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Review

Micronutrients limiting pasture production in Australia

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Abstract. Low levels of plant-available micronutrients were an inherent feature of many agricultural soils in Australia, mostly due to the prevalence of highly weathered soil parent materials. The diagnosis and correction of the widespread deficiencies of micronutrients, especially copper (Cu), molybdenum (Mo) and zinc (Zn), were prerequisites for the development of productive, legume-based pastures in southern Australia. In subtropical and tropical regions, Mo deficiency commonly limited pasture-legume production. Soil treatments involving micronutrient fertiliser incorporated in soils, or applied as additives to superphosphate, were generally effective in alleviating micronutrient deficiencies. In the low-output dryland pasture systems, the annual removal of micronutrients in wool and meat is small compared with rates added in fertiliser. Hence, in general, the residues of soil-applied micronutrient fertilisers remain effective for many years, for example, up to 30 years for Cu. By contrast, shorter residual values occur for manganese (Mn) fertiliser on highly calcareous soils, and for Zn in high-output pasture systems such as intensive dairy production. In the last two decades since the recommendations for micronutrient management of pastures were developed, there have been many changes to farming systems, with likely implications for micronutrient status in pastures. First, increased cropping intensity and low prices for wool and meat have meant lower nutrient inputs to pastures or to the pasture phase of rotations with crops. However, when pastures have been rotated with crops, ongoing small additions of Cu, Zn and Mo have been common. In cropping phases of farming systems, lime application and no-till may have altered the chemical and positional availability of micronutrients in soils to pastures. However, there has been little study of the impacts of these farming-systems changes on micronutrient status of pastures or profitability of the production system. The intensification of dairy production systems may also have altered the demand for, and removal rates of, micronutrients. Soil tests are not very reliable for Mn or Mo deficiencies, and well-calibrated soil tests for boron, Cu and Zn have been developed only for limited areas of pasture production and for a limited range of species. There is limited use of plant tests for nutrient management of pastures. In conclusion, there is limited knowledge of the current micronutrient status of pastures and their effects on animal health. Pasture production would benefit from targeted investigation of micronutrients status of pasture soils, pasture plants and micronutrient-linked animal-health issues.

Additional keywords: nitrogen fixation, residual value, subterranean clover pasture.

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Introduction

The micronutrient elements known to be essential for both grass and legume pasture plants are boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn) (Bell and Dell 2008). Legumes that depend on dinitrogen (N_2) fixation for their N supply require Mo in greater amounts for symbiotic function than for the growth of the host plant, and they also require cobalt (Co) as a nutrient for the rhizobia. In addition, sodium (Na), selenium (Se) and silicon (Si) have been shown to be beneficial to plants in some cases, without satisfying the criteria for essentiality for all plants (Marschner 2011). All of the elements essential for plants, with the exception of B, are essential for animals (Bell and Dell 2008). In addition, animals require iodine (I), Se and chromium (Cr) (Underwood and Suttle 1999). Under rigorously controlled laboratory conditions, fluorine (F) and Si have also been shown to be beneficial, particularly when added in minute amounts to purified diets for animals (Underwood and Mertz 1987; Underwood and Suttle 1999). However, there is no evidence of Cr, Ni, F or Si being deficient in pasture ecosystems, and they are not considered further in this paper.

In Australia, most micronutrients are supplied to animals from the direct consumption of pasture or forage species by the grazing animal. Both grass and legume plant species require micronutrients to be taken up from soil solution for adequate, normal or maximum growth. However, agricultural soils vary

widely in total content and plant-available forms of micronutrients and plant species may vary in their requirements (White and Zasoski 1999). Sillanpää (1982) reported micronutrient deficiency in plants from almost every country in their study.

A generalised map of the areas of agricultural soils with inherent micronutrient deficiency risk is presented in Fig. 1. In south-west Western Australia (WA), ~8–9 Mha of land was inherently deficient in Cu, Zn and Mo, and to a lesser extent Mn. Molybdenum deficiency was widespread in pasture legumes in subtropical and tropical pastures of Australia, particularly on acid basaltic soils. In southern Australia, the areas at risk correspond well with the extent of improved pastures.

A feature of agricultural production in southern Australian until the 1980s was the crop–pasture (ley farming) system in which the main pasture species was subterranean clover (*Trifolium subterraneum* L), which supplied the N required for crop production and suppressed crop diseases, especially those of wheat (*Triticum aestivum* L.) (Doole and Weetman 2009). On alkaline soils, particularly in South Australia (SA), medics (*Medicago* spp.) were commonly used instead of subterranean clover in the pasture ley in rotations with wheat

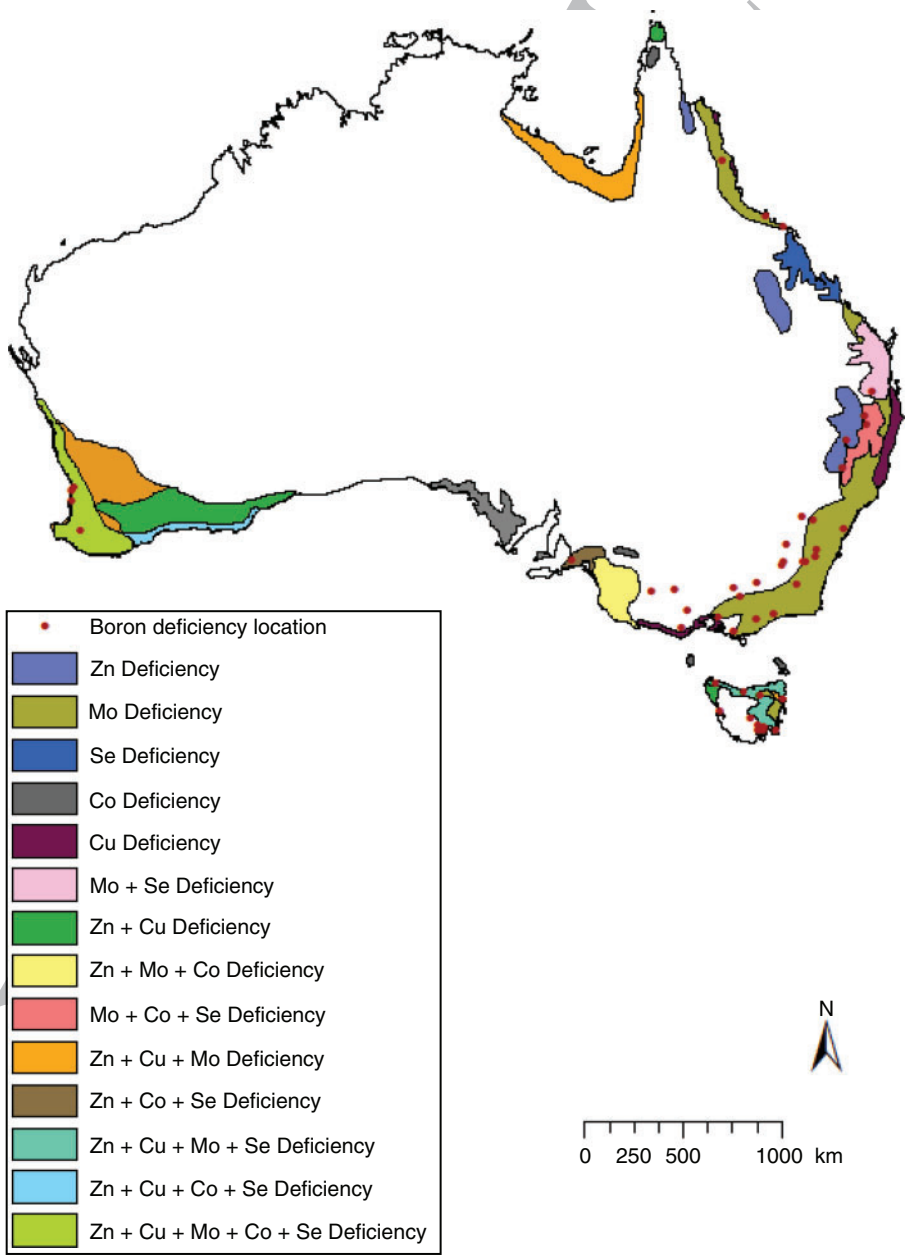

Fig. 1. Inherent and potential micronutrient deficiencies in agricultural soils. Modifed from Hayes *et al*. (2019).

and barley (*Hordeum vulgare* L.). A history of pastures in the ley farming system and their importance to agricultural production systems in southern Australia is outlined by Fitzpatrick (2011).

Since the 1980s, land use has changed towards more extended periods of cropping or continuous cropping. No-tillage planting of crops has become more prevalent, especially in WA and SA, where it covers 90% of the cropping area (Rochecouste and Crabtree 2014). In addition, low prices for wool and meat have led to to decreased inputs, including fertiliser, in the pasture phase. Soil acidification has continued because of inadequate use of lime. Even where programs of lime application have raised topsoil pH, subsoil acidification often continues (Gazey *et al*. 2014). A greater diversity of pasture legume and grass species has also been introduced, including more herbaceous and woody perennial species (e.g. Moore *et al*. 2006). Hence, there have been several changes in farming systems that have consequences for micronutrient supply and availability to pastures and grazing animals. Although micronutrient management packages for southern Australian (WA and SA) farming systems have been developed, these were mainly for cropping and mostly designed for farming systems >40 years ago. These packages may not be adequate for contemporary pasture systems. The recommendations for micronutrients may also be inadequate for more intensive grazing systems such as strip-grazing in dairy livestock systems.

According to Judson and McFarlane (1998), the main trace element deficiencies for grazing livestock are Co, Cu, I, Mn, Se and Zn. Mild mineral deficiencies are especially difficult to identify because their effects are rarely distinguishable from those due to underfeeding or intestinal parasitism. An initial assessment of the actual or likely occurrence of a dietary mineral inadequacy can be made by comparing the mineral composition of the diet with recommended levels (Underwood and Suttle 1999). These factors are frequently not integrated into fertiliser decision support systems for recommending micronutrients in the pasture–crop system.

Essential elements for pasture and animal production

Pastures plants in Australia generally come from the grass (Poaceae) and legume (Fabaceae) families. The function and importance of the essential micronutrients for plants, rhizobia and ruminants have been well reviewed (e.g. Minson 1990; Blevins and Lukaszewski 1998; Gerendás *et al*. 1999; Underwood and Suttle 1999; O'Hara 2001; White and Broadley 2001; Brown *et al*. 2002; Hänsch and Mendel 2009; González-Guerrero *et al*. 2014). Here we provide a brief overview of the function of these elements for plants, rhizobia and ruminants, and have indicated sources where more detailed accounts can be found.

Boron

Boron is required in plants for cell wall structure through its association with pectin, as well as having roles in membrane structure and function, detoxifying reactive oxygen species (ROS), and phenol metabolism (Blevins and Lukaszewski 1998; Brown *et al*. 2002).

In the legume–rhizobia symbiosis, B is fundamental to *nod*-gene activation by root exudates and is required for nodule initiation, infection thread development and nodule invasion (Bolaños *et al*. 1996; Redondo-Nieto *et al*. 2001).

Chlorine

Chlorine is important to plants for osmotic regulation and turgor in the vacuole, reactivity of enzymes, regulation of intercellular pH gradients, membrane potential, and photosynthesis (Welch and Shuman 1995; White and Broadley 2001).

Cobalt

In rhizobia, Co forms the coenzyme cobalamin (vitamin B12), which is used for methionine synthesis, the synthesis of DNA precursors and the synthesis of leghemoglobin, which provides the oxygen required for the reduction of N_2 to ammonia (NH_3) during N fixation (Drennan *et al*. 1994; Becana *et al*. 2000; O'Hara 2001).

Rumen microorganisms, similar to rhizobia, require Co for the synthesis of vitamin B12. Cobalt deficiency leads to a reduction in methylation, abnormal lipid metabolism, decreased blood haemoglobin and protein, urea and cholesterol in the serum, and impaired disease resistance (Minson 1990; Spears 1999; Underwood and Suttle 1999).

Copper

In plants, Cu plays important roles in photosynthesis and electron transport, as an enzyme co-factor, in cell-wall metabolism and oxidative stress response, and in abiotic stress signalling (Yruela 2009).

In rhizobia, Cu is required for N fixation, is needed for rhizobial respiration, and is involved in detoxification of ROS produced in the N-fixation process (Preisig *et al*. 1996; González-Guerrero *et al*. 2014).

In ruminants, Cu is a component of many important enzymes including lysyl oxidase, ceruloplasmin, tyrosinase, cytochrome oxidase and superoxide dismutase, and is required for reproduction, bone development, and growth and development of connective tissue (Spears 1999). Insufficient Cu intake can lead to anaemia, bone disorders, connective-tissue disorders, neonatal ataxia or 'swayback' in lambs born to Cu-deficient ewes, cardiovascular disorders, diarrhoea, infertility and increased susceptibility to infection (Underwood and Suttle 1999). Copper deficiency also causes 'steely wool', where the wool is weakened and the fibre is straight and lustrous and loses its characteristic crimp (Lee 1956); it can cause the fleeces of black sheep to lose their pigmentation (Smith and Gawthorne 1975).

Iodine

Iodine is crucial in ruminants for the function of the thyroid hormones, thyroxine and triiodothyronine, which control oxidation rates and protein synthesis in cells (Spears 1999; Underwood and Suttle 1999). These hormones are important for fetal development, lipid, carbohydrate and N metabolism, regulation of energy metabolism, digestion, growth, muscle function, reproductive performance, and immune defence (Minson 1990; Underwood and Suttle 1999). Iodine deficiency can result in an enlargement of the thyroid gland in the neck (goitre). Iodine deficiency can lead to impaired brain

development, impact on reproductive success, growth and postnatal mortality, and result in low milk yield (Underwood and Suttle 1999).

Iron

In plants, Fe is involved in photosynthesis, N assimilation, synthesis of hormones, regulation of ROS, osmoprotection, and mitochondrial respiration (Hänsch and Mendel 2009).

Many proteins involved in the legume–rhizobia symbiosis contain Fe. These include nitrogenase, which is integral to N fixation; ferredoxin, which is involved in electron transfer and reducing the Fe component of nitrogenase; and leghemoglobin, which helps to control oxygen concentrations for N fixation and respiration (Brear *et al*. 2013).

In ruminants, Fe is an important constituent of haemoglobin and myoglobin, which are vital to oxygen transport in the blood. Iron is also involved in electron transport and is a component of many enzymes (Spears 1999; Underwood and Suttle 1999). Its deficiency in ruminants leads to anaemia, which can cause a loss of appetite, reduced growth, lethargy, lightening of mucous membranes, increased respiration rate, and death in severe cases (Underwood and Suttle 1999).

Manganese

Manganese plays important roles in plants by catalysing reactions and activating enzymes (Hänsch and Mendel 2009). Examples of its functions in plants include the water-splitting system of photosystem II, synthesis of ATP, ribulose-1,5-bisphosphate carboxylase reactions, and biosynthesis of chlorophyll, fatty acids, lipids, aromatic amino acids, lignins, flavonoids and phytohormones, and it is involved in defence against ROS (Campbell and Nable 1988; Hänsch and Mendel 2009; Millaleo *et al*. 2010). In rhizobia, Mn is required for enzyme function and in nodulation and N fixation (O'Hara 2001).

Manganese is a key component of several important enzymes in ruminants, including pyruvate carboxylase, arginase and mitochondrial superoxide dismutase (Spears 1999; Underwood and Suttle 1999). It has functions in cartilage and bone development, synthesis of prothrombin (involved in blood clotting), lipid and carbohydrate metabolism, and protecting cells from damage due to ROS (Minson 1990; Underwood and Suttle 1999). Manganese deficiency can cause skeletal abnormalities, reproductive disorders and disproportionate loss of female fetuses (Minson 1990; Underwood and Suttle 1999).

Molybdenum

Molybdenum is a key component of four important plant enzymes: nitrate reductase, which reduces nitrate to nitrite; peroxisomal sulfite oxidase, which detoxifies excess sulfite; aldehyde oxidase, which is integral to the biosynthesis of abscisic acid; and xanthine dehydrogenase, which is important in purine catabolism, response to pathogens and other stressors, and senescence (Schwarz and Mendel 2006). In rhizobia, Mo is required as it is a key component of nitrogenase, which enables N fixation (O'Hara 2001).

In ruminants, Mo is a component of the enzymes xanthine oxidase, sulfite oxidase and aldehyde oxidase (Spears 1999). High Mo concentrations reduce the availability of Cu, and this apparent Cu 'deficiency' due to high Mo is often exacerbated by low Cu status in the animal (Underwood and Suttle 1999; Whitehead 2000).

Nickel

Nickel is important for urease activity and ureide metabolism, as well as seed viability (Welch and Shuman 1995; Hänsch and Mendel 2009). In rhizobia, Ni is required for efficient N fixation because it is needed by hydrogenase, which recycles the H_2 produced by nitrogenase (Gerendás *et al*. 1999).

Selenium

Selenium is required by rhizobia because it is a crucial component of several seleno-amino acids including selenocysteine, which is present in several important enzymes, and selenomethionine, which is an antioxidant important for detoxifying ROS (Ekanayake *et al*. 2017).

In ruminants, Se is a component of some enzymes and selenoproteins including glutathione peroxidase and iodothyronine deiodinases, and works with vitamin E to detoxify ROS (Spears 1999; Underwood and Suttle 1999). Selenium is required for growth, reproduction and protection from disease (Underwood and Suttle 1999). Selenium deficiency can cause reductions in growth rate, milk production and fat percentage, wool production and fertility (Minson 1990).

Zinc

Zinc is a cofactor of many plant enzymes (Brown *et al*. 1993) including zinc finger proteins, which bind DNA, RNA, proteins and other molecules, regulate stomatal closure and provide protection from ROS (Broadley *et al*. 2007).

In rhizobia, Zn is involved in carbonic anhydrase, which is important for root nodulation (Vance 2008). Zinc is also required for N fixation in the nodule, although its role(s) in N fixation are not fully elucidated (León-Mediavilla *et al*. 2018).

Zinc is a constituent in many ruminant enzymes including DNA and RNA polymerases, alcohol dehydrogenase and pyruvate dehydrogenase. It is important in vitamin A metabolism, is involved in gene expression and membrane stability, and regulates appetite (Spears 1999; Underwood and Suttle 1999). Zinc deficiency can reduce growth, fertility and milk production, cause a loss of appetite and skeletal disorders, and impair testicular development (Minson 1990; Underwood and Suttle 1999). Zinc deficiency can also cause wool to become brittle and thin and to lose its crimp (Mills *et al*. 1967; Underwood and Somers 1969).

Soil factors affecting micronutrient availability

Pasture plants and their associated symbiotic microorganisms obtain most of their micronutrients via the soil (see example of Zn in Fig. 2). However, the availability of these micronutrients for uptake is significantly affected by several soil factors including concentration of the element, soil type, clay percentage and clay type, organic matter concentration, soil pH and soil moisture (Whitehead 2000; Bell and Dell 2008).

In general, the availability of the micronutrients occurring as cations, especially Fe, Mn, Zn and Co, tends to increase with declining soil pH, whereas the availability of the micronutrients

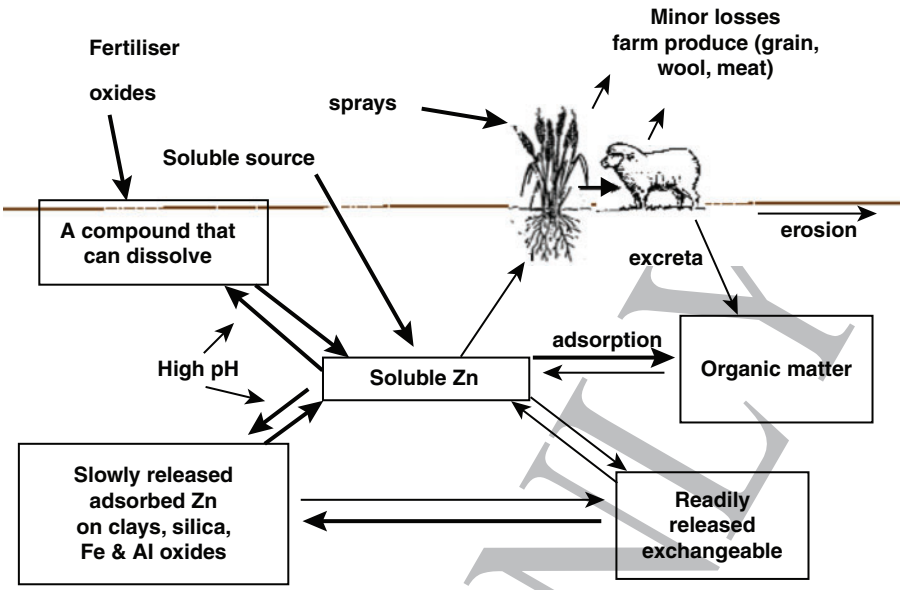

Fig. 2. The soil–plant–animal cycle, using zinc (Zn) as an example, with possible Zn additions and losses to this system for soils of Western Australia (Brennan 2005). Note that the leaching process is non-existent for zinc.

occurring as anions (B, Mo and Se) tends to decrease with declining soil pH. The effects of lime on concentrations of micronutrient elements in pasture herbage are due partly to the addition of Ca and partly to the increase in soil pH. When liming results in an appreciable increase in soil pH (e.g. from pH <5.5 to ≥7.0), there is usually a substantial reduction in the concentrations of Fe, Mn and Co, a small reduction or little difference in Zn and Cu, and an increase in Mo (Mitchell 1963; Stewart and McConaghy 1963; Price and Moschler 1965, 1970; John *et al*. 1972; Edmeades *et al*. 1983).

Soil pH in particular has a large effect on the availability of micronutrients for plant uptake, with B, Co, Cu and Mn being most available at pH in the range 5.0–7.0 (Bell and Dell 2008), and Mo at pH 5.0–6.0 (Sillanpää 1982). Victoria, Tasmania, coastal New South Wales and Queensland, and south-west WA have generally acidic topsoils (pH 4–5.5) (de Caritat *et al*. 2011), which can make micronutrients such as Mo relatively unavailable for pasture uptake (Fig. 1). These areas also happen to include important areas for improved pastures supporting dairying (Dairy Australia 2018), beef production (MLA 2018*a*) and sheep production (MLA 2018*b*); therefore, the low pH in these regions may significantly affect Australian pasture and animal production as a whole, in part through effects on micronutrient availability.

Species and varietal differences in micronutrient concentrations

There can be considerable differences in micronutrient concentrations among species of grasses and legumes (Whitehead 2000). Legumes often contain higher concentrations of Fe, Zn, Cu and Co than grasses, whereas Mn concentrations are sometimes higher in grasses than in legumes (O'Hara 2001). However, whether legumes or grasses have higher concentrations also depends on the soil concentration of the element (i.e. high or low; Whitehead 2000).

Differences in shoot micronutrient concentrations also exist among cultivars or varieties of the same species. Significant differences in micronutrient concentrations have been found among cultivars of prairie grass (*Bromus willdenowii* Kunth) for Fe, Mn, Zn and Cu (Rumball *et al*. 1972); Rhodes grass (*Chloris gayana* Kunth) for B, Mn and Zn (Jones *et al*. 1995); and red clover (*Trifolium pratense* L.) for Fe and Zn (Lindström *et al*. 2013). Differences in micronutrient concentrations were also found in cocksfoot (*Dactylis glomerata* L.) for Co, Cu, Mn and Zn (Forbes and Gelman 1981) and in perennial ryegrass (*Lolium perenne* L.) for B, Co, Cu, Fe, Mn, Mo, Se and Zn (Crush *et al*. 2018). However, inter-varietal differences in micronutrient concentrations were not always consistent among sampling times or sites. More data are needed to establish whether it is feasible to breed varieties of pasture grasses or legumes with consistently higher shoot micronutrient concentrations.

Residual value of micronutrient fertiliser additions

A distinctive feature of micronutrient management for pastures is the long residual value of micronutrient additions to soils relative to that of macronutrient fertilisers. Hence, after diagnosis of deficiency and determination of the optimum rate to correct deficiency in pastures, the next key step in fertiliser decision making is to estimate the residual value of the applied fertiliser. The residual value refers to how long after the initial application an adequate supply of nutrient to the pasture plant is maintained for maximum pasture and animal production. Knowledge of the residual value of micronutrient fertiliser is therefore important for determining when a further application of the micronutrient is required to prevent deficiency re-occurring and reducing pasture herbage yield or animal production (including wool and milk output). To estimate the residual value of a micronutrient

fertiliser, it is necessary to know which soil properties control chemical reactions, losses and additions in the soil–plant cycle because these determine the availability of the nutrient within the soil for pasture plants (Fig. 2).

Reactions of applied micronutrients with the soil constituents are the major cause of reduction in nutrient availability with time. Losses by leaching appear negligible even in sandy soils for most micronutrients (e.g. Cu, Gartrell 1981; Zn, Brennan and McGrath 1988). Boron, by contrast, is leachable on sands (Bell 1999). The amounts of micronutrients removed in harvested products from pastures (hay, wool, body mass) vary markedly for each element but generally are low or minute compared with the amounts added in fertiliser (Table 1). The typical removal of Zn for wool and meat (<10 g Zn ha^{-1}) is 60–80% less than for dairy cattle production for milk (27–46 g ha^{-1} $year^{-1}$). However, in dairy production systems, cattle are fed grain and other supplements bought onto the farm. Further studies are needed to determine the micronutrient balance in typical dairy systems, after accounting for all input and outputs.

Based on the rates of Zn fertiliser applied to soils of WA for cereal and pasture production, Zn is predicted to have a long residual value (Brennan and Bolland 2007). Even if 70% of an initial Zn application is strongly sorbed by the soil, based on the small rates of Zn removal, the residual Zn is likely to supply crop and pasture requirements for 17 years (Brennan 2005). According to Brennan and Bolland (2007), 1 kg Zn ha^{-1} added as fertiliser would remain effective for 40 years of supply on a yellow duplex soil. In another study, after 17 years, the 1 kg Zn ha^{-1} remained fully effective in correcting Zn deficiency in six grain crops (Brennan and Bolland 2006); however, like much of this work, the study did not include pasture species, and data are still limited to a small range of soil types. Micronutrients may also be supplied in NPK fertilisers, as either intentional or incidental constituents. Some fertilisers contain appreciable amounts of micronutrients, especially those derived from phosphate rock. For example, Verloo and Willaert (1990) reported Zn concentrations varying from 6 mg kg^{-1} in potassium chloride and 12 mg kg^{-1} in ammonium nitrate to 244 mg kg^{-1} in superphosphate. Similarly, research with cereal crops in WA has shown that regular (usually annual) application of >150 kg superphosphate ha^{-1} incidentally containing 400–600 mg Zn kg^{-1} supplied sufficient amounts of Zn to meet the requirements of the current crop and pasture production indefinitely (Brennan 2005). Frequently, these additions of superphosphate have maintained adequate Zn levels in soils despite any decline in the effectiveness of the original Zn application as Zn fertiliser (Brennan 1998, 2000).

Table 1. Typical amounts removed of copper (Cu), molybdenum (Mo) and zinc (Zn) in wheat or barley grain, lupin seed, wool, meat or milk

Product	Cu	Mo	Zn
Wheat or barley grain (g t^{-1})	8[A], 3[B]	0.16–0.2[C]	5–25[B,D]
Lupin seed (g t^{-1})	5[E], 4[B]	1.8[E]	17–30[B,D]
Sheep for wool production (g ha^{-1})	0.3[A]		<10[D]
Sheep for meat production (g ha^{-1})	>12[A]		<10[D]
Dairy cattle for milk production (g ha^{-1})			27–46[F]

[A]Gartrell (1981). [B]White *et al*. (1981). [C]Gupta (1971). [D]Brennan (2005). [E]White *et al*. (2007). [F]Dr M Staines, DPIRD, Busselton, WA, provided milk production data used for the calculation, which accounts only for removal in milk, not for removal in bodyweight of animals removed; Zn concentrations in milk taken from Dunshea *et al*. (2019).

Micronutrient additions through applications of macronutrient fertiliser to agricultural soils are a major source of micronutrient supply for pasture plant growth (Naidu *et al*. 1996). It is unusual for the amount of micronutrients added in macro or compound fertiliser to be taken up and completely removed; hence, the remainder adds to the soil reserves of micronutrients. Also, a proportion of the fertiliser nutrient that is taken up is subsequently returned to the soil in plant residues or manures and urine of grazing animals, and hence adds to the micronutrient soil reserves. Other inputs from straw, hay, silage, sewage waste and animal manure are generally less important sources of micronutrients for pasture systems in Australian agriculture (Fig. 2). Similarly, industrial and manufacturing processes and the disposal of domestic and industrial wastes that contribute to micronutrient enrichment of soils are not currently of major importance for Australian agriculture. Increased recycling of urban composts or sewerage sludge and their derivative products would increase the recycling of Zn, Cu and Ni, in particular, onto agricultural land. In this situation, a risk assessment based on the increased load of micronutrients and soil reactivity would be needed.

Case study of the residual value of Zn for pasture

Zinc cycling in the soil–plant–animal system is a process not well documented in the literature. The Zn in herbage harvested as pasture hay is either returned to the soil via animal excreta or removed if the produce is exported off the farm (meat, wool, and milk). For example, pasture hay yielding 7 t ha^{-1} would remove ~175 g Zn ha^{-1} if taken away from the farm, as calculated from pasture Zn levels in WA from Masters and Somers (1980). The amounts removed in the produce of animals are typically low relative to the amount of fertiliser Zn applied. In animals, the whole body concentration of Zn on a fresh basis ranges from 20 to 30 mg kg^{-1} in cows (Miller *et al*. 1974) and sheep (Grace 1983), or on a dry-weight basis from 20 to 250 mg kg^{-1} (Underwood 1977; O'Dell 1979; Hill *et al*. 1983*a*, 1983*b*, 1983*c*). However, in the case of sheep, ~55% of the body's Zn can be in wool. Masters and Moir (1980) found ~110 mg Zn kg^{-1} in the wool of sheep from WA. Typical wool production is 60–80 kg ha^{-1} during spring (August–November) in intensively grazed pasture systems of WA (Thompson *et al*. 1994, 1997; Hyder *et al*. 2002). Hence, annual Zn removal in wool ranges from ~6.5 to 8.8 g ha^{-1}. Similarly, 50-kg mature Merino wethers grazed at 12 sheep ha^{-1} (Thompson *et al*. 1997) and containing 30 mg Zn kg^{-1} body mass (Grace 1983) would remove ~1.8 g Zn ha^{-1} from a grazed pasture system in WA. The annual loss of Zn from an intensively grazed system, assuming complete removal of the animals and wool (~8–10 g Zn ha^{-1}) from the system, represents ~1–1.5% of the amount of Zn typically applied initially as a fertiliser in agricultural systems of WA. In set-stocking-rate grazing systems (Thompson *et al*. 1994, 1997; Hyder *et al*. 2002), the loss of Zn from the system would be about one-third to one-half that calculated for the intensively grazed system. The set-stocking-rate grazing system is the more typical system for dryland pastures in WA and should remain adequately

supplied with Zn for >15 years after a typical initial application of 1 kg Zn ha^{-1}, or longer if pastures are topdressed with P fertiliser enriched with Zn.

Summary of the residual value of micronutrient fertiliser for pasture

Similar to Zn, Cu has a long residual value and frequent additions of Cu are not required (Table 2). The residual value of Mo in south-west WA was estimated to be 5–10 years, whereas in subtropical and tropical regions, the residual effectiveness was only 2–5 years (Table 2). By contrast, Fe applied to the soil surface for 1 year was ~60% as effective as Fe sulfate applied immediately before pasture growth commenced, whereas Fe applied 5 years before was about one-third as effective as the recently applied Fe for herbage production (Brennan and Highman 2001).

Most of the estimates of residual value of micronutrient fertilisers have been derived from studies with crops. For pasture species, differences are likely among species and cultivars for uptake of micronutrients such as Zn (Grewal and Williams 1999) that would need to be accounted for when determining the residual value of fertiliser. For example, among 15 lucerne cultivars that differed in Zn efficiency, there was a 2-fold difference in Zn uptake by shoots under Zn-deficient conditions, but with adequate Zn supply in the soil, all cultivars absorbed similar amounts of Zn into shoots (Grewal and Williams 1999). Cultivar differences in residual value of micronutrient fertiliser have not been researched. Similarly, there are no data on residual value for the newer pasture species such as legumes serradella (*Ornithopus sativus* Brot.), annual medics, tedera (*Bituminaria bituminosa*) and biserrula (*Biserrula pelecinus* (L.) C.H.Stirt.) and a range of grasses such as Italian ryegrass (*Lolium multiflorum* Lam.) now grown in pasture systems. The residual values of B, Se and Mn are poorly defined for Australia pasture–animal systems. Similarly, the residual value of micronutrients may have changed as a result of the effects of liming on acid soils.

Micronutrient diagnosis and prognosis of deficiency

Soil and plant tests are used for the initial diagnosis of micronutrient disorders, and to determine when a re-application of micronutrient fertiliser is needed. However, total soil levels of Cu, Zn, Mn, B or Fe in agricultural soils are poor predictors of micronutrient deficiency in pasture plants because plant availability depends on the form of the micronutrients in soils, which in turn is determined by soil pH, organic matter content, adsorptive surfaces, and other physical, chemical, and biological conditions in the rhizosphere (Bell and Dell 2008).

In general, inaccurate soil and plant test results are more likely with micronutrients than with macronutrients because, by definition, they are present in very low concentrations so that the risk of results being affected by contamination is high. Analytical methods such as inductively coupled plasma-mass spectrometry have greater sensitivity, and therefore greater ability to determine low concentrations than the methods used when much of the Australian soil micronutrient research was completed. Errors may arise at various stages of the soil or plant testing process. Appropriate procedures for sampling the soil or pasture are essential to achieving accurate analytical results, and are particularly important with soil because of the marked spatial variability that occurs in paddocks. Herbage may be contaminated by soil before or during collection, or by dust during the drying and grinding operations, and such contamination will increase the apparent concentration of micronutrient elements, especially Fe, Co and I, whose concentration is much greater in soil than in plant material.

Samples, particularly of plant material, can be subject to contamination from the packaging used during collection or storage; various types of plastic and paper contain appreciable amounts of some micronutrient elements, especially Zn and B (Bell and Dell 2008). In addition, soil, plant and animal tissue samples can all be contaminated during drying and grinding through abrasion of the grinding mechanism. Steel components may contaminate the sample with Fe, brass components may add Cu and Zn, and rubber fittings may add Zn (Bell and Dell 2008).

Soil tests

Micronutrient availability in soils can be assessed by using chemical and biological tests. Various chemical extractants including mineral acids (e.g. 1 N HCl), salt solutions (e.g. 0.01 M $CaCl_2$), buffer solutions (e.g. 1 M NH_4OAc) and chelating agents (e.g. DTPA) have been used to measure micronutrient availability in soils (Sutton *et al*. 1984; Payne *et al*. 1988; Sims and Johnson 1991; van der Watt *et al*. 1994). For micronutrient metals, chelating agents such as EDTA and DTPA are usually more reliable (Sims and Johnson 1991) because they are more effective in removing potentially plant-available soil fractions. One of the most well-calibrated soil tests for micronutrients in pastures in southern Australia is the DTPA Zn soil test, developed for prognosis of potential Zn deficiency in subterranean clover (Brennan and Gartrell 1990). Development of similar calibrations for Zn on other pasture species would require many new field experiments on a range of soil types. Considering that Zn deficiency rarely exists now owing to the widespread use of fertilisers that contain Zn, the conditions are not available to acquire such new experimental data readily. The more feasible approach will be to determine the response of the new species relative to that of subterranean clover on a limited selection of soil types. A similar approach was suggested by Conyers *et al*. (2013) to address the paucity of soil test data for pulses and oilseeds relative to wheat.

Table 2. Residual values proposed for a range of micronutrients for pasture production and animal nutrition, based on the recommended application to originally deficient soil for set-stocking systems in south-west Australia or for tropical pastures

Element	Residual value (years)	Source
Copper	15–20	Brennan 2006
Zinc	15–20	Brennan and Bolland 2006, 2007
Molybdenum	5–10	Brennan 2002
	2–5[A]	Johansen *et al*. 1977
Iron	2–3	Brennan and Highman 2001
Cobalt	1–2	Adams *et al*. 1969

[A]For tropical pasture legumes, on a range of soil types.

Reuter *et al*. (1983) suggested that plant species differ in characteristics of Cu uptake and translocation within the plant. Therefore, it is likely that separate calibrations for soil Cu will be required for different plant species, as has been found for soil testing for phosphorus (Bell *et al*. 2013*a*, 2013*b*). We consider it highly unlikely that soil-test Cu calibrations will now be developed for a range of pastures on different soils in Australia. This would require many field experiments over many years, as well as a range of soil types that are Cu-deficient. Such conditions are less common now owing to widespread use of fertiliser Cu on soils that were originally deficient across Australia. As discussed above for Zn, there would be merit in determining the response of new pasture species to Cu relative to the response of subterranean clover. It would then be feasible to adapt the clover Cu decision tools to the alternative pasture species.

Critical values for predicting micronutrient limitations in pastures are reported in Peverill *et al*. (1999). Most of the soil tests are based on sampling the 0–10 cm layer during the dry season and using standardised laboratory methods (Rayment and Lyons 2011).

Although soil tests are not as accurate as plant tests for predicting micronutrient deficiencies, they can be useful for a general assessment of the risk of deficiency, and to identify changes in availability due to soil-management practices such as lime application and no-till cropping and as a consequence of increasing acidity.

An alternative approach was developed by Wong *et al*. (2005) for B, for which no calibrated soil tests had been developed. This involved developing a risk-prediction map for B deficiency based on soil pH, soil texture, geology, and limited cases of B response in crops to B fertiliser in pot experiments. This approach could be applied across pasture-growing areas in Australia to develop deficiency risk maps that reflect current farming systems as well as the inherent risk of deficiencies as described by Hayes *et al*. (2019).

Plant tests

Plant tests are inherently more reliable than soil tests for predicting micronutrient deficiencies because the concentration in the plant relates directly to plant requirements and represents the integrated effect of various factors that determine uptake by the plant (Smith and Loneragan 1997). Plant tests are used for diagnosis of observed or suspected disorders (deficiency or toxicity), for the prognosis or prediction of a disorder that may emerge later in the growing season, or for monitoring long-term trends in nutrient status (Smith and Loneragan 1997). The most accurate plant tests are those based on defined young leaves of pasture species (Smith and Loneragan 1997). Such leaves tend to reflect current nutrient supply to the plant from soils and hence reflect the current availability for pasture growth.

Whole shoot samples are used by some commercial testing services (e.g. NUlogic; CSBP, Kwinana, WA). Whole shoots are easier to sample but may reflect earlier growth conditions and soil nutrient supply rather than current conditions. In the case of the phloem-immobile or variably mobile micronutrients (B, Cu, Fe, Mn, Zn), high concentrations that accumulated in old leaves during early growth may give a false diagnosis of adequate supply (Smith and Loneragan 1997); in the same plants, under current soil supply, young leaves may contain deficient concentrations.

Whether young leaves or whole shoots are sampled, diagnosis depends on calibrated critical concentration or critical ranges for that nutrient defined for a specified time of sampling. Reuter and Robinson (1997) provide the most comprehensive listing for pasture species in Australia of critical concentrations for the diagnosis and prognosis of micronutrient deficiencies. A selection of critical concentrations is provided in Table 3. However, there is a paucity of calibrated critical-range data for micronutrient deficiencies in new pastures species.

Fertiliser decision-making practices for micronutrients

For micronutrients such as Cu, Zn and Mo that generally have a long residual effectiveness in soils, paddock-by-paddock records of the last time of micronutrient fertiliser application probably provide the most useful information for micronutrient-fertiliser decision making. Simple models such as that of Brennan (2005), as reported in Bell and Dell (2008), based on estimated availability of fertiliser, annual removal and the input from fertiliser can be useful in estimating the frequency of re-application (Table 4). Based on this model, in cases where Zn-enriched fertilisers are applied regularly, Zn supply to pastures should be indefinitely adequate as long as there is no major change in rate of removal or an increase in Zn reaction with the soil. Lime application is a soil-management practice that may decrease availability and hence trigger a need to re-assess the residual value of the Zn fertiliser (Brennan *et al*. 2005).

Another approach would be to conduct soil tests every 5–7 years to monitor the micronutrient status in soils that have previously had additions of micronutrient fertiliser and are receiving small supplementary additions on a regular basis in macronutrient fertiliser. Although soil testing is not as reliable for predicting crop responses to micronutrient fertilisers, repeated soil testing over time can be useful for establishing a time trend. This use of soil testing should detect declines over time in availability, or significant changes in availability due to lime or other soil-management practices.

Plant tests early in the season can be used to determine whether remedial applications by foliar application are needed during the season.

Table 3. A selection of critical concentrations (mg kg^{-1}) of micronutrients for maximum pasture production, in youngest open leaves and whole shoots of subterranean clover before flowering (Pinkerton *et al*. 1997)

	Youngest open leaves	Whole shoots
Copper	4.3–5.5	<3.5–4.5
Zinc	15–25	10–15
Molybdenum	0.1–0.2	0.1–0.2
Boron	20–24	–
Iron	50–75	–
Manganese	15–20	–
Cobalt	<0.04	<0.04–0.10

Table 4. Budget for zinc (Zn) inputs and outputs for a typical pasture-ley rotation in south-west Australia on a low-Zn sandy loam soil with an initial application of 0.75 kg Zn ha^{-1}, as recommended
Source: Brennan (2005)

	Yield (t ha^{-1})	Zn in produce (mg kg^{-1})	Zn removed	Zn added (g ha^{-1})	Zn balance
Pasture and clean wool (P)	0.04	110	3.5	90[A]	86.5
Wheat (W)	1.5	22	33	0	–33
Lupin (L)	1.1	30	33	0	–33
Canola (C)	1.1	30	33	0	–33
Sum					–12.5
No. of cycles of P–W–L–C			42[B]		

[A]Assumes Zn-enriched superphosphate used to supply phosphorus and Zn during the pasture phase of the rotation.
[B]The number of cycles is based on the amount of Zinc available for uptake minus the amounts removed per cycle. Zinc available for uptake is the proportion of the applied fertiliser Zn that remains in the plant-available pool, and depends on the Zn-sorption capacity of the soil, which in the calculation was 70%, based on Brennan (2005).

Micronutrient additions in dairy systems are primarily focused on animal health rather than pasture production; therefore, these micronutrient deficiencies are usually corrected by using animal-based interventions such as licks, injections or boluses. Decisions about micronutrient interventions for animal health are usually informed by past or present deficiency symptoms in the animals on the farm or at a nearby farm, or, more rarely, by soil or forage test results (PJM Raedts, pers. comm.).

The majority of Australian dairy farmers are using N-fertiliser application to drive pasture growth and are wary of having a large legume component because of the risk to livestock of bloat. Therefore, they tend to have a small legume component in their sward. Hence, Co and Se, which are required by rhizobia but not for grass growth, are not often applied directly to pastures in dairy systems. Furthermore, even the models and courses that researchers, advisors and consultants use to make fertiliser decisions or give fertiliser guidance, such as DairyMod (Johnson 2016), SGS Pasture Model (Johnson 2016), Dairy N Fertiliser Advisor (Stott *et al*. 2015) and Fert$mart (Dairy Soils and Fertiliser Manual Team 2013), have little or no inclusion of micronutrient management and fertilisation. Inclusion of micronutrients in these models and courses could be useful to improve animal health and legume N fixation for organic and low-input systems.

Conclusions

For management of micronutrients in pastures, growers face a dilemma. On the one hand, for old clover-based pastures systems in WA and SA, there is rich literature on management of micronutrients, especially Co, Cu, Mo and Zn (less so Mn). However, it is not clear how much of this knowledge can still be applied in those areas because of changes in farming systems and practices, or whether it is reasonable to extrapolate to other parts of Australia with different soils, climates and pasture species. On the other hand, there is limited contemporary research on micronutrient status of pastures. Given this uncertainty, an updated assessment of micronutrient status in representative pasture systems in Australia is warranted, to define the knowledge gaps that are hampering pasture productivity or animal productivity and health.

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