in use in the UK and method recommended by ADAS at the time.

For EDTA-extractable soil Cu, statistics supported the fitting of curves with separate linear parameters for each of the crops winter wheat, winter barley and spring barley; there were no data for spring wheat. The fitted curves ($P<0.001$, $R^2=0.403$) confirm that barley is more susceptible than wheat to Cu deficiency, and that spring barley is more susceptible than winter barley (Figure 5). For barley, large yield responses can occur at sites with <1.0 mg/kg EDTA-extractable Cu, but yield responses tend not to occur where EDTA-extractable soil Cu is >2 mg/kg, or for winter wheat

(Figure 5). For DTPA-extractable soil Cu, a single curve was fitted, as all but one data point was for spring wheat. The fitted curve ($P<0.001$, $R^2=0.313$) suggests that spring wheat responds strongly to Cu treatment on soils with <0.5 mg/kg DTPA-extractable Cu. These significant correlations imply that the majority of the yield responses listed in Table 7 were to Cu as a nutrient rather than as a fungicide.

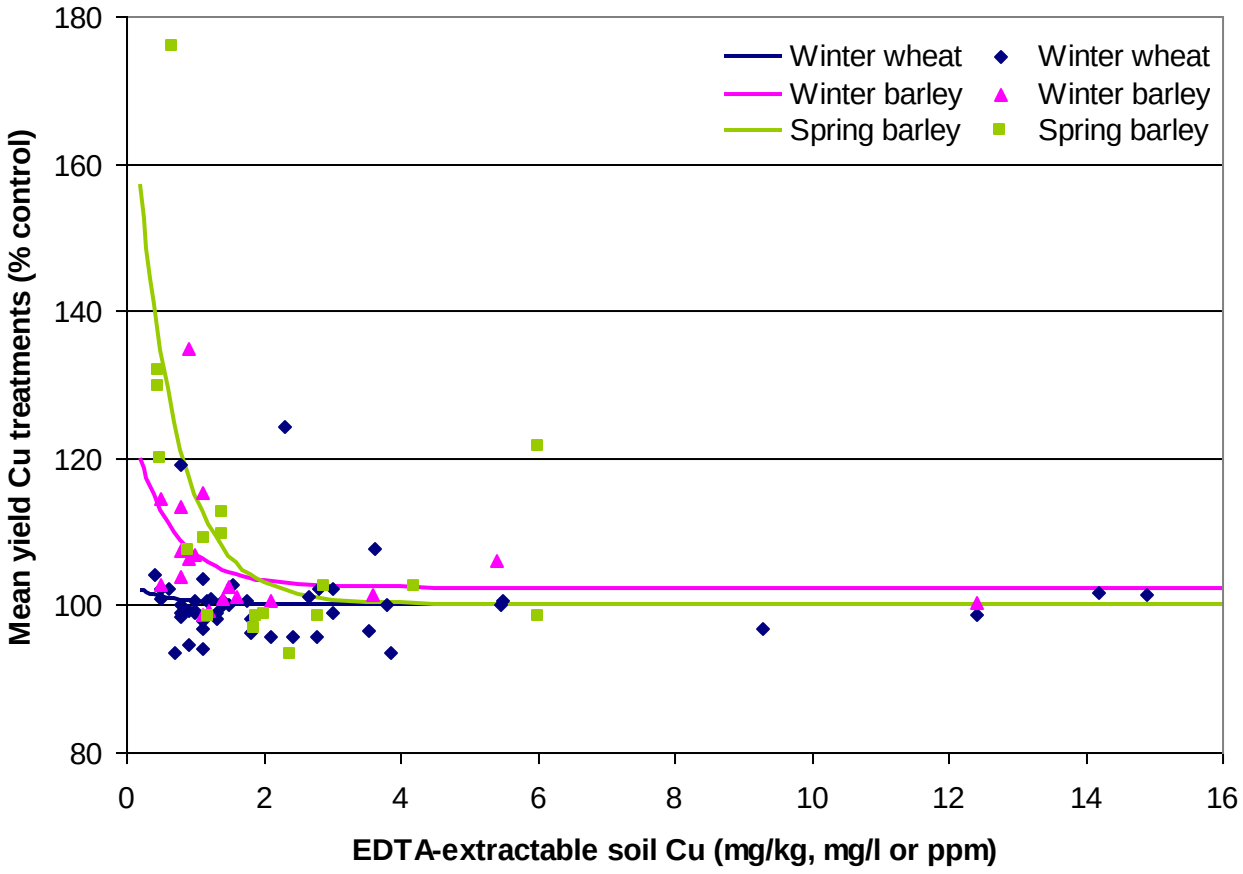

Figure 5. Relationship between EDTA-extractable soil copper levels and cereal yield responses to copper application for winter wheat, winter barley and spring barley ($P<0.001$; $R^2=0.403$). Mean treated yields are shown as a percentage of untreated control yield, and include foliar treatments, seed treatments, broadcast and soil incorporated treatments.

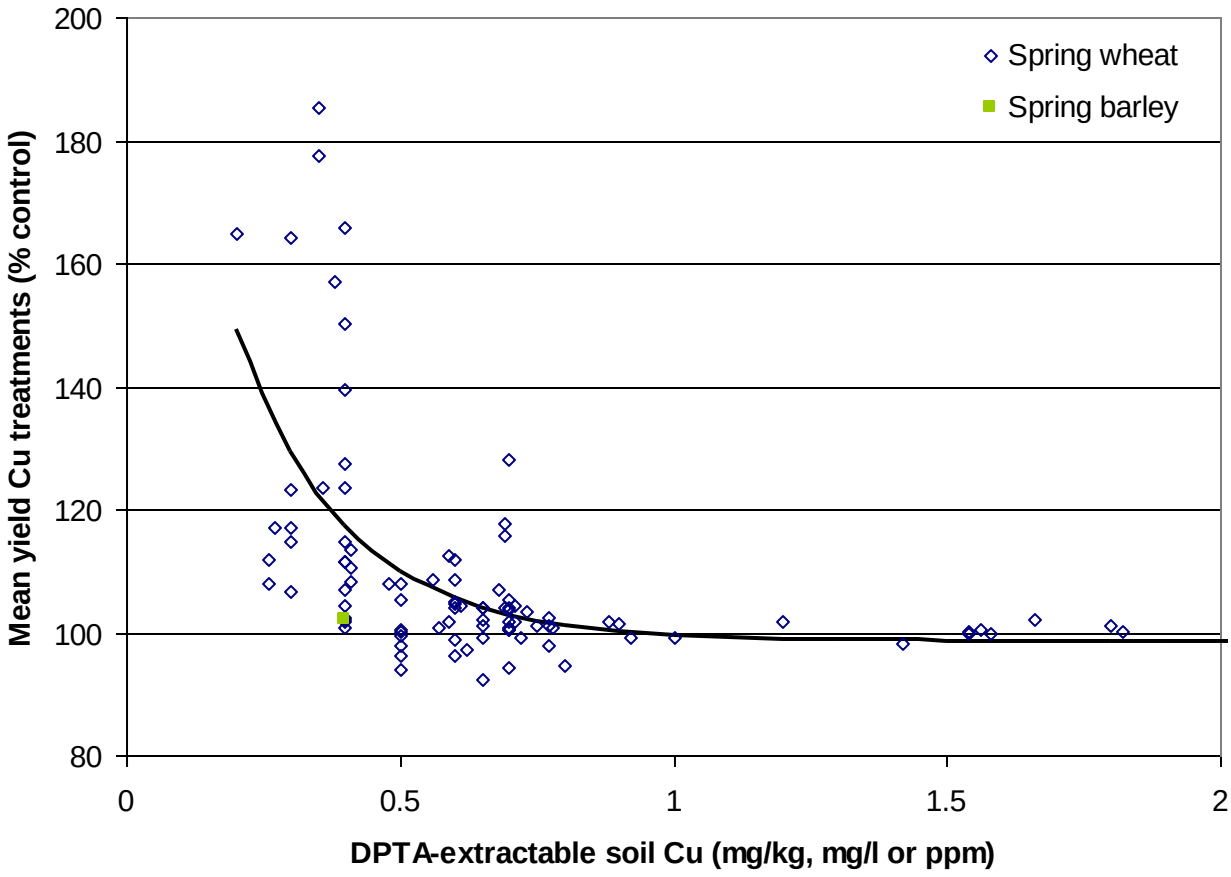

Figure 6. Relationship between DTPA-extractable soil copper levels and cereal yield responses to copper application for spring wheat and spring barley (P<0.001). Mean treated yields are shown as a percentage of untreated control yield, and include foliar treatments, broadcast and soil incorporated treatments.

Some studies have investigated the residual effect of Cu treatment in the years following applications; these have been reviewed by Sinclair & Withers (1995). Significant yield responses to residual Cu treatments have been recorded up to 18 years after application, showing that on deficient soils, applications of Cu sulphate to the soil can be effective for many years (Sinclair & Withers, 1995). This also suggests that soil Cu status is unlikely to change much from year to year, in the absence of Cu treatment, so it is unnecessary to test soil Cu levels every year even at high risk sites. There may be value in testing the soil in the year following a Cu treatment to check whether the soil Cu status has been sufficiently raised by the treatment.

Table 7. Yield responses to copper for field experiments carried out in the UK, Ireland, Canada and New Zealand for cereals. Bold treatments are those which led to significant yield responses.

Crop	Year	Soil type and copper content (EDTA-extractable, unless otherwise stated)	Responsive sites/ total number of sites†	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat	1952-1954	Light peat, loamy peat	2/3	Foliar	112-2020%	2.31	Cambridgeshire	Caldwell, 1971
Winter wheat	1965	-	1/1	Foliar	106%	4.34	Wiltshire	Davies *et al*., 1971
Winter wheat	1976	Peat; 2.3 mg/l Cu (analysis method not stated)	1/1	Foliar	124%	1.89	Bristol area	Wadsworth, 1977
Winter wheat	1983-1987	Silty clay loam; 0.4-1.1 mg/l Cu (analysis method not stated)	0/5	(Foliar)	99-105%	7.40	Hampshire	Wadsworth, 1989
Winter wheat	1988-1990	Shallow organic chalk soils	3/6	**-**	Mean 111% at responsive sites	-	Southern England	Sinclair & Withers, 1995
Winter wheat	2004	Flinty clay loam; 14.2 ppm Cu	0/1	(Foliar)	102%	12.42	Yorkshire	Frontier, 2004
Winter wheat	2005	Flinty clay loam; 14.9 ppm Cu	0/1	(Foliar)	101%	12.23	Yorkshire	Frontier, 2005
Winter wheat	2006	Sandy loam, flinty clay loam, limestone brash; 4.3-12.4 ppm Cu	0/3	(Foliar, seed treatment)	100%	10.33	Lincolnshire, Yorkshire	Frontier, 2006b
Winter wheat	2005-2007	Silt loam, sandy loam, sand; 0.5-3.7mg/kg Cu	1/23	Foliar, (broadcast**)**	90-107%	9.33	Canterbury, New Zealand	Curtin *et al*., 2008
Winter wheat	2010	Well drained calcareous silty soil over chalk. pH 7.9	0/1	(Foliar)	99%	10.11	East Yorkshire	NIAB TAG (TAG central treatments)

Crop	Year	Soil type and copper content (EDTA-extractable, unless otherwise stated)	Responsive sites/ total number of sites†	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat	2010-2012	Light, organic & calcareous soils; 0.79-9.28 mg/kg Cu.	1/15	Foliar	93-119%	7.97	Cambridgeshire, Norfolk, Bedfordshire, Lincolnshire, Hertfordshire, West Yorkshire	McGrath, 2012
Spring wheat	1948-1961	Light peat, calcareous loamy peat / peaty loam	10/10	Foliar	148-1431%	1.31	Cambridgeshire, Norfolk	Caldwell, 1971
Spring wheat	1961-1962	-	2/2	Foliar	116-149%	2.70	Wiltshire	Davies *et al*., 1971
Spring wheat	1984	Loam; 0.23-0.4 mg/kg Cu (DTPA extractable)	2/2	Broadcast & incorporation, (foliar)	87-140%	2.16	Northern Saskatchewan, Canada	Karamanos *et al*., 1986
Spring wheat	1991-2000	Various; 0.3-1.82 mg/kg Cu (DTPA extractable)	48/60*	Foliar, or broadcast & incorporation	92-177%	3.77	Northeastern Saskatchewan, Canada	Karamanos *et al*., 2003b
Spring wheat	1995-2002	Various; 0.11-0.704 mg/kg C (DTPA extractable)u	5/12	Foliar or broadcast & incorporation	95-216%	1.93	Alberta and Maitoba, Canada	Karamanos *et al*., 2004
Spring wheat	1995-2002	Various; 0.2-0.78 mg/kg Cu (DTPA extractable)u	7/16	Foliar, broadcast & incorporation or seedrow	93-218%	2.73	Ontario, Alberta, Canada	Karamanos *et al*., 2005a
Spring wheat	1995-2002	Silty clay loam; 0.2-0.8 mg/kg Cu (DTPA extractable)u	8/13	Foliar, broadcast & incorporation or seedrow	80-463%	2.63	Alberta, Minnesota, Saskatchewan, Canada	Karamanos *et al*., 2005b
Spring Wheat	1999-2001	Sandy loam; 0.4 mg/kg Cu (DTPA-extractable)	3/3	Foliar, broadcast & incorporation or seedrow	50-239%	1.48	Northeastern Saskatchewan, Canada	Malhi *et al*., 2005
Spring wheat	2005-2007	Sandy loam; 0.4 mg/kg Cu (DTPA extractable)	1/1	Seedrow or broadcast & incorporation	126-148%	1.65	Manitoba, Canada	Malhi, 2009

Crop	Year	Soil type and copper content (EDTA-extractable, unless otherwise stated)	Responsive sites/ total number of sites[†]	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Spring wheat	2001	Various; 0.30-0.88 mg/kg Cu (DTPA extractable)	1/6	Broadcast & incorporation	92-123%	6.88	Manitoba, Canada	Rehm, 2008
Mostly barley; some wheat	1962-1965	Various	19/52[§]	Foliar	-	3.46	Sussex, Berkshire, Hampshire, Oxfordshire, Eastern region	Davies *et al*., 1971
Winter barley	1976	Silty clay loam; 5.4 mg/l Cu (analysis method not stated)	0/1	(Foliar)	106%	4.69	Bristol area	Wadsworth, 1977
Winter barley	1983	Silty clay loam; 0.6-1.1 mg/l Cu (analysis method not stated)	2/3	Foliar	93-112%	5.34	Hampshire	Wadsworth 1989
Winter barley	1985	Sandy loam, 1.6-2.1 mg/kg Cu	0/2	(Foliar, incorporation)	98-107%	6.60	North-east Scotland	Sinclair & Withers, 1995
Winter barley	1985-1986	Sandy loam; 0.5, 1.1, 1.4, 1.5 & 3.6 mg/kg Cu	2/5	Foliar	99-116%	6.92	North-east Scotland	Sinclair *et al*., 1990; Sinclair & Withers, 1995
Winter barley	2006	Flinty clay loam; 12.4 ppm Cu	1/1	Foliar, (seed treatment)	100-101%	10.95	Yorkshire	Frontier, 2006c
Spring barley	1983	0.40 mg/kg Cu (DTPA extractable)	0/1	(Foliar, broadcast & incorporation)	101-103%	2.98	Northern Saskatchewan, Canada	Karamanos *et al*., 1986
Spring barley	1952-1964	Light peat, calcareous sandy peat, loamy sand	6/6	Foliar	131-2622%	1.47	Cambridgeshire, Suffolk	Caldwell, 1971
Spring barley and oats	1956-1964	Freely drained sands & loams; ≤0.7 ppm Cu	18/20	Broadcast	101- >200%	2.59	North-east Scotland	Reith, 1968
Spring barley and oats	1956-1964	Freely drained sands & loams; 0.8-1.0 ppm Cu	2/5	Broadcast	Mean 107%	2.38	North-east Scotland	Reith, 1968

Crop	Year	Soil type and copper content (EDTA-extractable, unless otherwise stated)	Responsive sites/ total number of sites†	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Spring barley and oats	1956-1964	Freely drained sands & loams; >1.0 ppm Cu	0/5	(Broadcast)	Mean 97%	3.46	North-east Scotland	Reith, 1968
Spring barley	1961-1965	-	10/10	Foliar	111-260%	2.62	Wilshire, Sussex	Davies *et al*., 1971
Spring barley	1968-1969	Calcareous sandy loam	0/1	-	102%	3.96	Cambridgeshire	Richardson, 1969
Spring barley	1969	Calcareous silty loam; 2.4-4.2 mg/l Cu	0/2	-	94-103%	5.28	Bedfordshire, Hertfordshire	Eagle, 1970
Spring barley	1976	Sandy loam, silty clay loam; 1.4-2.9 mg/l Cu (analysis method not stated)	0/3	(Foliar)	99-110%	2.86	Bristol area	Wadsworth, 1977
Spring Barley	1980-1982	Peat pH 5.6; 5.0-8.0mg/kg Cu.	2/3	Broadcast & incorporation, (spray & incorporation, foliar)	78%-165%	3.32	Ireland	MacNaeidhe & Fleming, 1984a
Spring Barley	1992	Clay loam, loam, gravelly loam; 1.2-2.8 mg/l Cu	2/3	Foliar	100-113%	6.36	Co. Louth, Co. Wiclow, Co. Cork, Ireland	Barclay trials (data provided by Teagasc)
Winter OSR	2007		0/1	(Foliar)	103%	4.12	East Yorkshire	NIAB TAG (Daltons)

- Insufficient detail in report.

† A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

* All sites with yield increases counted as responsive; significance not determined in publication.

§ Unreplicated trials consisting of adjacent sprayed and unsprayed strips; all sites with yield response >0.38 t/ha counted as responsive

A series of seven experiments in Alberta and Manitoba in Canada analysed the effects of soil and foliar applied Cu ($CuSO_4 \cdot 5H_2O$) on yield in spring wheat (Karamanos *et al*., 2004; Table 8). Five of the experiments were carried out on Cu deficient soils (≤4 mg/kg DTPA-2 extractable Cu) and the remaining two on soils containing marginal Cu concentrations. On average, soil treatment alone had the largest effect on yield, with an increase of 1.06 t/ha in comparison to the untreated control. It should be recognised that the soil applied treatment was at a higher rate (4 kg Cu/ha) than the foliar treatment (0.2 kg Cu/ha). The experiments carried out on soils with marginal Cu levels showed no significant increase in yield in response to soil or foliar copper treatment. A number of additional experiments which were carried out on marginal Cu soils also showed no yield increase in response to Cu application (Karamanos *et al*., 2004). When assessing the relevance of Canadian data to UK crops, it should be noted that many Canadian sites have 'humic' soils, with high organic matter, which are at greater risk of Cu deficiency than soils with <5% organic matter. Soil organic matter ranged from 4.4 to 7.9% at the sites shown in Table 8.

Table 8. Yield responses of spring wheat to soil and foliar applied copper in a series of experiments in Alberta and Manitoba. Canada. Data from Karamanos *et al*., 2004. Data in this table are also summarised in Table 7.

Year	Trial No	DTPA-2 extractable Cu (mg/kg)	Rate of soil applied Cu (kg/ha)	Stage at foliar application of 0.2 kg/ha Cu		
				None	GS31	GS47
				Yield (% of untreated control)		
1995	1	0.38	0	100	140	151
			4	173	155	166
1996	2	0.7	0	100	104	103
			4	107	106	101
1996	3	0.4	0	100	165	203
			4	216	192	192
1997	4	0.35	0	100	178	161
			4	205	184	202
1998	5	0.4	0	100	140	141
			4	173	174	190
1998	6	0.56	0	100	104	
			4	107	106	
1999	7	0.3	0	100	128	177
			4	163	162	191
		Average yields (t/ha)	0	1.93	2.54	2.73
			4	2.99	2.82	2.94

A small series of experiments carried out between 2000 and 2001 on spring wheat in Northwestern Minnesota, Canada showed a number of positive effects of Cu on yield (Table 9; Rehm, 2008). A

significant yield increase in response to broadcast Cu fertiliser application before drilling was present at one of the six sites tested. However, the average least significant difference (LSD) was 1.97 t/ha, which is much greater than the yield increase which would be required for an economic gain; significant and economic yield responses might have been detected at more sites, with greater experimental precision. Overall, application of the higher rate of Cu chelate led to the largest yield increase.

Table 9 Yield responses of spring wheat to broadcast copper fertilisers in a series of experiments in Northwestern Minnesota, Canada (Rehm, 2008). Treatment means in each column followed by the same letter are not significantly different at the 95% confidence level. Data in this table are also summarised in Table 7.

Treatment	Cu applied (kg/ha)	Site						
		1	2	3	4	5	6	Mean
		Yield (t/ha)						
None	0	7.59a	9.61a	5.11a	6.19a	8.38a	4.38a	6.43
Copper sulphate	6.7	9.21a	11.29a	5.49a	7.51a	9.86a	4.71a	8.01
Copper sulphate	13.4	8.89a	9.16a	6.32b	7.24a	8.05a	5.44a	7.52
Copper chelate	6.7	8.49a	9.34a	9.32b	6.92a	8.16a	5.22a	7.91
Copper chelate	13.4	10.95a	9.34a	6.00ab	8.82a	8.16a	5.13a	8.07
LSD (0.05)		3.36	1.98	1.08	2.73	1.71	0.94	

Relatively few experiments have investigated oilseed rape yield responses to Cu. A series of ADAS experiments from 1985 to 1988 found significant responses to Cu oxychloride at two out of 14 sites, both of which had 1.8 mg/l soil Cu (Withers, 1988). The 12 non-responsive sites had higher soil Cu levels.

5.1.3. Manganese

Although Mn deficiency is thought to be the most prevalent micronutrient deficiency in the UK for cereals, yield responses to applied Mn are inconsistent. Table 10 summarises cereal and oilseed rape Mn response experiments carried out from 1976 to 2012 in the UK, Ireland and New Zealand. Significant yield responses to Mn were found in 28 out of 77 UK experiments, three out of eight Irish experiments and two out of 23 New Zealand experiments.

A series of spring barley experiments in north-east Scotland demonstrated that the same sites tend to respond to Mn applications year after year: the significant spring barley yield responses listed in Table 10 in north-east Scotland, 1982 to 1987 (Chalmers *et al*., 1999; Clayton *et al*., 1987; Sinclair, 1983) were all at the same site, while the non-significant responses listed in the same rows were from a range of other sites.

For each crop, paired t-tests were done to compare untreated yield and mean Mn treated yield in all the experiments listed in Table 10. A paired t-test was not carried out for oilseed rape since there was only data for a single experiment. There was a significant effect of Mn treatment for winter barley (P=0.004) and spring barley (P=0.001), with the average treated yield being 110 to 111% of untreated control yield. There was no significant effect for winter wheat, and insufficient data to run a t-test for spring wheat.

To investigate the relationship between soil Mn status and yield response, an analysis was done of all the experiments from Table 10 for which soil analyses by EDTA-extraction were available. There were too few data points to discern any relationship for other extraction methods, and too little consistency of extraction methods to allow assumptions about the methods used where not stated in the original report. The average yield of the Mn treatments in each experiment, as a percentage of the untreated control yield, was plotted against the EDTA-extractable soil manganese status in mg/kg, mg/l or ppm (which are all equivalent units). The resulting graph shows that yield responses to Mn do not correlate with EDTA-extractable soil Mn (Figure 7). In contrast, when yield response to Mn is plotted against pH, a positive correlation is observed, although with a high level of scatter ($P<0.001$, $R^2=0.179$; Figure 8). The correlation with pH is consistent with published literature showing that soluble Mn decreases at greater pH levels (Lindsay, 1972). Mean yield was also plotted against Mn tissue levels, mostly measured in early spring, and in this case there is a negative correlation ($P=0.003$, $R^2=0.221$; Figure 9). Significant yield responses are common when tissue Mn is <20 mg/kg, but rare at higher levels.

The failure of the winter wheat t-test to show a significant effect of Mn treatment on winter wheat yield may be because the majority of the winter wheat experiments were done on acidic soils (Figure 8), hence it should not be assumed that wheat would not respond to Mn at sites with higher soil pH.

Table 10. Yield responses to manganese for field experiments carried out in the UK, Ireland and New Zealand for cereals and oilseed rape. Bold treatments are those which led to significant yield responses.

Crop	Year	Soil type and manganese content	Responsive sites/ total number of sites[†]	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat	1976	Peat; 9 mg/l exchangeable Mn; 250 g/l easily reducible Mn (analysis methods not stated)	1/1	Foliar	117%	1.89	Bristol area	Wadsworth, 1977
Winter wheat	1980-1982	-	2/6	Foliar	95-195%	3.91	Buckinghamshire, Cambridgeshire, Oxfordshire	Royle, 1984
Winter wheat	1987-1988	-	0/2	(Foliar)	-	-	Berkshire, Buckinghamshire	Royle, 1988
Winter wheat	1988	Site not Mn deficient	1/1	Seed treatment	118%	-	Leicestershire	Smedley, 1991[§]
Winter wheat	1997	Loamy peat with history of deficiency	1/1	Foliar	114-163%	3.87	Cambridgeshire	Anon, 1997
Winter wheat	2001	-	0/1	(Seed treatment, foliar)	99-100%	10.8	Lincolnshire	NIAB TAG (Daltons)
Winter wheat	2005-2007	Silt loam, sandy loam, sand; 19-80 mg/kg Mn (EDTA-extractable)	2/23	(Foliar)	92-112%	9.33	Canterbury, New Zealand	Curtin *et al*., 2008
Winter wheat	2010	Well drained calcareous silty soil over chalk. pH 7.9	0/1	(Foliar)	99%	10.11	East Yorkshire	NIAB TAG (TAG central treatments)
Winter wheat	2011	145 mg/l Mn (EDTA-extractable)	0/1	(Seed treatment and foliar)	98-101%	9.40	Meath, Ireland	Teagasc Better Farms
Winter wheat	2010-2012	Light, organic & calcareous soils. 3.9-64.9 mg/kg Mn.(EDTA extractable)	0/15	(Foliar)	95-107%	7.97	Cambridgeshire, Norfolk, Bedfordshire, Lincolnshire, Hertfordshire, West Yorkshire	McGrath, 2012

Crop	Year	Soil type and manganese content	Responsive sites/ total number of sites[†]	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Spring wheat	1980-1981	-	0/2	(Foliar)	96-111%	4.52	Cambridgeshire	Royle, 1984
Winter barley	1976	Silty clay loam; 2 mg/l exchangeable Mn; 112 mg/l easily reducible Mn (analysis methods not stated)	0/1	(Foliar)	105%	4.69	Bristol area	Wadsworth, 1977
Winter barley	1984-1987	Organic sand loam, loam sand, organic fine sand loam, peat.	6/10	Foliar	92-213%	4.88	Lincolnshire, Lancashire, Nottinghamshire, Yorkshire, UK	Royle, 1988
Winter barley	1982	-	0/2	(Foliar)	89-109%	5.58	Gloucestershire, Yorkshire	Royle, 1984
Winter barley	1982	Sandy silt loam	0/1	(Foliar, seed treatment)	-	-	Aberdeenshire	Chalmers *et al*., 1999
Winter barley	1988	Sites not Mn deficient	0/3*	(Seed treatment)	-	-	Leicestershire, Lincolnshire, Bedfordshire	Smedley, 1991[§]
Winter barley	1992	Loam, 135 mg/l Mn (EDTA-extractable)	1/1	Foliar	106-121%	6.2	Co. Waterford, Ireland	Barclay trials (data provided by Teagasc)
Winter barley	2000	Fine sand; 63 ppm Mn (ammonium acetate + quinol extractable)	0/1*	(Seed treatment, foliar)	103-104%	9.30	Yorkshire	Frontier, 2000
Winter barley	2007	Sandy loam; 60 ppm Mn (ammonium acetate + quinol extractable)	1/1	Seed treatment	105%	7.34	Yorkshire	Frontier, 2007
Winter barley	2008	Flinty clay loam; 199 ppm Mn (ammonium acetate + quinol extractable)	1/1	Seed treatment, foliar	103-106%	10.37	Yorkshire	Frontier, 2008b

Crop	Year	Soil type and manganese content	Responsive sites/ total number of sites[†]	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter barley	2010	Silty clay loam; 33 ppm Mn (ammonium acetate + quinol extractable)	0/1	(Foliar)	99-100%	10.96	Cambridgeshire	Frontier, 2010a
Spring barley	1968-1969	Calcareous sandy loam	0/2	(Foliar)	103-105%	3.78	Cambridgeshire	Richardson, 1969
Spring barley	1976	Sandy loam, silty clay loam; 3-4 mg/l exchangeable Mn; 76-1015 mg/l easily reducible Mn (analysis methods not stated)	0/3	(Foliar)	80-96%	2.68	Bristol area	Wadsworth, 1977
Spring barley	1980	Loamy peat; 0.9 mg/l exchangeable Mn; 9.6 mg/l easily reducible Mn (analysis methods not stated)	1/1	Foliar	87%-145%	3.44	Staffordshire	Anon, 1980a
Spring barley	1980-1981	Sandy loam; 0.9-2.4 mg/kg Mn (ammonium acetate extractable)	2/3	Foliar	98%-123%	5.02	South-east Scotland	Holmes *et al.*, 1983
Spring barley	1981	Loamy peat; 2.1 mg/l exchangeable Mn; 9.6 mg/l easily reducible Mn (analysis methods not stated)	1/1	Foliar	96%-134%	2.82	Staffordshire	Webb & Richardson, 1981
Spring barley	1980-1982	-	3/7	Foliar	97%-154%	3.28	Nottinghamshire, Yorkshire, Essex, Shropshire, UK	Royle, 1984
Spring barley	1980-1982	Peat Ph 6.1; 15.5 mg/kg Mn (calcium nitrate extractable)	1/3	Spray & incorporation, foliar, (broadcast & incorporation)	86%-150%	5.13	Ireland	MacNaeidhe & Fleming 1984b

Crop	Year	Soil type and manganese content	Responsive sites/ total number of sites[†]	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Spring barley	1982	Sandy loam; Ph 6.6	1/1	Seed treatment	35-45%	-	North-east Scotland	Sinclair, 1983; Chalmers *et al*., 1999
Spring barley	1983	Sandy loam, sandy silt loam; Ph 6.5-6.6	1/2	Seed treatment, foliar	132-138% (responsive site)	3.57 (responsive site only)	North-east Scotland	Chalmers *et al*., 1999
Spring barley	1984	Sandy loam, shelly sand	1/2	Foliar, (seed treatment)	84-127% (responsive site)	5.18 (responsive site only)	North-east Scotland	Chalmers *et al*., 1999
Spring barley	1987	Sandy loam; Ph 6.6	1/1	Seed treatment, foliar	112-123%	-	North-east Scotland	Clayton *et al*., 1987; Chalmers *et al*., 1999
Spring barley	1986	Sand loam, loam sand.	2/2	Foliar	101-123%	4.59	Staffordshire, Nottinghamshire, UK	Royle, 1988
Spring barley	1986-1988	All deficient soils	2/3*	Seed treatment, foliar	108-128%	-	Scotland	Smedley, 1991[§]
Spring barley	1992	Clay loam and gravelly loam; 120-250 mg/l Mn. (EDTA-extractable)	1/2	Foliar	102-108%	5.55	Co. Louth and Co. Tipperary, Ireland	Barclay trials (data provided by Teagasc)
Spring barley	2011	487 mg/l Mn. (EDTA-extractable)	0/1	(Foliar.)	99-101%	7.41	Wexford, Ireland	Teagasc Better Farms
Winter OSR	2007	-	0/1	(Foliar)	100%	4.12	East Yorkshire	NIAB TAG (Daltons)

- Insufficient detail available.

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

* Statistics not available; sites counted as responsive with >5% yield response.

[§] Personal communication from M. Smedley, Seed Coating and Technology Unit, Nickerson Seeds Limited to P. Dampney, ADAS, 10 September 1991.

[‡] Treatments vary too much between experiments to average across experiment series.

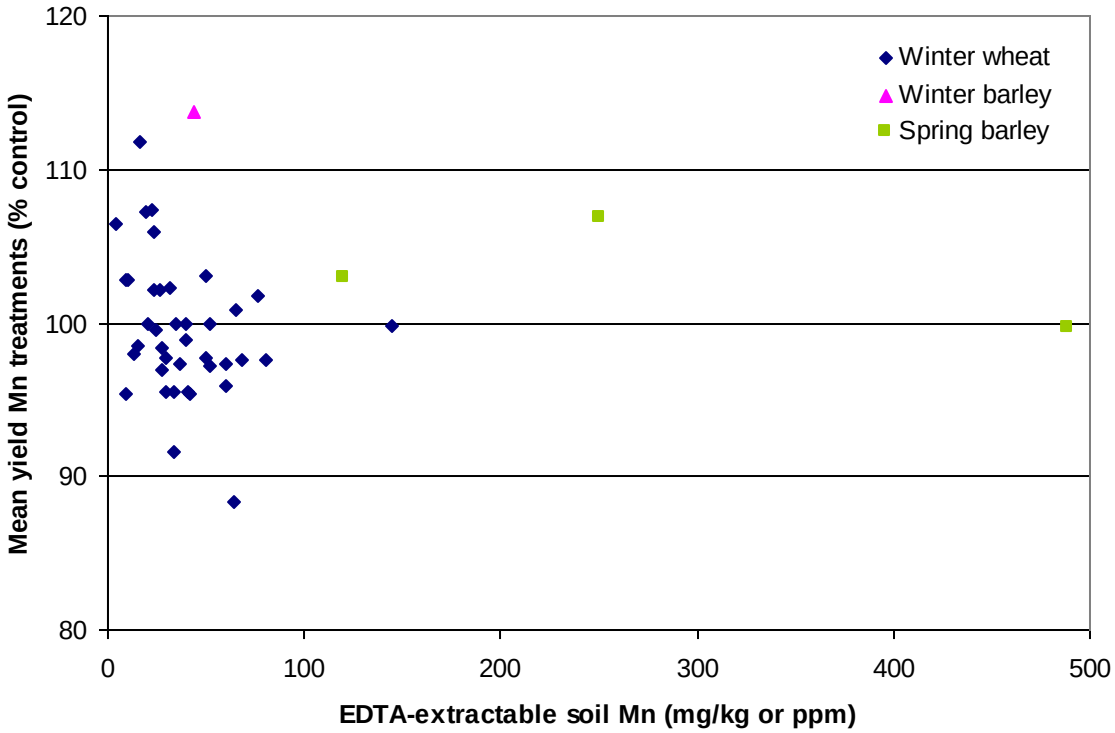

Figure 7. Relationship between EDTA-extractable soil manganese levels and cereal yield responses to manganese applications. Mean treated yields are shown as a percentage of untreated control yield, and include foliar treatments and seed treatments.

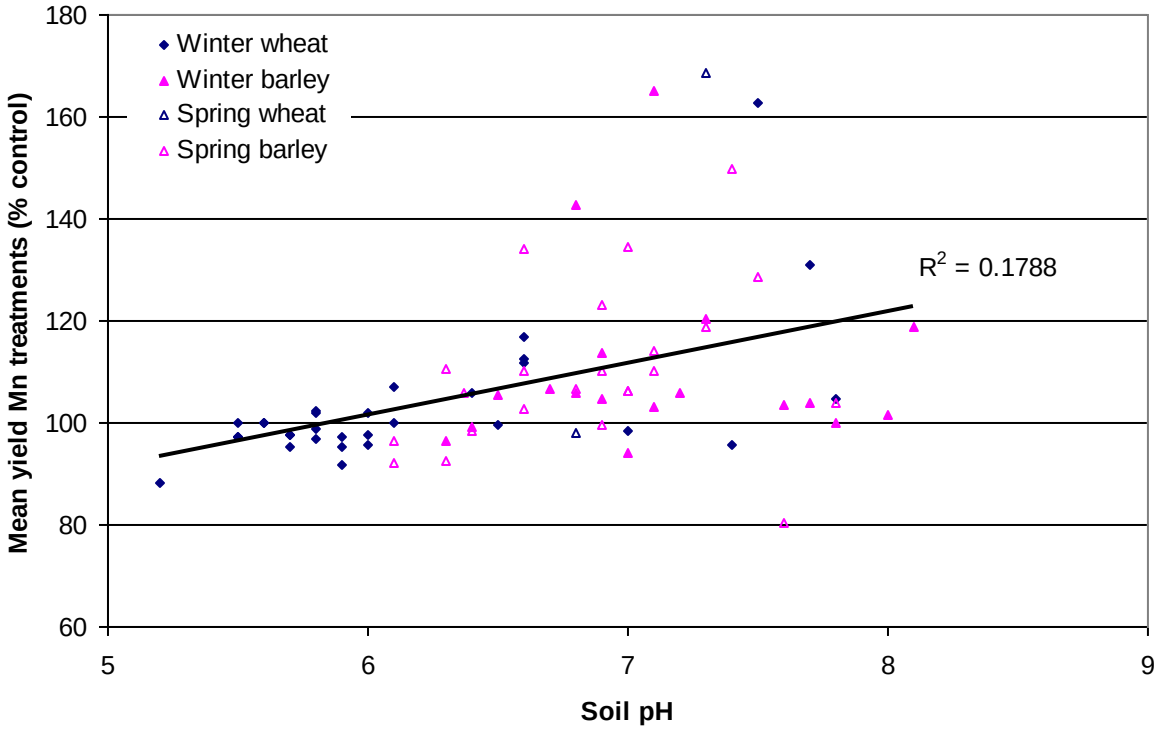

Figure 8. Relationship between soil pH and cereal yield responses to manganese applications (P<0.001). Mean treated yields are shown as a percentage of untreated control yield, and include foliar treatments, seed treatments, broadcast and soil incorporated treatments.

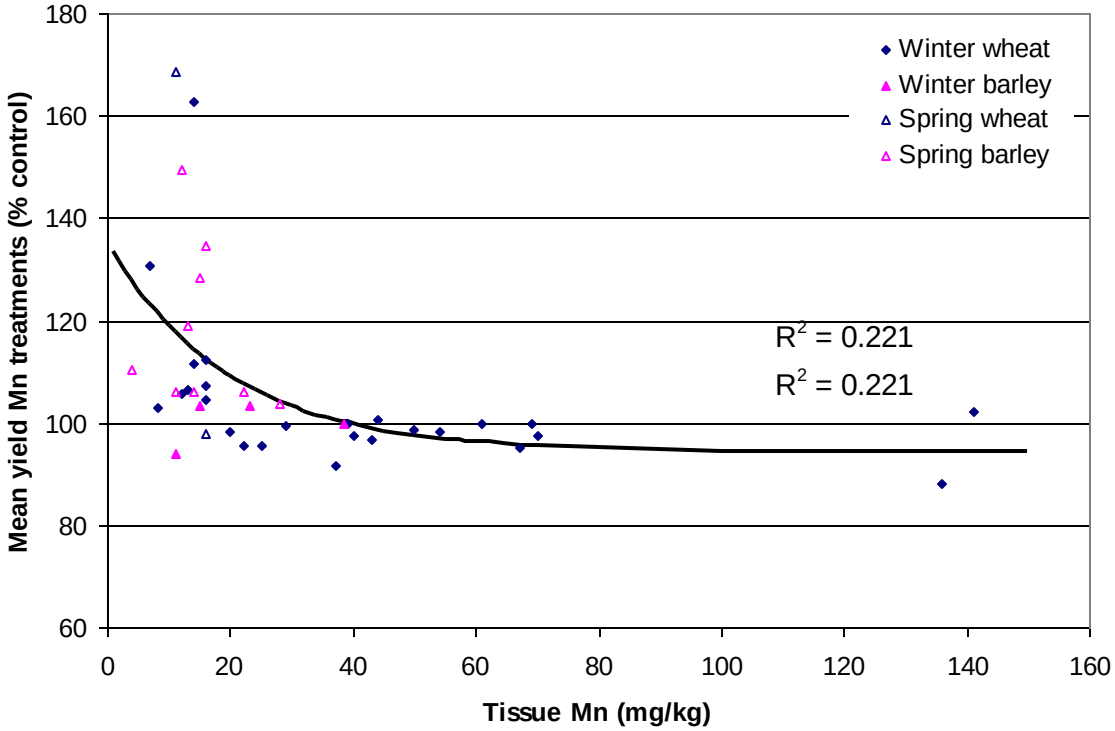

Figure 9. Relationship between tissue manganese levels and cereal yield responses to manganese applications (P=0.003). Mean treated yields are shown as a percentage of untreated control yield, and include foliar treatments, seed treatments, broadcast and soil incorporated treatments.

The high level of scatter in the correlations between yield response to Mn, soil pH and tissue Mn implies that these two factors may interact, and that other factors are also likely to have an effect. An attempt was made to determine the combined effects of soil pH and tissue Mn on yield response, for the experiments for which both test results were available. The best relationship found explained 31% of variation (Figure 10). It suggests that while the tissue threshold of 20 mg/kg may be an appropriate guide of whether to apply Mn on soils with pH <7, a higher threshold would be appropriate at pH 7 to 7.8, and Mn should always be applied soils with pH >7.8 (Figure 11). However, more data are necessary to confirm this relationship, as it based on too few data points for firm conclusions to be drawn, and there are clearly other factors affecting the yield response to Mn besides soil pH and tissue Mn.

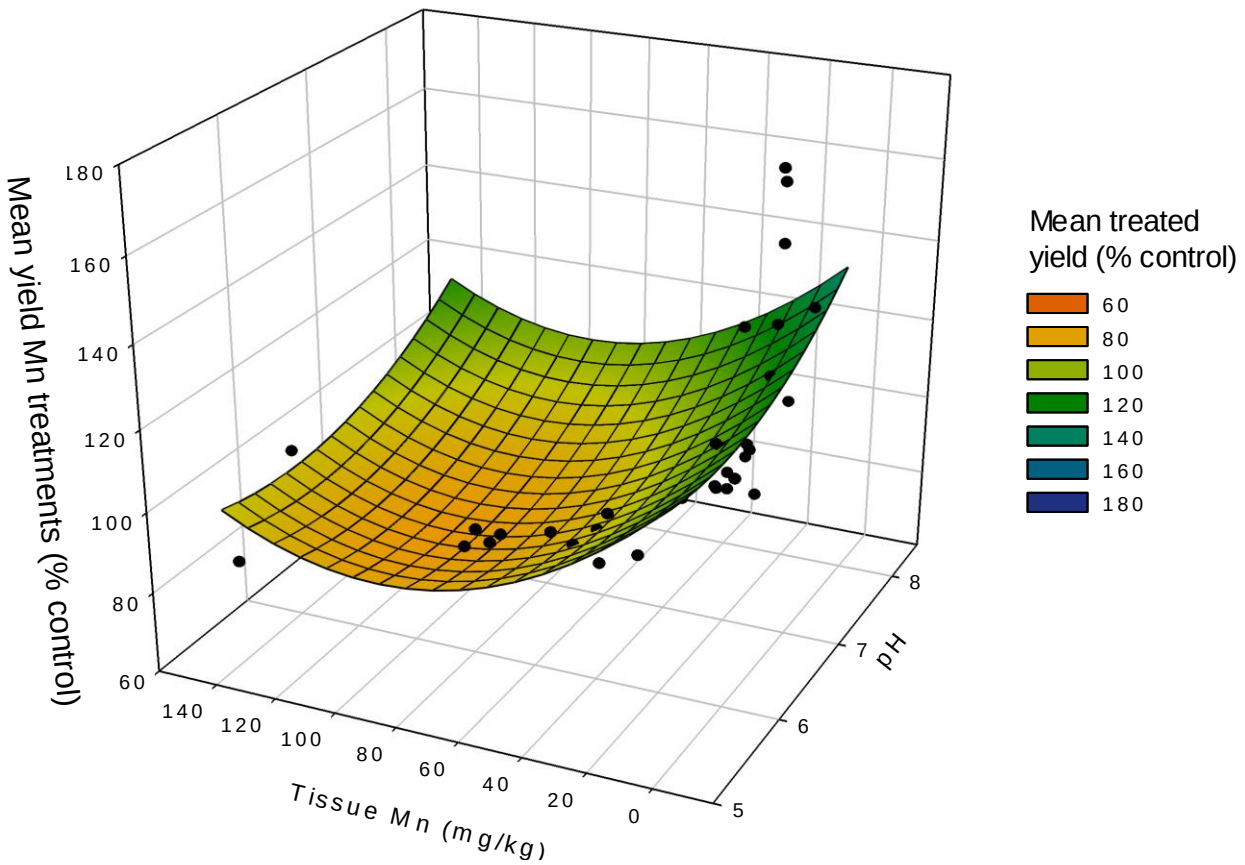

Figure 10. Relation ship between yield response to manganese (as % of untreated control yield), soil pH and tissue manganese concentration (mg/kg) for 36 experiments. Paraboloid relationship fitted using Sigma Plot: $f = 274.1697 - 51.569\ x - 0.7103\ y + 4.3026\ x^2 + 0.0039\ y^2$, where x = soil pH, y = tissue Mn and z = yield response. R^2=0.3141.

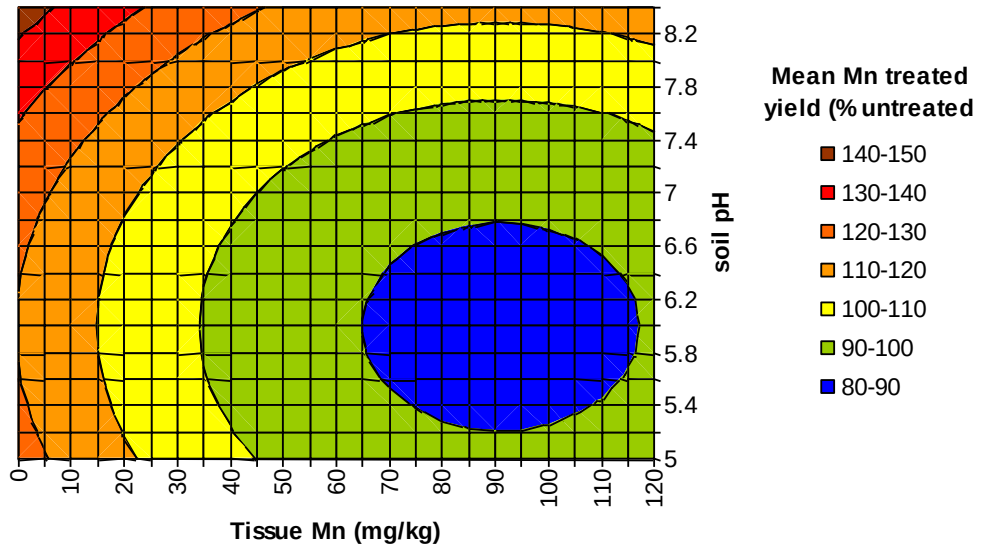

Figure 11. Multiple regression of yield response to manganese (as % of untreated control yield) against soil pH and tissue manganese concentration (mg/kg) as shown in Figure 10, demonstrating how the tissue Mn threshold to justify Mn treatment may vary with soil pH.

Relatively few experiments have investigated oilseed rape responses to Mn. In a series of seven ADAS experiments from 1985 to 1988, on sites with a history of cereal Mn deficiency, there were no significant responses to foliar applications of full-rate Mn EDTA in spring (Withers, 1988). However, this evidence is insufficient to conclude that Mn deficiency never occurs in oilseed rape.

5.1.4. Magnesium

Relatively few experiments have tested yield responses to Mg. Significant responses were found in one out of seven cereal experiments and one out of seven oilseed rape experiments (Table 11). When interpreting Mg experiments, it is important to note that Mg is usually applied as a sulphate (e.g. Epsom salts, kieserite), so if experiments do not ensure adequate sulphur nutrition using other sulphur fertilisers, there is a risk that what is presented as a Mg response may be, at least in part, a sulphur response.

The one wheat experiment showing a significant response to Mg was carried out by Masstock on a deficient soil (22.3 ppm Mg; index 0) in Hampshire in 1990 (Anon, 1990). Epsom salts (magnesium sulphate) were applied at total rate of 25 kg/ha with a range of single and split timings (GS 51, GS 59 and GS 80). All treatments significantly increased yield over the untreated control yield of 5.63 t/ha, with the responses ranging from 1.48 to 3.72 t/ha, but these yield responses could as easily be a response to sulphur as to Mg. There was a trend for greater yield responses to split applications and treatment programs, including earlier applications. Yield responses appeared to result from a reduction in the number of blind grain sites, particularly near the base of the ear; there were no effects on thousand grain weight.

The one oilseed rape experiment showing a significant response was carried out by Frontier on a soil with 121 ppm Mg, which would not normally be classed as deficient. However, plant tissue Mg analyses in autumn and spring were below the guideline value used by the analytical laboratory in question. Yield was increased significantly for only one of the two varieties tested, by foliar Mg applications in both autumn and spring, but not by applications only in autumn or only in spring (Frontier, 2008a).

There is no correlation between ammonium nitrate-extractable soil Mg and yield response to Mg (Figure 12); unfortunately the one large yield response to Mg (which might be a response to sulphur, as discussed above) occurred at a site at which a different extraction method had been used to analyse soil Mg. More data would allow this relationship to be more rigorously evaluated; however, Mg deficiency is known to be more likely as a result of poor soil conditions than due to a shortage of Mg in the soil (section 4.5.1).

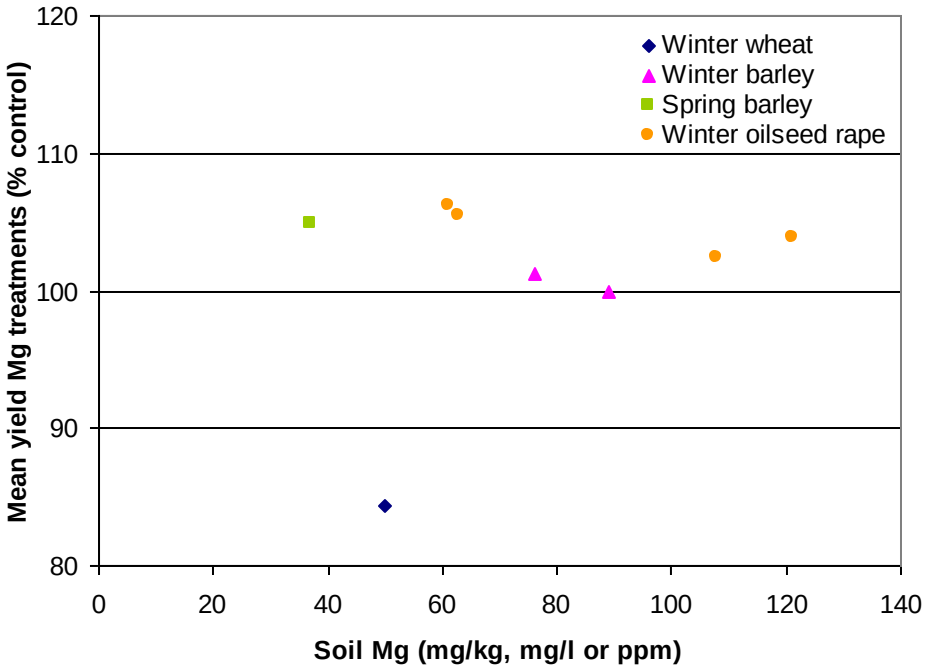

Figure 12. Relationship between ammonium nitrate-extractable soil magnesium levels and yield responses to magnesium applications. Mean treated yields are shown as a percentage of untreated control yield, and include foliar treatments and soil incorporated treatments.

Table 11. Yield responses to magnesium for field experiments carried out in the UK and Ireland for cereals and oilseed rape. Bold treatments are those which led to significant yield responses.

Crop	Year	Soil type and magnesium content (ammonium nitrate extraction, unless otherwise stated)	Responsive sites/ total number of sites[†]	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat	1972	50 mg/l Mg	0/1	(Incorporated)	84%	2.36	Suffolk	Draycott *et al*., 1975
Winter wheat	1990	Very thin loam over chalk, 22.3 ppm Mg (analysis method not stated)	1/1	Foliar	126-166%	5.63	Hampshire	Anon, 1990
Winter wheat	2010	305 mg/l Mg (sodium acetate extraction)	0/1	(Foliar)	98-101%	12.41	Co. Wexford, Ireland	Teagasc Better Farms
Winter wheat	2011	-	0/1	(Foliar)	96-99%	11.99	East Yorkshire	NIAB TAG
Winter barley	2010	Flinty clay loam; 76 ppm Mg	0/1	(Foliar)	101-102%	9.57	Yorkshire	Frontier, 2010b
Winter barley	2011	Flinty clay loam; 89 ppm Mg	0/1	(Foliar)	99-101%	9.55	Yorkshire	Frontier, 2011a
Spring barley	1972	37 mg/l Mg	0/1	(Incorporated)	105%	3.49	Suffolk	Draycott *et al*., 1975
Winter OSR	1985-1988	17-20 mg/l Mg (analysis method not stated)	0/2	(Incorporated)	-	-	-	Withers, 1988
Winter OSR	2007	-	0/1	(Foliar)	105%	4.12	East Yorkshire	NIAB TAG (Daltons)
Winter OSR	2008	Flinty clay loam, limestone brash; 61-121 ppm Mg	1/2	Foliar	100-111%	3.50	Lincolnshire, Yorkshire	Frontier, 2008a
Winter OSR	2012	Flinty clay loam, limestone brash; 63-108 ppm Mg	0/2	(Foliar)	103-104%	3.93	Lincolnshire, Yorkshire	Frontier, 2012a

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

5.1.5. Molybdenum

Frontier carried out eight Mo response experiments on winter oilseed rape between 2008 and 2012, of which four showed significant yield responses to foliar applications (Table 12). In all cases, two applications (autumn and spring) were required for a significant yield response; single applications in autumn or spring were not effective. Paired t-tests comparing untreated against mean treated yield or best treated yield across the eight experiments both showed no significant effect of Mo.

To determine the relationship between soil Mo status and yield response, an analysis was done of all the experiments from Table 10 for which soil analyses were available. The average yield of the Mo treatments in each experiment, as a percentage of the untreated control yield, was plotted against the soil Mo status in ppm, analysed by acid ammonium oxalate extraction. There was a negative correlation (P=0.003), suggesting that soil Mo status is a good indicator of deficiency and that modest oilseed rape yield responses may occur at sites with <0.12 ppm soil Mo (Figure 13). However, the regression line also suggests that molybdenum applications may reduce yield at sites with >0.13 ppm soil Mo; this is in accordance with published evidence of Mo toxicity to oilseed rape (McGrath et al., 2010a). McGrath et al (2010b) showed that the soil Mo concentration at which Mo toxicity occurs depends on other soil properties, with soil organic C and ammonium oxalate-extractable Fe concentration being the best predictors of Mo toxicity threshold. Further research is required to predict the risk of Mo toxicity on UK soils.

There was no correlation between tissue Mo level, measured in autumn or spring, and yield response to Mo, or between soil pH and yield response to Mo.

No cereal Mo response experiments were found in the literature search or the commercial data supplied.

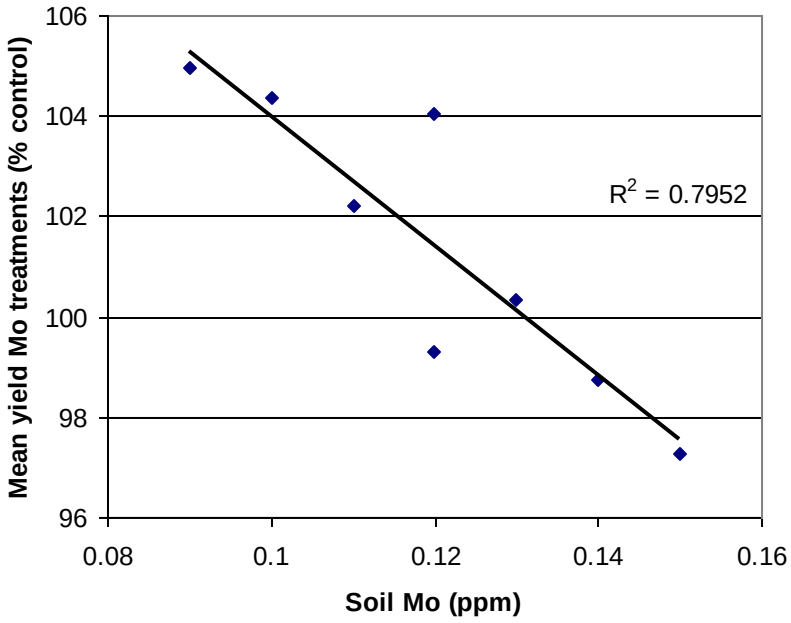

Figure 13. Relationship between soil molybdenum levels, analysed by acid ammonium oxalate extraction, and oilseed rape yield responses to foliar molybdenum applications (P=0.003). Mean treated yields are shown as a percentage of untreated control yield.

Table 12. Yield responses to molybdenum for field experiments carried out in the UK. Bold treatments are those which led to significant yield responses.

Crop	Year	Soil type, pH and molybdenum content (acid ammonium oxalate extraction)	Responsive sites/ total number of sites[†]	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter OSR	2008	Flinty clay loam, limestone brash; 0.09-0.1 ppm Mo; pH 7.8-8.0	2/2	**Foliar**	98-114%	3.50	Lincolnshire, Yorkshire	Frontier, 2008a
Winter OSR	2009	Flinty clay loam; 0.11 ppm Mo; pH 8.1	0/1	Foliar	102	4.51	Yorkshire	Frontier, 2009
Winter OSR	2011	Flinty clay loam, limestone brash; 0.14-0.15 ppm Mo; pH 7.9-8.0	0/2	Foliar	97-99%	4.80	Lincolnshire, Yorkshire	Frontier, 2011b
Winter OSR	2012	Flinty clay loam; 0.12 ppm Mo; pH 7.9	0/1	Foliar	99%	4.94	Yorkshire	Frontier, 2012b
Winter OSR	2012	Flinty clay loam, limestone brash; 0.12-0.13 ppm Mo; pH 7.7-7.9	2/2	**Foliar**	99-105%	4.03	Yorkshire	Frontier, 2012c

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

5.1.6. Zinc

Zinc deficiency was diagnosed in cereal crops in County Louth, Ireland in 1985, following which two experiments were carried out at these sites to investigate the zinc response (MacNaeidhe & Fleming, 1988). Zinc treatments increased yield at the two sites from 2.08 t/ha to up to 8.08 t/ha and from 2.96 t/ha to up to 6.34 t/ha. Yield responses were chiefly due to increases in ear number, but the authors recognise that these results are specific to the deficient sites and not representative of Ireland as a whole. The most effective treatment was Zn EDTA at 6.0 l/ha.

A significant yield response to Zn sulphate was detected in only one of a series of 15 UK experiments on winter wheat carried out between 2010 and 2012 on light, organic and calcareous soils with adequate Zn levels (Table 13; McGrath, 2012). Significant yield responses were detected in five out of 21 other UK experiments, three out of five other Irish experiments and none out of 23 New Zealand experiments (Table 13).

Zn applications were tested at two sites in western Canada thought to be marginal or Zn deficient (DPTA-extractable Zn levels 0.78 and 1.24 mg/kg) (Grant & Bailey, 1998) over three years (Table 13). However, there were no significant responses to 10 kg/ha $ZnSO_4$ which was broadcast and incorporated. In four of the six experiments there were negative yield responses to the Zn sulphate, although these were non-significant.

To investigate the relationship between soil Zn status and cereal yield response, an analysis was undertaken for all the experiments from Table 13 for which soil analyses by EDTA-extraction were available. For the unpublished ADAS report in which analysis method was not stated (Eagle, 1970) it was assumed that EDTA extraction was the method used, since this was the predominant method in use in the UK and the method recommended by ADAS at the time. The average yield of the Zn treatments in each experiment, as a percentage of the untreated control yield, was plotted against the soil Zn status in mg/kg, mg/l or ppm. There was no clear relationship between soil Zn status and cereal yield response to Zn (Figure 14), with large yield responses occurring at the two deficient sites in Ireland (MacNaeidhe & Fleming, 1988), but at no other sites, even though some had even lower soil Zn status. There was similarly little correlation between tissue Zn status and cereal yield response to Zn (Figure 15). A paired t-test of untreated and mean treated yields in all the experiments in Table 13 gave a significant effect of Zn treatment (P=0.043), but if the two experiments by MacNaeidhe & Fleming are excluded, there was no significant effect.

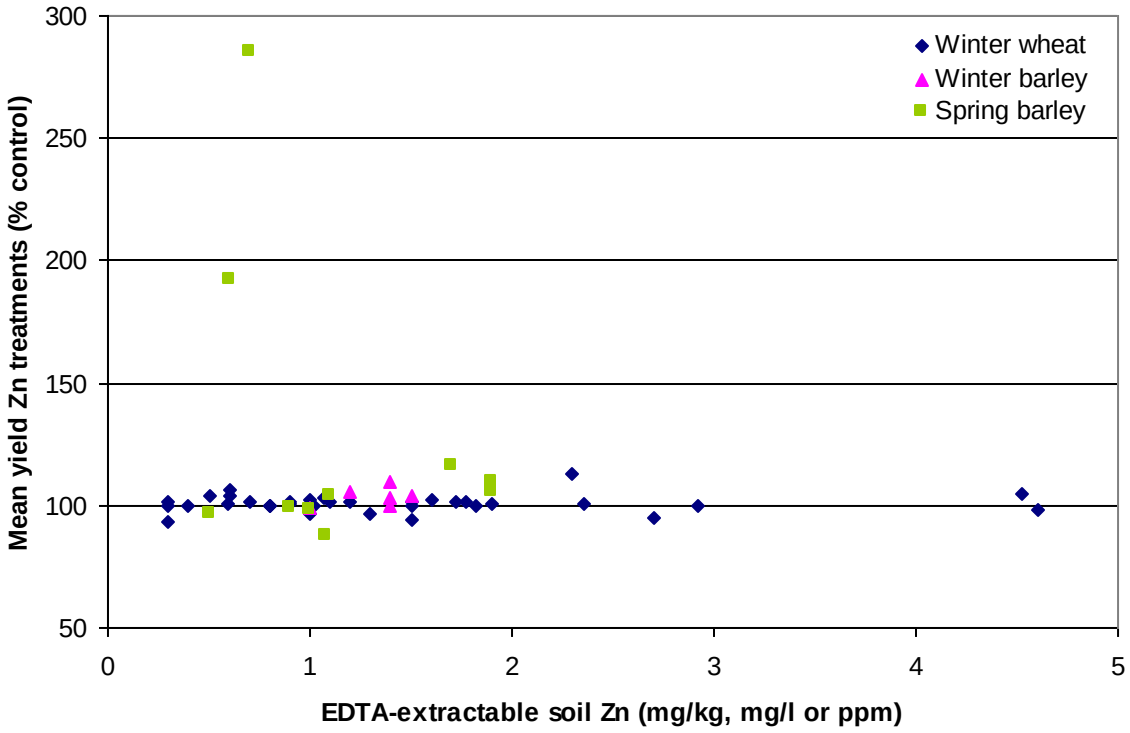

Figure 14. Relationship between EDTA-extractable soil zinc and cereal yield responses to zinc applications, for the experiments listed in Table 13 for which sufficient data was available. Mean treated yields are shown as a percentage of untreated control yield, and include foliar, broadcast and seed treatments.

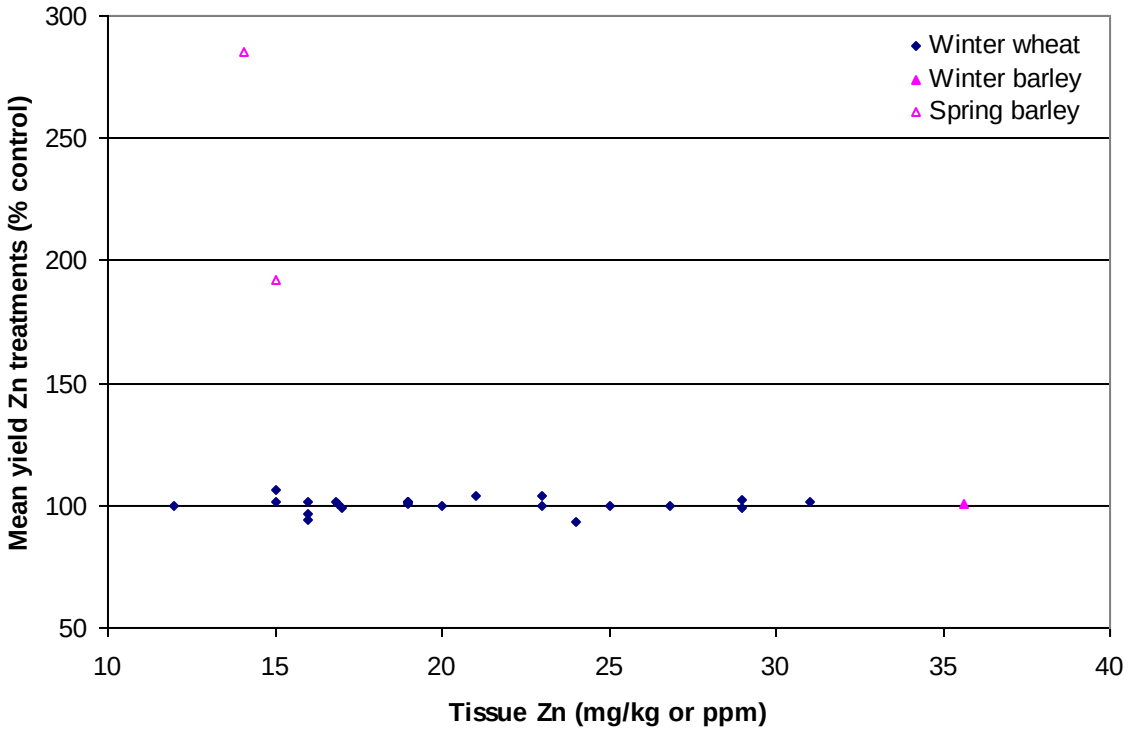

Figure 15. Relationship between tissue zinc status and mean cereal yield responses to zinc applications, for the 26 experiments listed in Table 13 for which sufficient data was available. Mean treated yields are shown as a percentage of untreated control yield, and include foliar, broadcast and seed treatments.

Table 13. Yield responses to zinc for field experiments carried out in the UK, Ireland and New Zealand for cereals. Bold treatments are those which led to significant yield responses.

Crop	Year	Soil type and zinc content (EDTA extractable, unless otherwise stated)	Responsive sites[†]/ total number of sites	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat	-	1.6 mg/kg Zn	0/1	(Foliar)	-	7.4	Aberdeenshire	Chalmers *et al*., 1999
Winter wheat	2006	Sandy loam, flinty clay loam, limestone brash; 7.6-30.3 ppm Zn	1/3	Foliar, (seed treatment)	99-103%	10.43	Lincolnshire, Yorkshire	Frontier, 2006d
Winter wheat	2005-2007	Silt loam, sandy loam, sand; 0.3-1.9 mg/kg Zn	0/23	(Broadcast)	94-107%	9.33	Canterbury, New Zealand	Curtin *et al*., 2008
Winter wheat	2010-2011	Clay loam & loam;1.02 & 0.59 mg/l Zn	0/2	(Foliar)	99-101%	10.90	Co. Wexford and Co. Meath, Ireland	Teagasc Better Farms
Winter wheat	2010-2012	Light, organic & calcareous soils. 1.07-12.43 mg/kg Zn	1/15	(Foliar)	95-113%	7.97	Cambridgeshire, Norfolk, Bedfordshire, Lincolnshire, Hertfordshire, West Yorkshire	McGrath, 2012
Spring wheat	1991-1993	Clay loam and silty loam. 0.62-1.32 mg/kg Zn (DTPA extractable)	0/6	(Broadcast & incorporation)	79-113%	2.21	Manitoba, Canada	Grant & Bailey, 1998
Winter barley	1984-1985	1.2-1.5 mg/kg Zn	1/5	Foliar	100-110%	7.48	North-east Scotland	Chalmers *et al*., 1999
Winter barley	1988-1989	Sandy loam; 1.0 mg/kg Zn	0/1	(Foliar, broadcast)	98-100%	6.12	South-east Scotland	Paterson *et al*., 1991
Winter barley	2006	Flinty clay loam; 11.6 ppm Zn	1/1	Foliar, (seed treatment)	100-101%	10.97	Yorkshire	Frontier, 2006e
Spring barley	1968-1969	Calcareous sandy loam	2/2	Foliar	110-118%	3.60	Cambridgeshire	Richardson, 1969
Spring barley	1969	Calcareous silty loam; 1.08-5.9 mg/l Zn (analysis method not stated)	0/2	(Broadcast)	88-101%	5.28	Bedfordshire, Hertfordshire	Eagle, 1970

Crop	Year	Soil type and zinc content (EDTA extractable, unless otherwise stated)	Responsive sites[†]/ total number of sites	Treatment type (treatments with non-significant effects shown in brackets)	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Spring barley	1985	0.6-0.7 mg/kg Zn	2/2	Foliar	161-388%	3.56	North-east Ireland	MacNaeidhe & Fleming, 1988
Spring barley	1988-1989	Sandy loam, sandy clay loam; 0.5-1.1 mg/kg Zn	0/4	(Foliar, broadcast)	90-107%	4.97	South-east Scotland	Paterson *et al*., 1991
Spring barley	1989	Sandy loam; 0.6-1.1 mg/kg Zn	0/2	(Foliar)	-	-	North-east Scotland	Chalmers *et al*., 1999
Spring barley	1992	Clay loam, loam, gravelly loam; 1.7-1.9 mg/l Zn	3/3	Foliar	107-119%	5.93	Co. Louth, Co Wiclow, Co. Tipperary, Ireland.	Barclay trials (data provided by Teagasc)

- Insufficient detail available.

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

5.1.7. Micronutrient mixtures

A number of independent experiments have tested proprietary products containing a mixture of micronutrients. In the case of unpublished work conducted several decades ago, it can be difficult to find out what nutrients were contained in each treatment, and at what rates, but the results have some value in testing the hypothesis that combined micronutrient dressings can be 'greater than the sum of their parts' due to Leibig's 'law of the minimum'. In 10 ADAS cereal experiments in 1976 and 1977, the few yield responses observed were too small to economically justify treatment (Table 14). None of the treatments tested were consistently effective, leading to the conclusion that 'the routine use of foliar sprays is not justified and a yield reduction is as likely as a yield increase' (Wadsworth, 1977; Anon, 1978). Similarly, in five Scottish cereal experiments from 1976 to 1978, there were no significant grain or straw yield responses to any treatment (Harkess *et al*., 1981). Significant responses to multi-nutrient products were found in two Frontier oilseed rape experiments, and one of three cereals experiments by Teagasc in Ireland (Table 14).

Table 14. Yield responses to foliar multi-nutrient products for field experiments carried out in the UK and Ireland for cereals.

Crop	Year	Soil type	Responsive sites[†]/ total number of sites	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat	1977		0/1	94-101%	6.07	Bristol area	Anon, 1978
Winter wheat	1976	Peat	1/1	117%	1.89	Bristol area	Wadsworth, 1977
Winter barley	1976	Silty clay loam	1/1	107%	4.69	Bristol area	Wadsworth, 1977
Winter wheat	1990	Grey brown podzolic	0/1	96%	5.25	Wicklow, Ireland	Seedtech trials (provided by Teagasc)
Spring wheat	1990	Brown Podzolic dervied from sandstone & shale mixture	0/1	110%	6.01	Waterford, Ireland	Seedtech trials (provided by Teagasc)
Winter barley	1977	-	0/1	100-102%	5.75	Bristol area	Anon, 1978
Spring barley	1976	Sandy loam, silty clay loam	0/3	N/A	2.68	Bristol area	Wadsworth, 1977
Spring barley	1976-1978	-	0/5	N/A	4.83	Scotland	Harkess *et al*., 1981
Spring barley	1977	-	0/3	92-107%	5.39	Bristol, Cardiff	Anon, 1978
Spring barley	1990	Brown Podzolic dervied from sandstone & shale mixture	1/1	138%	3.96	Cork, Ireland	Seedtech trials (provided by Teagasc)
Winter OSR	2008	Flinty clay loam and limestone brash	2/2	101-114%	3.92	East Yorkshire, Lincolnshire	Frontier 2008a

- Insufficient detail available.

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

5.1.8. Phosphite

Although phosphorus (P) is out of the scope of this review, an analysis of yield responses to phosphite, which is a reduced form of phosphate, has been included. A recent review by Thao & Yamakawa (2009) highlighted the confusion associated with the use of phosphite as a fungicide, fertiliser or a bio-stimulator. They suggest that the effect of phosphite is dependent on the level of phosphate anions (Pi) in the soil, and phosphite has a deleterious effect as the Pi levels are reduced. Numerous early studies carried out on citrus trees demonstrated that phosphite could replace Pi, thus acting as a P fertiliser and improving P nutrition (e.g Lovatt, 1990a, 1990b; Albrigo, 1999). However, there are also numerous studies which show that phosphite is not oxidised or metabolised by the plant and has negative effects on plant growth and development (Carswell et al., 1996, 1997; Guest & Grant 1991). Thao & Yamakawa (2009) suggest that benefits in response to treatment with phosphite are due to its fungicidal properties whereby it is able to control a number of diseases caused by pseudofungi belonging to the order Oomycetes.

Four of the six Frontier experiments which investigated the effects of different phosphite products and application methods in winter wheat showed significant increases in yields, of which the maximum was a 6% increase over the control yield (Table 15). In winter barley, phosphite treatment gave a significant yield increase in only one of three experiments (Table 15). In two of the winter barley experiments there were significant decreases in yield in response to foliar applications of phosphite. In contrast to the Frontier experiments, a series of experiments carried out by Teagasc on their Better Farms showed no significant yield responses to foliar or seed treatment with phosphite for winter wheat or spring barley. At four of the six sites tested there were only negative responses to phosphite, although these differences were not significant.

To understand the relationship between yield responses to phosphite and soil and tissue phosphate levels, mean yields for phosphite treatment as a percentage of the control yield was plotted against soil or tissue phosphate levels. There was no correlation for either soil or tissue levels of phosphate with the phosphite treated yields (Figure 16 and Figure 17). It should also be recorded that there have been documented cases of phytotoxicity from phosphite. In two experiments in Germany to evaluate the nutritional effect of phosphate on courgette, significant damage resulted from phosphite treatments and the researchers concluded (i) 'that P-deficient plants are very sensitive to phosphite, which represents a nutritionally ineffective form of P' and (ii) that phosphite 'should not be considered as a form of P suitable for fertiliser manufacture' (Ratjen & Gerendas, 2009).

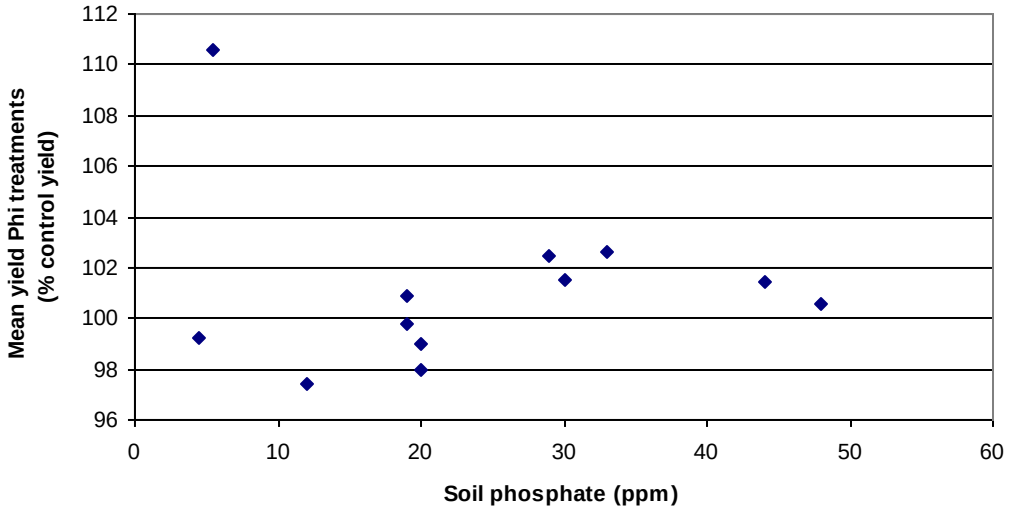

Figure 16. Relationship between soil phosphate levels and the mean yield response to phosphite (Phi) treatments for the experiments in Table 15.

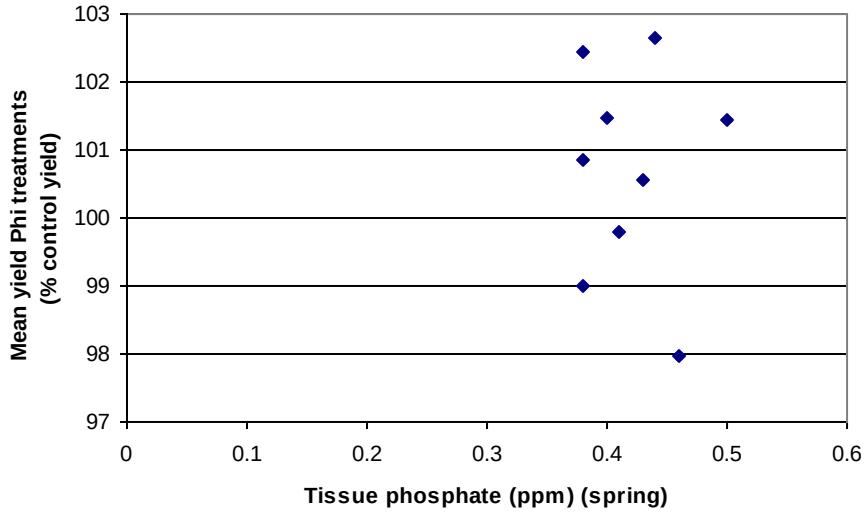

Figure 17. Relationship between tissue phosphate levels in the spring and the mean yield response to phosphite (Phi) treatment for the experiments in Table 15.

Table 15. Yield responses of cereals to phosphite products in the UK and Ireland.

Crop	Year	Soil type	Treatment type (treatments with non-significant effects shown in brackets)	Responsive sites[†]/ total number of sites	Yield response range (% control; includes non-significant results)	Mean untreated yield (t/ha)	Site Locations	Reference
Winter wheat and winter barley	2008-2011	Flinty clay loam, limestone brash; 19-44 ppm P	Foliar, seed treatment.	4/9	97-106%	9.25	East Yorkshire, Lincolnshire, Cambridgeshire, UK	Frontier 2008c, 2010c, 2011c, 2011d, 2011e.
Winter wheat and spring barley	2011-2012	Loam, clay loam, shallow loam; 1.98-12 mg/l P	(Foliar, seed treatment)	0/6	95-112%	7.73	Meath, Wexford, Louth, Carlow: Ireland	Teagasc Better Farms

[†] A responsive site is defined as one where the nutrient treatment produced statistically significant effect ($P<0.05$)

5.2. Agronomist survey

Agronomists were consulted to find out their perception of the incidence of non-NPKS nutrient deficiencies in wheat, barley and oilseed rape. Twenty agronomists responded to the consultation, including one from North East England, four from Yorkshire and the Humber, two from the East Midlands, four from the East of England, five from South East England, and four from the West Midlands. They were asked to:

- estimate the percentage of winter wheat, winter oilseed rape, winter barley and spring barley crops with visible symptoms of B, Ca, Cl, Cu, Fe, Mg, Mn, Mo and Zn deficiency;
- give an opinion on whether the same nutrient deficiencies have increased, decreased or stayed the same in the last 10 to 15 years.

The most common deficiency observed in cereals was Mn, thought to affect 16% winter wheat crops (Table 16), 20% winter barley crops (Table 17) and 15% spring barley crops (Table 18). 95% agronomists claimed to have seen Mn deficiency in at least some crops. Mg deficiency was also thought to be common (10% winter wheat, 7% winter barley and 9% spring barley). A minority of agronomists also claimed to have observed symptoms of Ca, Cu and Zn and Fe deficiency in cereals.

In oilseed rape Mg was thought to be the most common deficiency (13% crops affected; observed by 75% respondents), followed by B (8% crops, 55% respondents), Mn (6% crops, 70% respondents) and Mo (4% crops, 20% respondents) (Table 19).

Table 16. Results of agronomist consultation into non-NPKS nutrient deficiencies in winter wheat.

	Visible deficiency symptoms		Changes in past 10-15 years (% respondents)	
	Mean % crops	% responses >0	Increase	Decrease
B	0	0	10	0
Ca	0	0	0	0
Cl	0	0	0	0
Cu	2.2	30	10	0
Fe	0.1	5	0	0
Mg	9.9	65	45	0
Mn	15.7	95	40	5
Mo	0	0	5	0
Zn	3.0	15	15	0

Table 17. Results of agronomist consultation into non-NPKS nutrient deficiencies in winter barley.

	Visible deficiency symptoms		Changes in past 10-15 years (% respondents)	
	Mean % crops	% responses >0	Increase	Decrease
B	0	0	0	0
Ca	0	0	5	0
Cl	0	0	0	0
Cu	2.2	30	0	0
Fe	0.03	5	0	0
Mg	7.1	45	40	0
Mn	19.9	90	35	10
Mo	0	0	5	0
Zn	0	0	10	0

Table 18. Results of agronomist consultation into non-NPKS nutrient deficiencies in spring barley.

	Visible deficiency symptoms		Changes in past 10-15 years (% respondents)	
	Mean % crops	% responses >0	Increase	Decrease
B	0	0	0	0
Ca	0.01	5	0	0
Cl	0	0	0	0
Cu	2.3	25	20	0
Fe	0	0	0	0
Mg	9.1	50	35	0
Mn	15.4	90	30	5
Mo	0	0	5	0
Zn	0.3	10	10	0

Table 19. Results of agronomist consultation into non-NPKS nutrient deficiencies in winter oilseed rape.

	Visible deficiency symptoms		Changes in past 10-15 years (% respondents)	
	Mean % crops	% responses >0	Increase	Decrease
B	7.8	55	30	5
Ca	0	0	0	0
Cl	0	0	0	0
Cu	0.01	5	5	0
Fe	0	0	0	0
Mg	12.7	75	35	0
Mn	6.3	70	25	0
Mo	3.8	20	20	0
Zn	0	0	0	0

Across all four crops, about a third of agronomists think that the most common deficiencies (Mg and Mn in all crops and B in oilseed rape) have become more common in the past 10 to 15 years. There have been no long-term surveys of soil or tissue nutrient status to support this, but some information can be gleaned from the analysis results of soil samples sent to UK labs. Analysis by NRM of data from several thousand soil samples shows no strong trend in soil magnesium levels from 1994 to 2012 (Figure 18; NRM, 2012) or boron levels from 2002 to 2012 (Figure 19; Sean Stevenson, personal communication). It must again be recognised that incidence of Mg deficiency has in the past been more often associated with poor soil and rooting conditions as a result of compaction, impeded drainage or pest attack (section 4.5.1). There has been similarly little change in levels of zinc, calcium, copper, iron or sodium in arable soils analysed by NRM from 2002 to 2012 (Sean Stevenson, personal communication; data not shown). The soil samples sent to labs

for analysis are unlikely to be representative of all UK soils, as growers and agronomists are more likely to submit samples of soils at high risk of deficiency, e.g. sandy soils, but there is no reason to assume that this bias should change over time.

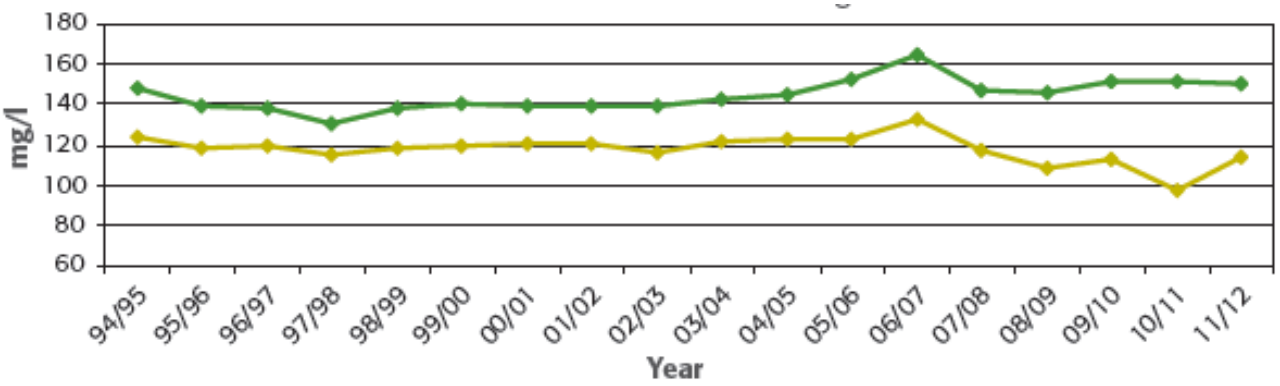

Figure 18. Trend in mean soil magnesium level of samples analysed by NRM from 1994 to 2012. Darker green line represents grassland and lighter green line represents arable soils. From NRM (2012).

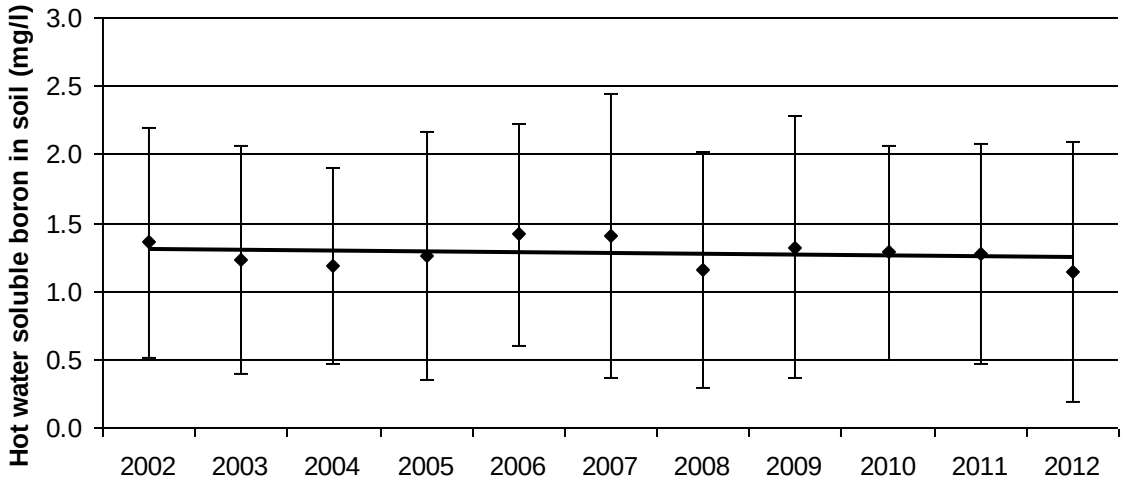

Figure 19. Trend in mean soil boron level of arable soil samples analysed by NRM from 2002 to 2012. Error bars show ± 1 standard deviation; bold line shows regression (R^2=0.06). (Sean Stevenson, personal communication).

6. Diagnostic methods

Diagnosis of micronutrient deficiencies is carried out in three ways: through crop symptoms, soil analysis and tissue analysis. As highlighted in section 6.12, there is considerable variability in the critical values which are recommended by different organisations, and this is compounded by the added complexities involving soil type, pH, timing of sampling, method of analysis, etc.

6.1. Visual symptoms

A thorough description of micronutrient visual symptoms in wheat is discussed by Snowball and Robson (1991) and is summarised below and in Figure 20. Orlovius (2003) describes the main visual symptoms for micronutrient deficiencies in oilseed rape and this is summarised below

6.1.1. Boron

Wheat

Symptoms of B deficiency include dieback of the apical growing point on the main stem, the development of side shoots and a bushy appearance of the plant. In wheat one of the first symptoms of B deficiency is splitting of the newer leaves close to the midrib. This is accompanied by some unusual indentations along the length of the leaf on the opposite side to the splitting.

Oilseed rape

Oilseed rape leaves are usually paler in colour with reddish discolouration and/or interveinal mottling in some cases. Leaves may become crinkled. The edges of young leaves are unrolled and, as B deficiency accelerates, new leaves are deformed and stems may be hollow and cracked. Leaves at the base of the plant begin to die back.

6.1.2. Calcium

Wheat

Calcium has an important role in meristematic growth, and so symptoms of Ca deficiency appear in new growth. Unlike many other micronutrient deficiencies, Ca deficiencies do not lead to chlorosis, and instead the dark green colour is maintained. Necrotic spotting around the middle of the leaf of newest growth occurs, and this spotting expands and the leaf then collapses before unrolling.

Oilseed rape

Deficiency causes stunting of new growth in stems, flowers and roots. Symptoms range from distorted new growth to black spots on leaves. Yellow leaf margins may also appear.

6.1.3. Copper

Wheat

Both old and new leaves of plants which are Cu deficient tend to show a withered appearance and are paler than non-deficient plants. One of the first symptoms of Cu deficiency is ‘withertip’, which shows as a sudden dying and curling of the tip end of the leaf blade. The base end of the tip can remain green until senescence occurs. In wheat, shrivelled grains are also symptomatic of Cu deficiency. Additionally, Cu deficiency can lead to depositions of the pigment melanin, which can result in purpling of the stem and nodes.

Oilseed rape.

Given that the sensitivity of oilseed rape to Cu deficiency is low, it is unusual for deficiencies to occur. General symptoms of a lack of Cu in oilseed rape include distortion, wilting, bleeding and death of the younger leaves. The whole plant phenotype resembles a plant suffering from water deficiency with permanent wilting and limp leaves.

6.1.4. Iron

Wheat

Given the importance of Fe in chlorophyll biosynthesis, it is not surprising that plants which are deficient in Fe are chlorotic. Chlorosis occurs in new leaves, whilst older leaves remain green. Iron deficient plants remain erect

Oilseed rape

Symptoms of Fe deficiency in oilseed rape are similar to those symptoms of Mn and Mg deficiency. However, in contrast to Mg deficiency, where the plants first show symptoms in the older leaves, a lack of Fe first appears on the young leaves. This is also true of Mn deficiency, which can make diagnosis difficult.

6.1.5. Magnesium

Wheat

The new leaves of Mg deficient plants are pale and chlorotic and remain unopened. Severe Mg deficiency can completely prevent leaves from opening; however this level of deficiency is not common. In cereals, yellow mottling appears, whilst in oilseed rape a marbled patterning of yellowing can be seen.

Oilseed rape

Symptoms of Mg deficiency in oilseed rape resemble that of Fe or Mn deficiency. Interveinal chlorosis of the leaf occurs, and purpling of the leaf margin.

6.1.6. Manganese

Wheat

Plants which are deficient in Mn display symptoms which can be similar to plants deficient in Fe or Mg. In wheat deficient plants, symptoms occur in new leaves which become pale and limp. This is followed by light grey flecking and striping which occurs at the base of the youngest fully opened leaf. In time, more chlorophyll may be lost leading to paler leaves which eventually become necrotic and collapse.

Oilseed rape

In oilseed rape, interveinal chlorosis of middle and younger leaves is the typical symptom of Mn deficiency, which begins at some distance from the veins. This chlorosis is normally distributed all over the leaf blade in the form of spots. Leaves of Mn deficient plants appear spotted and mottled with a greenish-yellow and yellow colour.

6.1.7. Molybdenum

Wheat

Symptoms of Mo deficiencies depend on the nitrogen status of the plant. Under high N, molybdenum deficient plants are much paler than those with adequate Mo. Yellow striping may also occur longitudinally on middle-aged leaves. New growth is largely unaffected, whilst there may be some necrosis to older leaves.

Oilseed rape

The total demand of Mo for oilseed rape is not very high because of the low Mo-content in the plant. Therefore, Mo deficiency symptoms are not frequently observed under field conditions. Under severe Mo deficiency, only the midrib continues to grow and the leaf lamina is not formed. Marginal chlorosis and necrosis occur on older leaves which have a high content of nitrate, and leaves may become pale and limp.

6.1.8. Zinc

Wheat

Symptoms of Zn deficiency, which include the change in colour from green to muddy grey-green in central leaf areas, appear on middle aged leaves. These areas appear to be drought stressed, and necrotic patches soon develop which become larger and are surrounded by mottled yellow-green areas.

Oilseed rape

Oilseed rape is not highly sensitive to Zn deficiency and therefore symptoms are not often described. The most typical symptoms are stunted growth with shortened internodes leading to a bushy habit of the plant. Leaf size is also greatly reduced and can be combined with chlorosis.

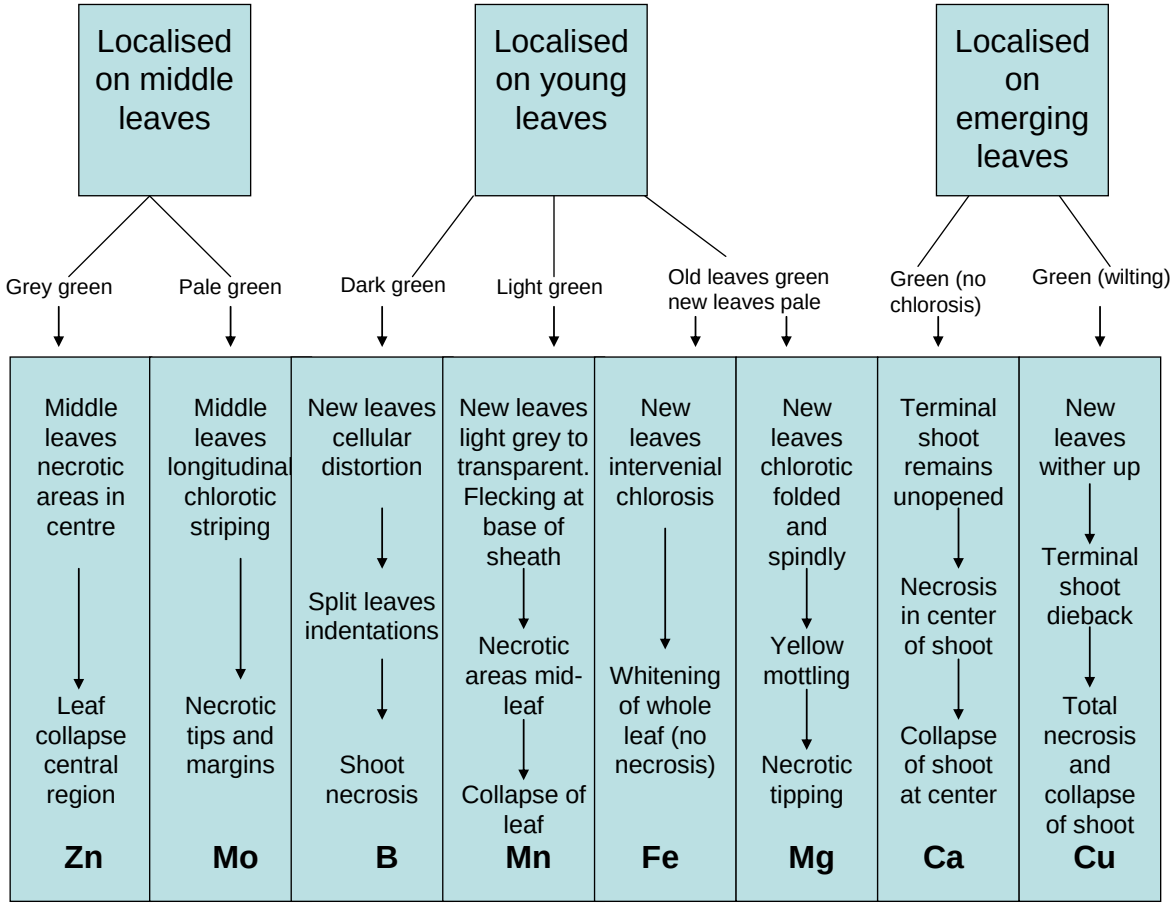

Figure 20. Diagnostic key for identifying micronutrient deficiencies in wheat. Taken from Snowball and Robson 1991.

6.2. Soil diagnostic methods

A range of different extractants are used to determine potential plant-available micronutrient levels in the soil, including acids (HCl, HNO_3), chelating agents (ethylenediamine tetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), buffered salt solutions (NH_4OAc) and unbuffered salt solutions ($CaCl_2$, $MgCl_2$, $NaNO_3$, NH_4NO_3). The most suitable extractant depends on the micronutrient being investigated, due to differences in the basic soil chemistry of different micronutrients.

No technique is universally accepted for determining the concentration of plant-available micronutrients, and hence large differences arise between laboratories and different countries. The benefits of using a soil diagnostic method to determine the presence of deficiencies is that it allows for correction to be carried out before the crop is established. Soil type can have a large effect on whether micronutrient levels in soils are adequate or not. For example, on light soils copper deficiency is likely to occur when EDTA-extractable levels reach 2.5 mg/kg or less, whereas on heavy soils extractable levels of copper must be below 1.0 mg/kg before a deficiency would occur (McGrath *et al*., 2008).

A comparison of three different extractants for determining soil available Cu, Zn and Mn (Table 20) highlights the potential for large differences in levels of available micronutrients when different methods are used for extraction. EDTA extraction resulted in twice the level of Cu and Zn and twelve times the level of Mn relative to extraction using DTPA. For Zn, extraction using 0.1M HCl gave the highest concentration, which was approximately three times that using DTPA.

Table 20. Mean values for EDTA, DTPA and HCl extractable Cu, Zn and Mn for 44 study soils in New Zealand (Haynes, 1997).

	Cu (µg/g)	SE	Zn (µg/g)	SE	Mn (µg/g)	SE
EDTA	1.81	1.61	1.3	0.68	32	30
DTPA	0.95	0.88	0.65	0.46	2.8	2.5
HCl	1.3	0.34	1.8	1.3	21	18

One of the main issues with the extraction methods outlined above is their inability to incorporate biological and chemical processes which take place in the soil, in particular soil-plant interactions in the rhizosphere zone. In an attempt to mitigate this problem, a Chinese group have developed a 'rhizosphere based method' which involves using fresh moist rhizosphere soil and low-molecular-weight organic acids (LMWOAs) as extractants, to obtain labile metal fractions in the soil solution which have been shown to be correlated with metal contents in plants (Feng *et al*., 2005; Shan *et al*., 2003).

When soil Cu and Zn levels were compared to the levels in barley roots, significant correlations occurred for the rhizosphere-based and DTPA extraction methods; the EDTA extraction method provided a significant correlation between soil and root Zn levels but not between soil and root Cu levels (Table 21). However, when the Zn content of barley shoots was compared to soil levels, the DTPA and EDTA soil extractions showed significant correlations, whereas the rhizosphere-based method showed a poor correlation. Interestingly, for Cu there was no significant correlation between shoot tissue levels and any of the soil extraction methods. Additionally, when soils were separated according to pH, the rhizosphere-based method showed better correlation between soil levels and root levels for Cu and Zn.

Table 21. Linear correlation coefficients (R) between extractable copper (Cu) and zinc (Zn) from the rhizosphere soils by different extraction methods and metal content of barley shoots and roots (n=15) (Feng *et al*, 2005). * and ** indicate statistical significance at the probability level of P<0.05, and P<0.01 respectively.

Tissue		Rhizosphere method	DTPA	EDTA
Shoots	Cu	-0.041	0.213	0.309
	Zn	0.203	0.793**	0.760**
Roots	Cu	0.709**	0.726**	0.25
	Zn	0.709**	0.717**	0.544*

Stepwise linear regression models, which are based on extractable micronutrient levels and soil properties (pH, C and N content, textural properties and total content of Zn, Cu and Mn), have been successfully used for the prediction of shoot Zn and Cu concentrations in cereals (Lombnæs & Singh, 2003). Plant tissue Zn concentrations were predicted in this case most accurately (R^2=0.96) when the citric acid soil extraction procedure is used whilst DTPA extractable soil Cu gives the best prediction of plant Cu concentration (R^2=0.59). In contrast, neither soil extraction method was a good predictor of plant Mn concentration. Clay content, total Zn content (measured by AAS following extraction with aqua regia) and pH have an important effect on the correlation between soil Zn and tissue Zn, whereas total N and C do not have important roles in predicting Zn concentration.

6.3. Plant tissue diagnostic methods

The use of plant tissue diagnostic methods varies among the different micronutrients. It is generally perceived that plant analyses should not be carried out in isolation, but in conjunction with soil analyses can be used as a valuable tool to diagnose micronutrient problems (Sinclair & Edwards, 2008). Heywood *et al*., (2004) highlight that the main role of commercial plant tissue analyses is to determine gross nutrient deficiencies rather than to optimise fertiliser use. The interpretation of plant tissue micronutrient levels is complicated by variation in the distribution and concentration of a micronutrient in different plant parts due to nutrient mobility and physiological age of the plant part. Plant analysis should be carried out early in the growing season when the plants are young, to allow sufficient time for correction of any arising deficiencies. Carrying out analyses on whole plant samples is not recommended for arable crops, since deficiencies which could be determined from analysis of young tissues can be masked by the incorporation of older tissues. Instead, only the youngest fully expanded leaves should be sampled.

Numerous studies have attempted to define critical tissue analysis values indicating a risk of deficiency or a likely yield response to particular nutrients. These studies usually consist of field, pot or hydroponic experiments in which plants are grown at a range of nutrient availabilities,

avoiding yield limitation by other factors; plant tissue analysis and eventual yield are analysed to determine their relationship and so determine critical values. Reuter (1986) carried out a detailed review of published studies and unpublished data, which is summarised below for wheat (Table 22), barley (Table 23) and oilseed rape (Table 24). The studies included looked at a range of plant parts and growth stages, with these details included by Reuter but not in the condensed tables below. Relatively few studies have looked at oilseed rape, and for all crops the majority of studies have been done in Australia, Canada or the US.

Table 22. Interpretation of wheat tissue analyses. Condensed from a review of published research (Reuter, 1986). Values vary with study and with growth stage and plant part.

Nutrient	Concentration range (mg/kg)				Number of studies
	Deficient	Marginal	Critical	Adequate	
Calcium	<1500-1800	1200-2500	2000-2500	>2000-3000	4
Magnesium	<500-1100	500-1500		>1200-1500	6
Copper	<1.0-1.6	1.1-2.1	1-2.5	>1.0-2.2	10
Zinc	<12-18	12-15	5-20	>15-22	7
Manganese			10-82		8
Iron			>25		1
Boron	<5-8			>3-14	2
Molybdenum	<0.05	0.05-1	0.075	>0.09-0.16	4

Table 23. Interpretation of barley tissue analyses. Condensed from a review of published research (Reuter, 1986). Values vary with study and with growth stage and plant part.

Nutrient	Concentration range (mg/kg)				Number of studies
	Deficient	Marginal	Critical	Adequate	
Calcium		<3000		>2000-3000	2
Magnesium		<1500		>1500	2
Copper	<1.0-2.3		1.0-4.8	>4.8	7
Zinc	<5	5-24		>20-25	5
Manganese	<5-13	5-24	11-20	>15-25	6
Iron				>25-50	2
Boron	<3.5-8	<5		>3-14	7
Molybdenum				>0.3-1.2	4

Table 24. Interpretation of oilseed rape tissue analyses. Condensed from a review of published research (Reuter, 1986). Values vary with study and with growth stage and plant part.

Nutrient	Concentration range (mg/kg)				Number of studies
	Deficient	Marginal	Critical	Adequate	
Calcium				>14000	1
Magnesium	<1400	1600-1900		>1500-4000	2
Copper			2	>4	2
Zinc				>22	1
Manganese				> 31	2
Boron	<6-10.6	9		>17-25	3
Molybdenum				>0.28	1

A recent study has assessed the ability of portable X-ray fluorescence (PXRF) to predict micronutrient levels in wheat, corn, soybean and cotton (McLaren *et al*., 2012). PXRF measures the energy levels of X-rays which are emitted from elements when irradiated with an excitation source (Kilbride *et al*., 2006). For corn, soybean and cotton there were significant linear relationships between acid digest values and PXRF values for Ca, Fe, Mn and Zn. In contrast, for wheat the PXRF method only seemed to show a consistent significant linear relationship for Mn. PXRF has also been shown to be a suitable method for determining micronutrient levels in soil samples (McLaren *et al*., 2010)

6.4. Climate

Soil moisture has a large effect on the availability of micronutrients to the plant. Examples of soil and plant tissue levels of B, Cu, Mn and Zn measured in winter cereals on the same soil in a wet year and a dry year are shown in Table 25. Although soil levels are similar for the four micronutrients in the wet and dry years, there are large differences in the tissue levels. In all cases, plant tissue levels were higher in the wetter year than the drier year due to improved nutrient uptake from the moist soil. Micronutrient availability is also affected by temperature, with deficiencies occurring more frequently in cold periods in comparison to warm months.

Table 25. The effect of rainfall on micronutrient levels in soil and winter cereal tissues. (Data from McGrath *et al*., 2008).

Year	Rainfall/Month (May – Sep)	Soil test concentration (mg/l)				Plant tissue concentration (mg/kg)			
		B	Cu	Mn	Zn	B	Cu	Mn	Zn
1990	6.4	0.91	3.7	84	2.1	34	5.1	51	19
1991	37.4	0.88	3.6	91	2.4	82	7.4	111	27

6.5. Boron

The RB209 Fertiliser Manual (Defra, 2010) recommends that both hot water-extractable soil B and the B content of leaf tissue can be useful indicators of boron deficiency.

Levels of B in the soil are generally measured using the hot water extraction method (modified method of Berger & Truog, 1944). Levels of hot water extractable B generally correlate well with B concentrations in leaves and total uptake by plants in pot experiments (Rashid *et al*., 1994). However, in field experiments B availability and yield responses to boron fertilisation can be influenced by additional site specific factors which soil analysis does not take into account.

For tissue analyses to be useful in determining B levels, it is important that the correct part of the plant at the correct time is sampled since boron taken up by the roots is largely phloem-immobile. This means that once deposited at the leaves, B is not removed or translocated to other organs in the plant. Therefore it is possible that leaves of different ages will contain different B levels, with B levels building up in older, mature leaves. For example, Oertli (1993) observed toxic B concentrations in old leaves and deficient B concentrations in growing young leaves concurrently in the same plant when it was transferred from nutrient solutions containing very high B concentrations to B deficient solution. The mobility of micronutrients around the plant differs for different micronutrients. For example remobilisation of Mn is poor, whereas Zn shows good transport from the leaves to the grain (Pearson & Rengel 1994).

A study carried out by Huang *et al*., (1996) correlated boron measurements from different plant parts with shoot dry weight to determine the best tissue for analysis under different levels of B supply. The study concluded that B levels in mature leaves of oilseed rape are physiologically irrelevant, and samples for tissue analysis need to be taken from growing, immature leaves. Subedi *et al*., (1998, 1999) showed that there was no consistent difference in the B concentration of flag leaves from wheat cultivars which are tolerant to B deficiency to those which are susceptible.

Not only does B distribution differ between different parts of the plant, but there is also spatial distribution of B within an organ. B levels differ within the leaf in response to increased water use where it concentrates in the leaf tip in monocotyledons and in the leaf margins of dicotyledons in response to high evapotranspiration (Nable *et al*., 1990). Therefore, inclusion or exclusion of leaf tips or leaf margins in samples has the potential to sway total leaf and shoot concentrations. Nable *et al*., (1990) suggest that sampling whole leaves or shoots for B concentrations acts as a poor diagnostic measure of the B status of the plant. The effect of evapotranspiration rate on accumulation of B acts as an example of the implication that environmental factors can have on the

application of critical levels which are determined from experiments carried out in greenhouse conditions to field grown crops.

It has also been shown using barley cultured in nutrient solutions that B may be leached from leaves by water sprays, leading to a reduction in B concentration and content in whole shoots and young leaves (Nable & Moody, 1992). Similarly, moderate rainfall on a wheat field experiment on a soil with high B concentration also reduced the B concentration of whole shoots and young leaves (Nable *et al*., 1990). These results suggest that rainfall and irrigation in field situations and watering in greenhouse situations could also affect the usefulness of tissue analyses as a diagnostic method for B deficiency. Rainfall was found to have little effect on tissue concentrations of other nutrients (Ca, Cu, Mg, Mn, P, S and Zn) (Nable *et al*., 1990).

6.6. Copper

The RB209 Fertiliser Manual (Defra, 2010) recommends that EDTA-extractable soil Cu can be used to indicate Cu deficiency, but that the Cu content of plant tissue is an unreliable indicator of a crop's Cu status. Chalmers *et al.* (1999) point out that there is little difference in Cu tissue levels between healthy and deficient plants and so tissue testing has little use in comparison to soil testing.

Plant available Cu levels in the soil are usually measured using the chelating agents EDTA or DTPA. A recent study examined the suitability of a new method called Diffusive Gradients in Thin Films (DGT) for determining plant available Cu and Zn (Tandy *et al*., 2011). This method analyses the diffusive supply of the element, thus mimicking a plant root. Plant available Cu and Zn were tested using DGT for a range of Scandinavian soils and compared to levels determined by EDTA or DTPA extraction. A comparison between Cu and Zn soil levels and plant tissue levels measured in the youngest fully developed leaf of barley showed that, although all were significantly correlated, the effective Cu concentration in the soil measured by DGT correlated best with plant tissue levels. It is noteworthy that the significant correlations between EDTA and DGT extracted Cu levels and plant tissue levels are influenced by a small number of soils which contained high levels of Cu, and when these soils are removed from the analysis, the correlation is greatly reduced. In contrast to Cu, DGT was the only method which produced a significant correlation between soil Zn levels and plant tissue Zn levels.

The authors of this study conclude that using EDTA or DTPA extraction methods to predict available levels of micronutrients such as Cu and Zn is not very reliable (Tandy *et al*., 2011). This observation has been described numerous times (Feng *et al*., 2005;Takeda *et al*., 2006; Brennan *et al*., 2008; Curtin *et al*., 2008). This suggests that current methods for determining levels of available Cu in the soil may not be accurate tools for assessing the prevalence of deficiencies,

although the negative correlation between EDTA-extractable soil Cu and cereal yield response to Cu shown in Figure 5 provides support for the EDTA method.

Experiments carried out by McGrath (2012) found significant yield increases in response to Cu treatment in only one of fifteen experiments. A range of methods were used to determine soil Cu levels, which included EDTA, DTPA, ammonium nitrate and DGT. The DGT method was the only analysis in which the predicted soil levels at the responsive site were distinct from the other sites. In this case levels were between two and ten times lower than the other sites. Collectively, these results suggest that prediction of crop responsiveness to Cu might be improved if the DGT soil test method was used instead of EDTA, which is currently the most common method in the UK.

6.7. Iron

The use of tissue analysis for determining Fe deficiency is limited as there is often no relationship between total leaf Fe content and deficiency symptoms (Bell & Dell 2008). Additionally, Fe levels in leaves which are chlorotic are frequently higher than those in healthy leaves, and this phenomenon is know as the 'chlorosis paradox', which is caused by the inactivation of iron in the leaf (Bell & Dell 2008).

In a pot study carried out by Garnett and Graham (2005), the authors found that fertilisation with $FeSO_4.7H_2O$ had no effect on Fe tissue concentrations of wheat plants. Two conclusions may be drawn from this result: either the method for determining Fe tissue concentrations may be inadequate or fertilising with $FeSO_4$ could be ineffective. Like B, large differences in the concentration of Fe may be found between different plant organs, and organs of different maturity. Garnett & Graham (2005) showed that iron levels are approximately 3.5 times higher in lower leaves and flag leaves in comparison to stems and dead leaves at anthesis.

For these reasons, the RB209 Fertiliser Manual (Defra, 2010) recommends that neither soil nor plant analysis is reliable for diagnosing Fe deficiency.

6.8. Magnesium

RB209 indicates that soil analysis can be used to determine the quantity of readily available Mg in the soil and that soils should be maintained at an index of 1 (26 to 50 mg Mg/l).

A recent study by Ayala-Silva & Beyl (2005) has investigated the potential of using spectral reflectance measurements to determine Mg deficiencies. Magnesium deficient wheat plants have increased reflectance in both the visible and infrared parts of the spectrum and have decreased chlorophyll concentrations (Ayala-Silva & Beyl 2005). As leaves become more chlorotic, leaf

reflectance increases as the reflectance peak normally centred at about a light wavelength of 550 nanometres (nm), broadens towards the red end of the light spectrum as absorption of incident light by chlorophyll decreases. Therefore spectral reflectance measurements could act as a powerful non-destructive technique for determining micronutrient deficiencies and deciding when to apply fertiliser. However, there is the potential that different micronutrient deficiencies (i.e. iron) may lead to similar alterations in reflectance patterns, and so distinguishing between different micronutrients deficiencies, as well as nitrogen and sulphur deficiencies, could be problematic.

6.9. Manganese

Current recommendations in RB209 for determining Mn levels are that leaf analysis should be used and that soil analysis is not a reliable guide to deficiency.

The appropriateness of the DGT method for determining soil Mn levels has also been recently tested in barley (Mundus *et al*., 2012). However, in contrast to copper and zinc, where soil levels determined using the DGT method correlate significantly with plant tissue levels, the correlation for manganese was poor and insignificant. Therefore the authors conclude that DGT cannot be used to accurately predict the plant available Mn (Mundus *et al*., 2012). This highlights the fact that diagnostic methods which are good for determining plant available levels of one micronutrient may not be suitable for other micronutrients. In contrast to some of the other micronutrients, there is evidence to suggest that plant tissue levels of Mn correlate relatively well with yields in both wheat and oats (Curtin *et al*., 2008; Karamanos *et al*., 1984). However, manganese easily changes oxidation state under varying redox conditions in soils, and so this can explain why relationships between soil and tissue manganese are not always evident (Lombnæs & Singh 2003).

As mentioned earlier, accurate plant tissue sampling is extremely important to ensure that the conclusions made regarding micronutrient deficiencies are as precise as possible. A study carried out in North West Saskatchewan, Canada, investigated the correlation between plant tissue levels of Mn determined at different growth stages with yield (Karamanos *et al*., 1984). The study found significant correlations between plant tissue Mn levels and yield for a range of growth stages, but concluded that sampling whole plants at growth stage 47 was more accurate than growth stage 31 (Karamanos *et al*., 1984). However, delaying tissue analysis until this growth stage reduces the time for correction, and the study showed that foliar Mn treatments applied at growth stage 31 produced greater yield response than treatments applied at growth stage 47. This suggests that in deciding when to sample for tissue analysis, there is often a compromise between accuracy of diagnosis and sufficient time for correction of deficiency.

6.10. Molybdenum

The RB209 Fertiliser Manual (Defra, 2010) recommends that Mo deficiency may be diagnosed using either soil or tissue analysis, although deficiency is not expected in arable crops or in limed soils.

Orlovius (2003) suggests that tissue analysis should be used rather than soil analysis to determine Mo deficiencies. This is because although high levels of Mo may be released by soil extractants, in acid soils Mo often complexes with iron oxides and availability to the plant is depressed. In the UK and Ireland, extraction using ammonium oxalate is the most common method for analysing soil Mo levels, although again measuring tissue levels is preferred (McGrath *et al*., 2008).

6.11. Zinc

Currently, both plant and soil analyses are used as indicators of Zn status, although the RB209 Fertiliser Manual (Defra, 2010) recommends that leaf analysis is the most useful indicator of deficiency. In the UK, the most commonly used method for Zn soil analysis is extraction using EDTA.

6.12. Current industry approaches

A large number of commercial laboratories in the UK offer soil and plant tissue testing for the full range of major and minor nutrients. As part of this review, laboratories were invited to provide information on the analytical methods they use, and the interpretation they offer with the test results. The responses were examined to determine the level of consistency between the services offered, and the level of agreement with the findings from the literature review. Current practices are also compared with the recommended standard analytical methods for soil and plant tissue published by MAFF in RB427, which was last revised in 1986 (MAFF, 1986).

There may be cause for concern about the breadth of nutrient analyses offered, given the consensus in the literature and the guidance in sources such as RB209 that for some nutrients, soil or tissue analysis is unreliable. Manganese deficiency, for instance, is probably the most common micronutrient deficiency in the UK, but soil analysis does not provide a useful indication of the risk of deficiency. Despite this, Mn is included in the broad spectrum soil analyses offered by all the major UK labs, in many cases with interpretation of the analysis result as deficient or adequate.

6.12.1. Soil extraction methods

The laboratories Hill Court Farm Research, NRM and Yara Lancrop all use the RB427 recommended extractants for analysis for B, Cu, Mg and Zn in soil, but for Ca, Fe and Mn there is

variation in the extractants used (Table 26). These different extractants are likely to cause substantial variation in the analysis results obtained by different labs. Even where the same extractants are used, minor differences in methods can lead to important differences in analysis results. This is because the levels of minor nutrients in arable soils are often extremely low, with the deficiency thresholds being near the limits of detection for standard methods such as EDTA extraction. Furthermore, contamination during the analysis process can lead to significant effects on the results, for example by extraction of B from glassware (Steve McGrath, pers com.)

Table 26. Extractants for nutrient analysis of arable soils, as recommended by RB427 (MAFF, 1986), and currently used by NRM and Yara Lancrop laboratories. Hill Court Farm Research use RB427 methods for all nutrients.

Nutrient	RB427	Yara Lancrop	NRM
Boron	Hot water	Hot water	Hot water
Calcium	Ammonium acetate	Ammonium nitrate	Ammonium nitrate
Copper	EDTA	EDTA	EDTA
Iron	No recommendations	EDTA	DTPA
Magnesium	Ammonium nitrate	Ammonium nitrate	Ammonium nitrate
Manganese	Ammonium acetate + quinol	Ammonium acetate + quinol	DTPA
Molybdenum	Acid ammonium oxalate	Acid ammonium oxalate	Not routinely analysed
Zinc	EDTA	EDTA	EDTA

6.12.2. Tissue extraction methods

Internationally certified plant tissue samples are available for laboratories to check and calibrate their own methods, giving the potential for greater accuracy and consistency in tissue analysis than soil analysis.

All mineral analysis of plant tissue begins with destruction of the organic material by ashing, followed by acid extraction to dissolve the nutrients. RB427 recommends hydrochloric acid for this extraction (MAFF, 1986); Yara Lancrop use hydrochloric acid and NRM nitric acid, but this difference is unlikely to impact significantly on the results.

6.12.3. Analysis interpretation

Some laboratories, including SAC, report only the quantitative test results, leaving interpretation to growers and agronomists; others include some interpretation with the test report. Interpretation typically involves provision of a scale for each nutrient with categories such as deficient, adequate or high, against which the test results can be assessed; it is rare for laboratories to include advice on rectifying nutrient deficiencies.

Interpretative scales for soil have been collected from several labs and other sources, as follows:

- NRM and Richard Austin Agriculture a scale based on ICI research;
- Hill Court Farm Research use a scale which was first published by ADAS in 1982, and derived from the conclusions of a 1980 conference of ADAS Advisory Soil Scientists;
- Levington Agriculture published a scale, thought to be based on the ADAS scale;
- SAC do not provide interpretation in soil analysis reports, they do have an interpretative scale as described by Edwards *et al*. (2012);
- RB209 (Defra, 2010) includes threshold levels of boron, copper, manganese and zinc in soil which indicate a risk of deficiency, but detailed interpretative scales for soil analysis are not given;
- Teagasc publish scales in the Irish equivalent of RB209 (Coulter and Lalor, 2008).

Some other laboratories, including Yara Lancrop and Emerald Crop Science, use more complex interpretative systems in which the scales vary with soil type, soil pH and crop, based on a combination of internal research and published data. These scales have not been submitted to this review, due to their commercial sensitivity.

Different interpretative scales use different category or threshold descriptions, leading to some difficulties in comparing the scales. An attempt has been made to match up the categories accurately to allow the comparisons shown below, for B, Cu and Zn in soil (Figure 21, Figure 22, Figure 23) and B, Mn and Zn in plant tissue (Figure 24, Figure 25, Figure 26).

For each soil nutrient there is moderate agreement between the scales; for instance, 0.2 mg/l boron would be counted as very low and 1.6 mg/l as adequate by every scale (Figure 21). However, close to the thresholds there are inconsistencies such that 1.8 mg/l zinc would be interpreted ‘very low, deficiency very likely in susceptible crops’ by ADAS (Anon, 1980a), ‘risk’ by NRM and ‘moderate, no deficiency expected’ by SAC (Edwards *et al*., 2012) (Figure 23); and a soil with 1.2 mg/l Cu would be above the RB209 threshold for ‘possible deficiency’ but would be interpreted by NRM as ‘very low’ and by SAC as ‘low, deficiency possible’ (Figure 22).

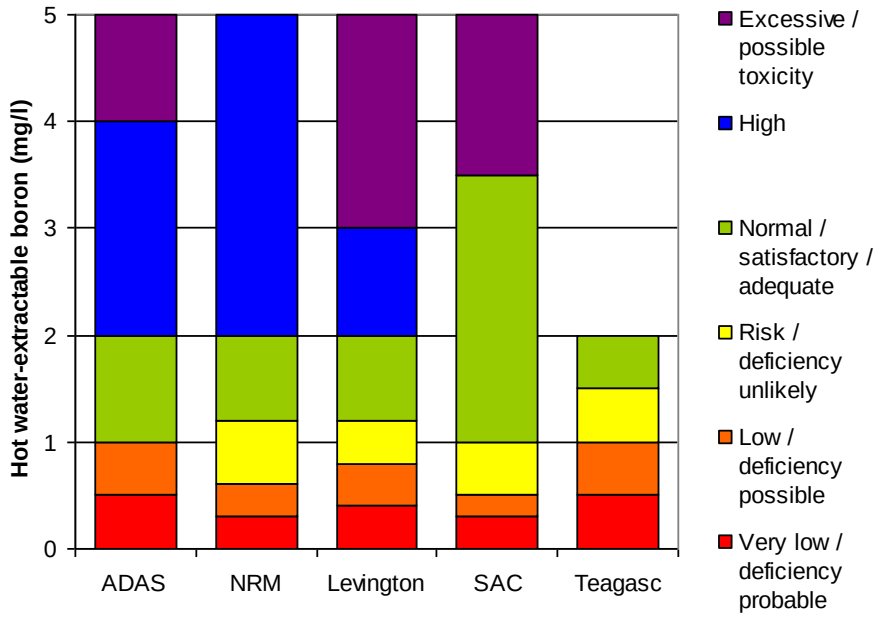

Figure 21. Interpretative scales for hot water-extractable boron in arable soils. Some sources specify that scales are only appropriate for boron-responsive crops such as oilseed rape (not cereals). Scales included are ADAS (MAFF, 1976; Anon, 1980b), NRM (Sean Stevenson, personal communication), Levington (Levington Agriculture, date unknown), SAC (Edwards *et al*., 2012), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010). Exact figures given in Appendix, Table 28.

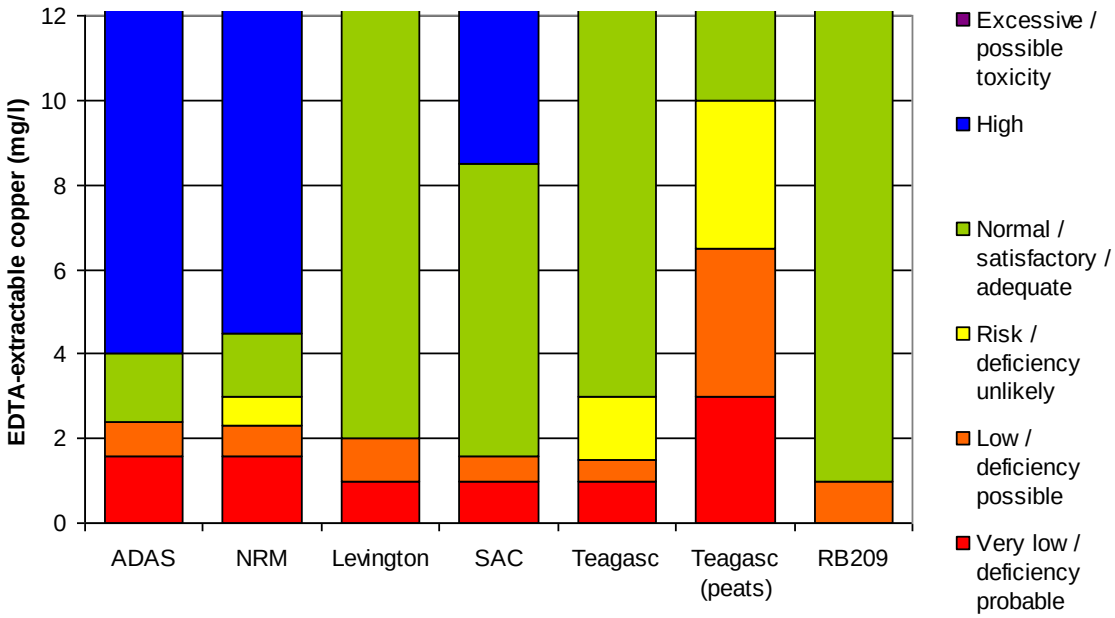

Figure 22. Interpretative scales for EDTA-extractable copper in arable soils. Scales included are ADAS (MAFF, 1976; Anon, 1980b), NRM (Sean Stevenson, personal communication), Levington (Levington Agriculture, date unknown), SAC (Edwards *et al*., 2012), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010). Teagasc provide separate scale for mineral soils and peats. Most scales include a threshold for excessive / possible toxicity, but this is not shown in order to focus on the deficient end of the scale. Exact figures given in Appendix, Table 29.

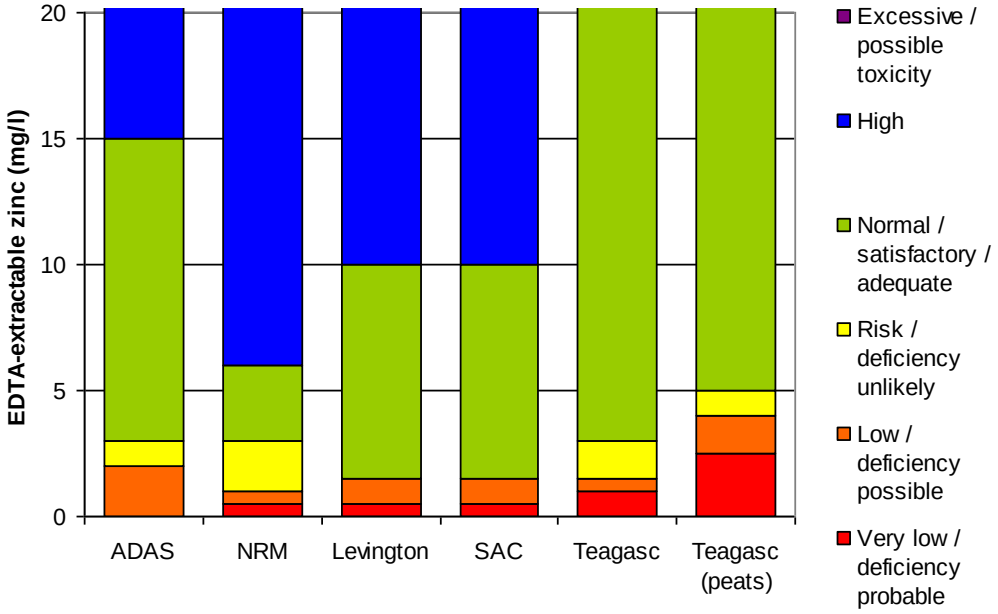

Figure 23. Interpretative scales for EDTA-extractable zinc in arable soils. Scales included are ADAS (Anon, 1980b), NRM (Sean Stevenson, personal communication), Levington (Levington Agriculture, date unknown), SAC (Edwards *et al*., 2012), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010). Teagasc provide separate scale for mineral soils and peats. Most scales include a threshold for excessive / possible toxicity, but this is not shown in order to focus on the deficient end of the scale. Exact figures given in Appendix, Table 30

The tissue analysis scales published in the UK, below, can be compared to the critical values from the scientific literature as summarised by Reuter (1986) (Table 22, Table 23, Table 24). In most cases there is reasonable agreement between the scales below and the values in Reuter (1986); exceptions include the NRM oilseed rape and the Teagasc scales for B (Figure 24), and the NRM wheat and oilseed rape scales for Zn (Figure 26), all of which are more sensitive than the values in Reuter (1986), i.e. tending to diagnose deficiency more readily than may be justified.

The interpretative scales for soil Cu (Figure 20) can also be compared to the analysis of yield responses shown in Figure 5. The RB209 and SAC scales most closely describes the relationship shown in Figure 5, which suggested a threshold of about 1.0 mg/kg soil Cu.

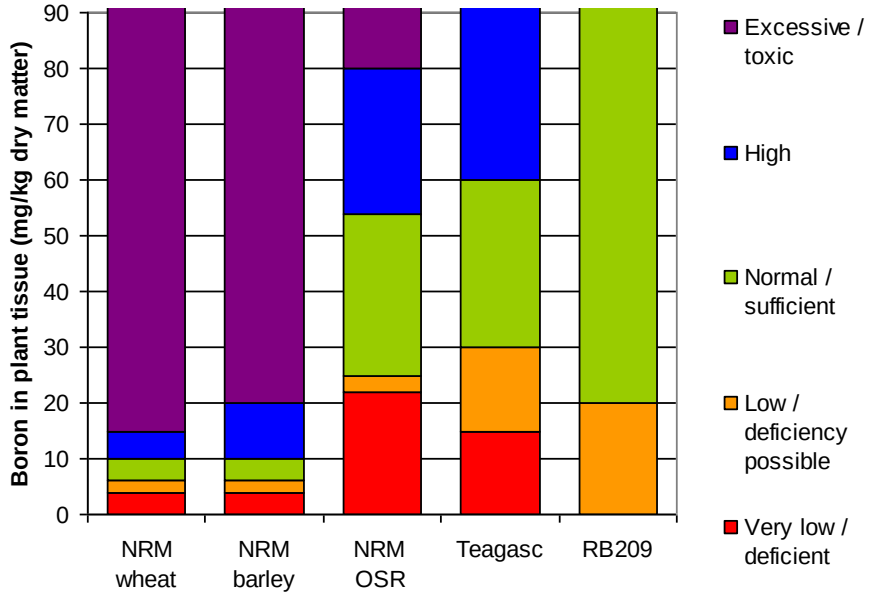

Figure 24. Interpretative scales for boron in plant tissue. Scales included are NRM (Sean Stevenson, personal communication), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010). Exact figures given in Appendix, Table 31.

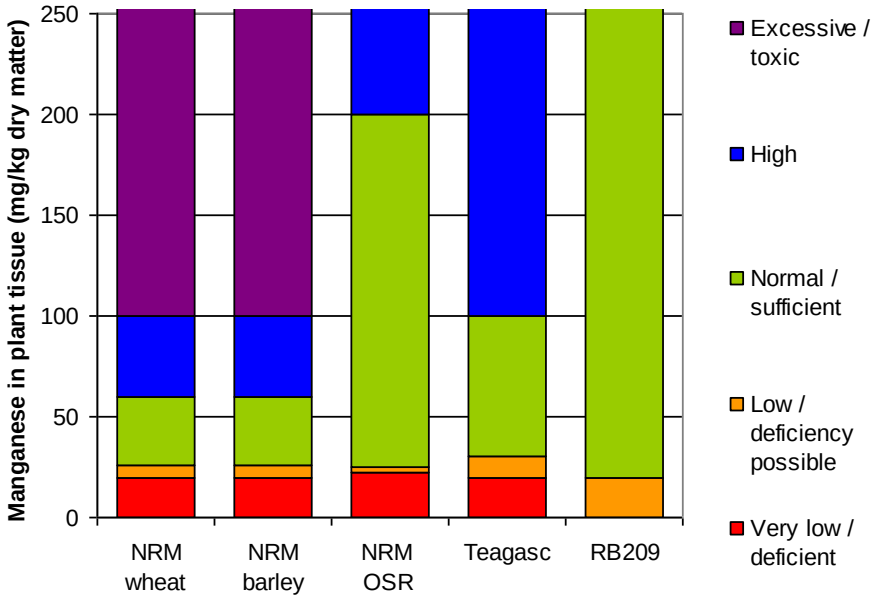

Figure 25. Interpretative scales for manganese in plant tissue. Scales included are NRM (Sean Stevenson, personal communication), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010). Exact figures given in Appendix, Table 32.

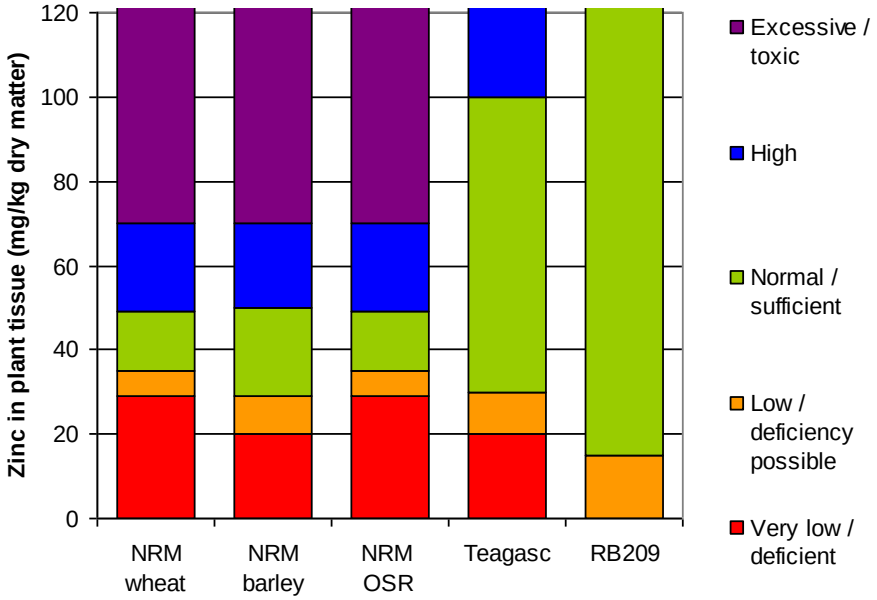

Figure 26. Interpretative scales for zinc in plant tissue. Scales included are NRM (Sean Stevenson, personal communication), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010). Exact figures given in Appendix, Table 33.

There is a consensus between the interpretative scales for Mn in plant tissue that deficiency occurs below about 20 mg/kg; this is consistent with the relationship between experimental yield responses to Mn and tissue Mn status shown in Figure 9.

7. Treatment strategies

7.1. Boron

B fertilisers which are commonly used to treat deficiencies include Borax (11.3% B), Solubor (20.5% B), liquid organics and also B in blended fertilisers. Solubor (disodium octaborate) can be either soil or foliar applied. Foliar application of 10kg/ha Solubor increased oilseed rape yields by approximately 0.5 t/ha and whether or not this application was made in the autumn or spring did not significantly affect the yield response (Table 4). In contrast, a split application of 10 kg/ha Solubor in the autumn and spring significantly reduced yield in comparison to the single treatment. Malhi *et al*., (2003) concluded that the methods which were most effective for improving yield in oilseed rape were incorporation>seedrow>foliar after testing a range of products and placement methods.

7.2. Copper

Soil and foliar applications of Cu fertiliser are commonly used to overcome deficiencies. However, confusion is apparent in the literature as to whether soil or foliar application of Cu fertilisers treats

deficiencies most successfully (Malhi *et al*., 2005). Reith (1968) observed higher yields from 22.7 kg/ha broadcast copper sulphate than from 1.1 kg/ha sprayed on the crop.

Soil applied fertilisers include Cu sulphate which contains approximately 25% Cu and Cu oxychloride powder which contains approximately 52% Cu. The correcting effect of soil applied Cu fertilisers may last up to 10 years depending on the amount applied and soil texture (Sinclair and Edwards, 2008).

There are three main sources of copper foliar fertilisers: Cu sulphate, Cu oxychloride and Cu chelates. Cu chelates (e.g. EDTA), which are an organic salt of copper contain approximately 9% Cu w/v whilst Cu oxychloride contains approximately 25% Cu in liquid formulation. Foliar fertilisers are very useful if a deficiency is determined through tissue analysis, as there is no longer time for soil applications. Typically, for Cu oxychloride application rate is between 200 and 500 g Cu/ha and approximately 70 g Cu/ha for chelated Cu (Sinclair & Edwards, 2008). Foliar 'cocktails' which contain Cu often contain smaller amounts of Cu than specific inorganic or chelated products. Getting the timing of application of foliar products correct is essential for overcoming deficiency. Generally it is thought that foliar application at the late tillering stage is most effective. Karamanos *et al*. (2004) compared the effect of a variety of different foliar products representing different formulations (chelate, lignin sulphonate, humic acid, oxychloride and citric acid) at different growth stages and found that application at early tillering was ineffective, whilst application at approximately GS 47 was not as effective as application at GS 31. Foliar application of a total of 0.435 kg Cu/ha spread over two applications (GS 30 to 31 and GS 32) increased yield significantly by 1.39 t/ha at one of three sites where soil levels indicated deficiency (McGrath, 2012).

7.3. Magnesium

The most common sources of Mg are Mg sulphate, Mg carbonate and Mg oxide. Chelated Mg products have also been produced for foliar application. Kieserite (25% MgO, 50% SO_3) and Epsom salts (16% MgO, 33% SO_3) contain Mg in the sulphate form. Epsom salts are usually applied as foliar sprays whilst Kieserite, which is available in both powder and granular form is soil applied.

7.4. Manganese

Foliar application of Mn fertilisers is the recommended method for dealing with deficiencies. The most common Mn fertiliser used is Mn sulphate, which contains around 24% Mn in solid form but concentration varies with the degree of hydration and the application rate ranges from 1.5 to 3.0kg Mn/ha. Foliar application of Mn chelates can also be used to treat deficiency. Chelates are usually based on EDTA as the chelating agent and typically contain 6 to 7% Mn in liquid form as supplied

for subsequent dilution. Treatment of crops with Mn fertilisers is recommended only when tissue analysis results indicate that a deficiency is present, except where moderate to severe deficiency has occurred regularly in the past and an 'insurance' spray would be recommended. Foliar application of 1.17 kg/ha Mn sulphate which was spread over two applications (GS 30 to 31 and GS 32) had no significant impact on yields of winter wheat even though tissue testing suggested deficiencies at three sites (McGrath, 2012).

7.5. Molybdenum

Ammonium molybdate and sodium molybdate are the usual sources of Mo in the UK and both can be either soil or foliar applied. Additionally, sodium molybdate can be used as a seed treatment.

7.6. Zinc

Treatment of Zn deficiency with either soil or foliar applications of Zn sulphate is the most common method. If soil is known to be deficient, soil application of Zn sulphate at a rate of 60 to 120 kg Zn/ha can be used and this treatment should have a residual effect for a number of years. Foliar applications of chelated forms of Zn, Zn chloride and Zn oxide are also sometimes used to eliminate deficiencies. In the series of experiments summarised in Table 13 it is only foliar applications and not soil applications of Zn fertilisers which led to a significant increase in yield. In a recent study McGrath (2012) found that foliar application of Zn sulphate applied at 0.273 kg/ha over two applications (GS 30 to 31 and GS 32) increased yield significantly by 0.27 t/ha at one site which had 1.07mg/kg EDTA extractable zinc, whilst there was no significant effect at the other 14 sites.

8. Economic evaluation

Agronomists were asked to provide typical costs for micronutrient products (Table 27). Prices varied depending on the formulation of the product (liquid or powder) and whether the dose was intended as a maintenance application, or a higher rate to correct deficiency. The costs in Table 27 refer to single applications; where deficiencies are perceived; up to three applications would often be recommended.

The low costs of micronutrient applications, relative to the current high grain prices means that, for most nutrients, even multiple application timings can be paid for by a yield response of less than 0.1 t/ha. This means it is difficult to determine whether or not applications are economically justified because conventional small plot experiments are only capable of detecting statistically significant ($P<0.05$) yield responses down to about 0.3 to 0.5 t/ha.

Table 27. Price ranges for single and multi-nutrient products, as supplied by agronomists in January 2013, and yield responses required to justify application, assuming no costs of application (products tank-mixed with other maintenance applications).

Nutrient	Price range for a single application (£/ha)	Yield response required to break even (t/ha)*	
		Wheat	Oilseed rape
Boron	4.90 – 6.00	0.025 – 0.030	0.014 – 0.017
Magnesium	1.50 – 4.20	0.008 – 0.021	0.004 – 0.012
Manganese	1.25 – 6.60	0.006 – 0.033	0.004 – 0.019
Multinutrient mixtures	6.50 – 9.50	0.033 – 0.048	0.019 – 0.027

*Assuming grain prices of £200/t for wheat and £350/t for oilseed rape.

9. Recommendations for further work

9.1. Yield response experiments

The greatest problem in determining whether and in what circumstances non-NPKS applications are justified is the inability of conventional plot experiments to detect statistically significant yield responses of 0.1 t/ha (or less) that are required to pay for such applications. Conventional experiments consist of plots, in area rarely exceeding 50 m^2, with treatments usually replicated three or four times and arranged in replicated blocks. 'Least significant differences (LSD)' from this approach are typically 0.3 to 0.5 t/ha, currently worth around £60 to £100/ha for cereals and £120 to £200/ha for oilseed rape. Greater accuracy could be obtained from conventional methods by increasing the level of replication. If a typical randomised block experiment with four treatments and five replicates had a yield LSD of 0.5 t/ha, then increasing the replicate number to approximately 17 would reduce the LSD to 0.25 t/ha. Figure 25 gives an illustration of how changing replicate number may affect the LSD for a specific experiment with four treatments. This analysis shows that increases in replicate number have a diminishing effect on reducing the LSD and it indicates that it will be very difficult to reduce the LSD of a modest sized conventional randomised block experiment to <0.1 t/ha through simply increasing the number of replicates. Therefore, alternative experimental methods should be investigated to enable small yield differences to be statistically tested.

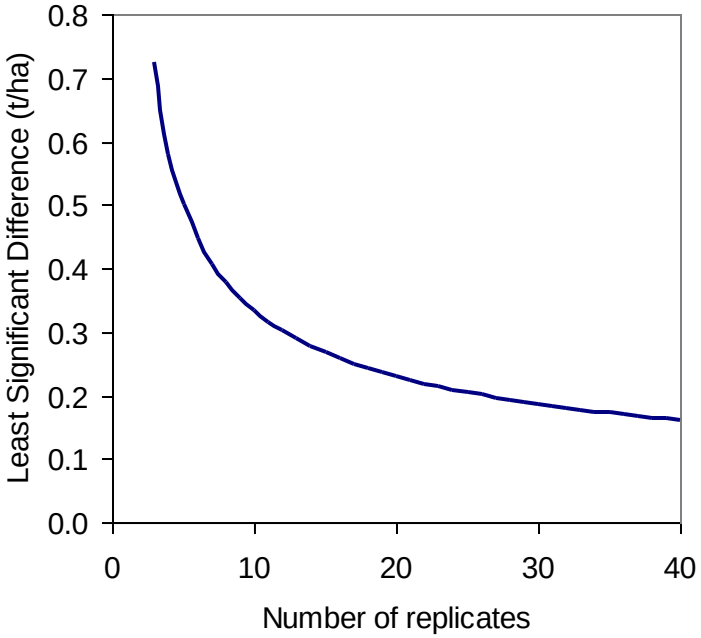

Figure 25. Illustration of how increasing replicate numbers in a randomised block field experiment with four treatments is likely to affect the least significant difference.

Non-NPKS experiments should also change approach to compare treatments with a key nutrient missing against multi nutrient cocktail controls, rather than single nutrients against nil controls. Good experimental practice demands that when investigating the yield response to one factor, yield limitation by other factors should be avoided as far as possible; for example, in nitrogen response experiments, best practice involves robust pesticide programmes to minimise weeds, pests and disease, sulphur applications, and soil testing to ensure adequate levels of P, K and Mg. Although non-NPKS nutrients are rarely a major cause of yield limitation, non-NPKS nutrient experiments are often conducted on light or organic soils where the risks of deficiency are higher; the results will be more robust and defensible if maintenance applications of non-NPKS are used to ensure nutrients other than the one being tested are not yield-limiting.

Further nutrient response experiments are required particularly for those nutrients for which this review has found very limited data.

- Magnesium: cereal and oilseed rape experiments on a range of soil Mg indices, to confirm whether the current advice to maintain soil index 1 is appropriate. If Mg treatments are applied as sulphates, experimental crops should receive adequate sulphur nutrition to ensure that treatment responses are to Mg, not S. Alternatively, Mg may be applied in a form not containing S, such as calcined magnesite. Whilst the impact of soil and rooting conditions on the incidence of Mg deficiency is recognised, it would be inappropriate to attempt crop response experiments under such adverse conditions.

- Boron: further oilseed rape experiments are required to clarify the frequency of yield responses to B. Experiments should include both soil and tissue testing, to determine which is the better diagnostic method, or whether both tests may be combined to give a more accurate prediction of deficiency. Experiments must include soils with very low B levels to determine where the critical soil and tissue thresholds lie.
- Molybdenum: oilseed rape experiments on a wider range of soil types, to investigate the relationship between soil Mo level and yield response to Mo. Experiments must include soils with very low Mo levels to determine where the critical soil and tissue thresholds lie.
- Test the effectiveness of foliar sprays against soil applied treatments for non-NPKS nutrients.

9.2. Soil and tissue testing

Confidence in soil testing for non-NPKS nutrients could be improved by standardisation of testing methods between labs and ring tests to ensure that each lab is giving comparable results. The Profession Agricultural Analysis Group (PAAG) already coordinate quality standards and ring tests for 'standard' soil tests, for P, K, Mg and pH. Given that this system is already in place, PAAG may be able to introduce similar ring tests for other nutrients.

Research should also be conducted to clarify the effects of factors such as soil type and pH on nutrient availability and the risk of deficiency. Some soil testing labs already use models which take account of these and other factors to interpret soil and tissue test results, but these models are based on internal research and there is minimal relevant published research. Important nutrients to study include B, Mn, and Mo. For example, this review has found that many cereal crops respond to Mn, and the yield response is correlated with soil pH and tissue test, but the correlations were not strong, indicating that other factors may be important. An improved diagnosis to predict Mn deficiency would probably involve testing for tissue Mn and soil pH, and possibly other factors, followed by the development of a decision matrix to derive a risk factor or likelihood of yield response.

9.3. Crop requirement and nutrient sources

Information about maximum crop uptake and offtake of different nutrients could not be found for all crops, e.g. Mo offtake in oilseed rape. Further work should be undertaken to rectify this knowledge gap. There were also knowledge gaps for the amount of nutrients contained in organic materials, e.g. B and Mn in manures. A nutrient budget should be calculated for each element; however, to do this, more up to date information is required for atmospheric deposition and reliable data are also required on the rate of nutrients loss via leaching.

10. Conclusions

10.1. Boron

The accepted wisdom that cereal crops are not susceptible to B deficiency was confirmed by this review. The susceptibility of oilseed rape to B deficiency is less clear: significant yield responses occurred in about 10% of experiments, but no correlation was found between yield response and soil or tissue B status. The significant responses to B which have been found justify further research into oilseed rape response to B. Experiments should include soil and tissue testing, to clarify which is more useful for predicting deficiency, or whether a combined approach should be used. Soil pH, soil organic carbon and clay content should also be measured to investigate the relationship between B deficiency and soil physico-chemical properties. The limited data available for this review do not support the RB209 thresholds of <0.8 mg/l hot water-extractable B in soil and 20 mg/kg B in tissue; more research is needed to confirm whether these thresholds are appropriate, and if not, to define more suitable thresholds.

10.2. Calcium

Calcium is an essential micronutrient, but deficiencies are thought be extremely rare in UK arable crops due to adequate Ca supplies in most soils, hence treatments are not justified and further research is not required.

10.3. Chlorine

Chlorine deficiency has not been observed in UK arable crops, probably due to high inputs from the atmosphere, manures and inorganic fertilisers. Treatments are not justified and further research is not required.

10.4. Copper

Cereals can show large yield responses to Cu applications. The relationship between EDTA-extractable soil Cu and yield response to Cu treatment in experiments included in this review supports RB209 advice that soil testing is useful for predicting deficiency and that deficiency is possible on soils with <1.0 mg/kg EDTA-extractable Cu, particularly for barley; winter wheat appears to be relatively unsusceptible to Cu deficiency. Experiments on the residual effects of Cu treatments indicate that applications of copper sulphate to the soil can give yield responses for a number of years, suggesting that soil Cu indices are generally slow to change. Further research may be justified to investigate whether DGT soil analysis could provide a more reliable threshold than EDTA extraction, and whether the threshold should vary with soil type or other soil factors.

For now, however, applications are probably justified to barley on soils with <1.0 mg/kg EDTA-extractable Cu.

10.5. Iron

Iron is an essential micronutrient, but deficiency is thought be extremely rare or non-existent in UK arable crops, due to adequate soil supplies. Where Fe deficiency does occur in susceptible crops (such as fruit crops), it is due to low availability or uptake, rather than low supply. Consequently, deficiencies can be best prevented by ensuring good soil structure, drainage and rooting. Treatments are not justified and further research is not required.

10.6. Magnesium

Data on yield responses to Mg are very limited for both cereals and oilseed rape, which is surprising given that Mg is a major nutrient. It is not possible to draw conclusions on the suitability of existing advice about Mg thresholds and applications. Further experiments should be done on soils with Mg index 0 and 1 to confirm whether or not the RB209 guideline soil level is appropriate and what type and timing of Mg fertiliser is most effective.

10.7. Manganese

Mn applications to cereal crops often give economic yield responses. The results of this review support the current advice that soil testing is of little value, that tissue testing is a better way to predict deficiency, and that there is a greater risk of deficiency on more alkaline soils. The RB209 advice that a tissue test of <20 mg/kg indicates possible deficiency seems appropriate, but with further work it should be possible to refine this threshold to take soil pH into account: the threshold is likely to rise with increasing soil pH. Other factors may also influence the tissue threshold.

10.8. Molybdenum

This review has found few data on oilseed rape responses to Mo applications, and no information about cereals. The limited results available suggest that Mo applications may be justified on some sites, and that soil testing may be a better indicator of deficiency than tissue testing, but that applications may also reduce yield on soils with high Mo (>0.13 ppm). Research should be done to assess the risks of Mo toxicity on UK soils, and to investigate the impact of soil pH on crop Mo requirement, since lime addition has in the past been found to be a more effective treatment than Mo application. No data could be found on the amount of Mo taken up by the crop. Since there are insufficient data to justify firm conclusions in this review, the main finding is that there is a justification for further research into oilseed rape responses to Mo and identifying the threshold levels.

10.9. Zinc

While Zn deficiency for cereals has been shown to occur in many parts of the world, including on some peaty soils in Ireland, this review finds only moderate evidence of zinc deficiency in the UK: significant yield responses occurred in six out of 36 UK experiments. Given this lack of data on yield responses, it is not possible to support or improve on existing advice on soil and tissue thresholds.

10.10. Phosphite

The conclusions of Thao & Yamakawa (2009) and Ratjen & Gerendas (2009), that phosphite does not act as a P fertiliser, are supported by recent experiments on phosphite. These experiments showed no correlation between yield response and soil or tissue P status. However, four out of 15 experiments showed significant yield responses to phosphite which indicates that further work is justified to understand the mechanism of effects.

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13. Appendix: Interpretative scales for soil and tissue analyses

Table 28. Interpretative scales for hot water-extractable boron in arable soils. Some sources specify that scales are only appropriate for boron-responsive crops such as oilseed rape (not cereals). Scales included are ADAS (MAFF, 1976; Anon, 1980a), NRM (Sean Stevenson, personal communication), Levington (Levington Agriculture, date unknown), SAC (Edwards et al., 2012), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010).

Scale	Very low / deficiency probable	Low / deficiency possible	Risk / deficiency unlikely	Normal / satisfactory / adequate	High	Excessive / possible toxicity
ADAS	<0.5	0.5-1		1-2	2-4	>4
NRM	<0.3	0.3-0.6	0.6-1.2	1.2-2	>2	
Levington	<0.4	0.4-0.8	0.8-1.2	1.2-2	2-3	>3
SAC	<0.3	0.3-0.5	0.5-1	1-3.5	>3.5	
Teagasc	<0.5	0.5-1	1-1.5	1.5-2		
RB209		<0.8				

Table 29. Interpretative scales for EDTA-extractable copper in arable soils. Scales included are ADAS (MAFF, 1976; Anon, 1980b), NRM (Sean Stevenson, personal communication), Levington (Levington Agriculture, date unknown), SAC (Edwards et al., 2012), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010). Teagasc provide separate scale for mineral soils and peats. Most scales include a threshold for excessive / possible toxicity, but this is not shown in order to focus on the deficient end of the scale.

Scale	Very low / deficiency probable	Low / deficiency possible	Risk / deficiency unlikely	Normal / satisfactory / adequate	High	Excessive / possible toxicity
ADAS	<1.6	1.6-2.4		2.4-4	4-50	>50
NRM	<1.6	1.6-2.3	2.3-3	3-4.5	>4.5	
Levington	<1	1-2		>2		
SAC	<1	1-1.6		1.6-8.5	8.5-80	>80
Teagasc	<1	1-1.5	1.5-3	>3		
RB209		<1				

Table 30. Interpretative scales for EDTA-extractable zinc in arable soils. Scales included are ADAS (Anon, 1980b), NRM (Sean Stevenson, personal communication), Levington (Levington Agriculture, date unknown), SAC (Edwards et al., 2012), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010).

Scale	Very low / deficiency probable	Low / deficiency possible	Risk / deficiency unlikely	Normal / satisfactory / adequate	High	Excessive / possible toxicity
ADAS		<2	2-3	3-15	15-130	>130
NRM	<0.5	0.5-1	1-3	3-6	>6	
Levington	<0.5	0.5-1.5		1.5-10	10-80	>80
SAC	<0.5	0.5-1.5		1.5-10	40-80	>80

Teagasc	<1	1-1.5	1.5-3	>3
Teagasc (peats)	<2.5	2.5-4	4-5	>5
RB209	<0.5	0.5-1		>1

Table 31. Interpretative scales for boron in plant tissue. Scales included are NRM (Sean Stevenson, personal communication), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010).

Scale	Very low / deficient	Low / deficiency possible	Normal / sufficient	High	Excessive / toxic
NRM (wheat)	<4	4-6	6-10	10-15	>15
NRM (barley)	<4	4-6	6-10	10-20	>20
NRM (OSR)	<22	22-25	25-54	54-80	>80
Teagasc	<15	15-30	30-60	>60	
RB209		<20			

Table 32. Interpretative scales for manganese in plant tissue. Scales included are NRM (Sean Stevenson, personal communication), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010).

Scale	Very low / deficient	Low / deficiency possible	Normal / sufficient	High	Excessive / toxic
NRM (wheat)	<20	20-26	26-60	60-100	>100
NRM (barley)	<20	20-26	26-60	60-100	>100
NRM (OSR)	<22	22-25	25-200	200-300	>300
Teagasc	<20	20-30	30-100	100-500	>500
RB209		<20			

Table 33. Interpretative scales for zinc in plant tissue. Scales included are NRM (Sean Stevenson, personal communication), Teagasc (Coulter & Lalor, 2008) and RB209 (Defra, 2010).

Scale	Very low / deficient	Low / deficiency possible	Normal / sufficient	High	Excessive / toxic
NRM (wheat)	<29	29-35	35-49	49-70	>70
NRM (barley)	<20	20-29	29-50	50-70	>70
NRM (OSR)	<29	29-35	35-49	49-70	>70
Teagasc	<20	20-30	30-100	100-500	>500
RB209		<15			