

Benefits of Liming

Context & Overview

Natural and anthropogenic processes and influences cause soil acidification, the latter accelerating it. It is estimated that 30% of the world's ice-free land is affected by topsoil acidity and of these lands, 75% suffer from subsoil acidity (Sumner & Noble, 2003). Therefore the issue of soil acidity is one of global significance. The abundant use of legumes in agroecosystems contributes to such a process, as does the use of synthetic fertilisers, especially those that are nitrogen- and sulphur-based. In New Zealand, agriculture is an industry of significant economic importance, with pastoral land covering almost one third of the nation's total land mass. Such pastures typically consist of di-cultures of a grass and a legume species (Goldson *et al.*, 2020). The agricultural industry is also heavily dependent on fertiliser inputs. Thus, soil acidification is of significant concern to New Zealand.

Lime is applied to ameliorate soil acidity in New Zealand, though concerningly its use has declined since a peak in 2002 (Fertiliser Association of New Zealand, 2021; McLaren & Cameron, 1996). Liming also provides numerous other benefits; it improves soil structure and associated properties (e.g. aeration, drainage, water retention), reduces elemental toxicities (e.g. aluminium, manganese), increases the availability of nutrients that are already present in the soil or have been added (e.g. from fertilisers), promotes earthworm and microbial activity, and increases pasture palatability, all of which can result in improved productivity.

Lime is also a calcium provision, of which is particularly important for the legumes that are prominent in New Zealand's pastures. However, it is believed that our soils do not require additions of calcium, and that liming occurs for the purpose of reducing soil acidity only, though this generalisation may be up for debate.



1. What is soil acidity?

Soil acidity refers to the relative concentrations of hydrogen (H^+) and hydroxyl (OH⁻) ions in soil solution (water contained in the soil), though it is the concentration of H^+ in soil solution that is typically referred to and expressed via the pH scale (Eq. 1) (McLaren & Cameron, 1996; Ritchie, 1989; Uchida & Hue, 2014):

 $pH = -log[H^+]$ (1)*1

(pH is equivalent to the negative log of the concentration of H^+)

*1(McLaren & Cameron, 1996)

According to Uchida & Hue (2014), the pH scale ranges from 0-14 with each decline of a pH unit indicating ten times more acidity, and vice versa. A neutral pH of 7 is obtained when concentrations of H⁺ and OH⁻ are equal. Thus, soils are considered acidic (pH<7) if the concentration of H⁺ is greater than the concentration of OH⁻, and considered alkaline (pH>7) if the concentration of H⁺ is less than the concentration of OH⁻. Therefore, the greater the concentration of H⁺ (relative to OH⁻), the greater the acidity and the lower the pH value.

As outlined in McLaren & Cameron (1996), the pH of soil solution is termed the 'active acidity'. However, there are also H⁺ present on the cation exchange sites of negatively charged soil colloids, termed 'reserve acidity'. These H⁺ are typically more abundant than the 'active acidity' H⁺ in soil solution. 'Reserve acidity' is inversely related to base saturation - the proportion of the cation exchange sites that is occupied by exchangeable bases (i.e. all nutrient cations except H⁺ and Al³⁺). Therefore, the lower the base saturation, the higher the reserve acidity of the soil. 'Active acidity' H⁺ and 'reserve acidity' H⁺ are in equilibrium, therefore pH (a measure of active acidity) and base saturation are also related; as base saturation decreases, so does pH (acidity increases). However, this function will vary between soils depending on their cation exchange capacities (number of cation exchange sites) and thus their buffer capacities (the extent to which a soil resists pH change). For example, soils with a high cation exchange capacity (many cation exchange sites), and therefore greater ability to store reserve acidity or base cations, will have a higher buffer capacity (resistance to pH change) than soils with low cation exchange capacities as more cation exchange sites must be occupied by base cations to result in a pH increase (McLaren & Cameron, 1996; Ritchie, 1989).

2. How do soils become acidic?

Soil acidification is inevitable due to natural soil processes e.g. weathering, plant-soil chemo-dynamics, as well as nitrogen fixation by legumes and associated leaching of nitrates (NO₃⁻) with base cations (Goulding, 2016; McLaren & Cameron, 1996; Sumner & Noble, 2003: Tang & Rengel, 2003). However, the anthropogenic use of fertilisers in agroecosystems, specifically those that are nitrogen- and sulphur-based, is a significant cause of the acceleration of soil acidification via increased leaching of base cations and their contribution to acid rain (Goulding *et al.*, 2016; Reid *et al.*, 2005; Uchida & Hue, 2014).

a) Soil weathering

All soils naturally become more acidic with time under conditions of weathering and leaching (Sumner & Noble, 2003). However, soils may vary in their rates of acidification due to differences in combinations of soil forming factors (climate, organisms, relief, parent material, and time) which control the rate and state of soil development (Jenny, 1994). Factors of greatest influence are the nature of the parent material, rainfall and temperature. Soil acidification is typically accelerated in humid areas with high temperatures and substantial rainfall, whilst highly basic parent material will weather quicker (releasing many base/nutrient cations) than other types of parent material under these conditions (Sumner & Noble, 2003; Uchida & Hue, 2014). As a result, the range of soil types and their rate and stage of natural weathering varies across the globe. Rain is slightly acidic (pH5-5.6) due to the dissolution of carbon dioxide (CO₂) and dissociation of the resulting carbonic acid (H2CO3) which releases H+ into the soil (Eq. 2) (Goulding, 2016). These H+ displace base cations on cation exchange sites into soil solution, resulting in their loss via leaching (Helyar & Porter, 1989; McLaren & Cameron, 1996). The same chemical reactions occur via microbes decomposing soil organic matter (OM); microbes respire CO2 which reacts with soil water. Plant roots also respire. However, these processes are unlikely to cause soil pH levels lower than pH5 as acid soil solution holds little CO2 (Bolan &



Hedley, 2003). Furthermore, microbes produce organic acids when decomposing OM, and OM itself contains chemical groups that behave as weak acids, thus contributing to natural soil acidification.

$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow HCO_3^- + H^+ (2)^{*2}$

*2(Bolan & Hedley, 2003)

b) Plant nutrient uptake - charge equilibrium

Plants obtain nutrients (in their ionic form) for their growth and function from the soil via their roots, and from the atmosphere in the case of nitrogen-fixing legumes. As plants are of neutral charge, the uptake of one or more nutrient cations must be matched with the uptake of one or more nutrient anions or the release of H⁺, all of which must equate in charge to maintain charge equilibrium between soil solution, cation exchange surfaces on soil colloids, and the plant itself (Goulding, 2016; McLaren & Cameron, 1996; Tang & Rengel, 2003) (Fig. 1). Similarly, plants release OH⁻ or HCO₃⁻ (hydrogen carbonate anion) upon the uptake of nutrient anions, however the uptake of cations is generally greater, thus the plant produces a net acidifying effect of soil surrounding the plant's roots (Goulding, 2016; Sime, 2001; Tang & Rengel, 2003).



Fig. 1. Schematic of the charge balancing exchange of cations and anions between plant roots, soil solution (water) and negatively-charged clay or organic matter within soil colloids (Fang et al., 2019).

c) Legumes: nitrogen fixation & leaching

Non-leguminous plants cannot naturally obtain nitrogen unless it has first been 'fixed' from the atmosphere by legumes. Atmospheric nitrogen is fixed by legumes within their root nodules via their symbiotic relationship with rhizobia bacteria (Eq. 3) (Uchida & Hue, 2014). Most of the nitrogen fixed by legumes is either used by the legume itself or taken up by other plants, via the facilitative service of legumes. Some plants die, providing OM directly to the soil, whilst others are consumed by grazing livestock which then excrete excess nitrogen in the form of urea (Goulding, 2016). Mineralisation, also termed ammonification, of this OM results in the formation of ammonium (NH₄⁺), followed by nitrification which produces nitrate anions (NO₃⁻) (Eq. 4, 5) (Chapin III *et al.*, 2011). Nitrification produces H⁺ as a by-product (Eq. 5). Typically, plants do not take up all nitrate ions produced, therefore they are leached (Goulding, 2016). Since nitrate ions are negatively charged, they are accompanied by nutrient cations (e.g. calcium; Ca²⁺) which are displaced from cation exchange sites by the H⁺ released through nitrification. Soil acidification occurs as a result (McLaren & Cameron, 1996; Sime, 2001; Uchida & Hue, 2014). A schematic of terrestrial nitrogen cycling is shown in Fig. 2.



 $N_2 + H_2O + 2R-OH \rightarrow 2RNH_2 + 1.5O_2(3)^{*2}$

(nitrogen fixation)

$RNH_2 + H^+ + H_2O \rightarrow R-OH + NH_4^+$ (4)*²

(ammonification of organic matter)

 $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$ (5)*2

(nitrification)



Fig. 2. Terrestrial nitrogen cycling schematic displaying nitrogen fixation, mineralisation, nitrification, and denitrification processes (Chapin III et al., 2011).

d) Anthropogenic activity: fertilisers

The use of synthetic fertilisers, specifically those that are nitrogen- and sulphur-based (e.g. urea, ammonium sulphate, superphosphate) are significant contributors to soil acidification within agricultural production systems (Goulding, 2016; Reid *et al.*, 2005; Uchida & Hue, 2014). These compounds produce nitrates and sulphates (SO_4^{-}) upon oxidation and other microbe-driven reactions, of which subsequently leach through the soil if not taken up by plants, carrying nutrient cations with them (Goulding, 2016; Uchida & Hue, 2014).

Regarding fertilisers that contain sulphur, e.g. superphosphate, ammonium sulphate, H⁺ are produced when they are oxidised; the elemental sulphur is oxidised into sulphuric acid which dissociates into hydrogen cations and sulphate anions, the latter leaching nutrient cations with it if in excess after plant uptake (Eq. 6) (Bolan & Hedley, 2003; Goulding, 2016; Hinckley *et al.*, 2020).

$2S^{\circ} + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \rightarrow 2SO_4^{2-} + 4H^{+}$ (6)*2

Regarding nitrogen-based fertilisers, acidification occurs via the same chemical reactions outlined in section c), however, instead of legumes fixing their own nitrogen from the atmosphere, they and other non-leguminous plants take up nitrogen supplied by nitrogen-based fertilisers.

To provide context; soil microbes break down polymers within OM in order to release nitrogen to be used by plants and the microbes themselves. As described by McLaren & Cameron (1996), if the soil has a high carbon : nitrogen (C:N) ratio, i.e. there is a higher availability of carbon available to microbes relative to



nitrogen, microbes will assimilate nitrogen from the soil (e.g. NH_4^+ , NO_3^-), a process called immobilisation. This causes microbes to compete with the plant for nitrogen and reduces the leaching of nitrates with nutrient cations. Conversely, as the soil C:N ratio lowers, i.e. the difference in relative availability of carbon and nitrogen reduces, microbes carry out mineralisation/ammonification. This process entails the mineralisation (excretion) of excess nitrogen not utilised by microbes from the decomposition of OM. This excess nitrogen is excreted as ammonium (Eq. 4), which can then be nitrified into nitrate (Eq. 5). Nitrates can then be leached, taking nutrient cations with them. Ideally, soils should have a C:N ratio of 25:1 to obtain a balance between mineralisation and immobilisation in order to minimise nitrogen deficiencies in plants and soil acidification through nitrification and leaching.

Anthropogenic use of nitrogen-based fertilisers creates low soil C:N ratios, favouring mineralisation and nitrification, and therefore leaching of excess nitrates and soil acidification. Soil acidification occurs at rates dependent on the concentration of nitrogen in different fertilisers and the quantities and rates of application (Johnston *et al.*, 1986; Sumner & Noble, 2003). Therefore, the more nitrogen-based fertiliser used, the lower the C:N ratio, and the more the soil nitrogen pool is dominated by inorganic forms of nitrogen, promoting the acceleration soil acidification (Chapin III *et al.*, 2011) (Fig. 3).



Fig. 3. Changes in forms of nitrogen depending on nitrogen availability. Organic forms of nitrogen (DON) dominate when nitrogen availability is low (high C:N) due to immobilisation. As nitrogen availability increases (lower C:N), inorganic forms of nitrogen dominate (NH_4^*, NO_3^-) as a result of ammonification and nitrification (Adapted from Chapin III et al., 2011, Professor M. Turnbull, personal communication, 2019).

As of 2005, global manufacturing of nitrogen for fertiliser (and some industrial use) reached more than 100 teragrams (1 teragram = 1 million tonnes) of which is within the range of the natural rate at which nitrogen fixation occurs (*excluding* nitrogen fixation by legumes in agroecosystems) (Reid *et al.*, 2005) (Fig. 4). When including nitrogen fixed by agricultural legumes, this figure of 100 teragrams of anthropogenic nitrogen fixation is raised almost another 50 teragrams (Reid *et al.*, 2005) (Fig. 4). In other words, the amount of nitrogen manufactured for nitrogen fertilisers paired with the use of legumes in agroecosystems is approximately equivalent to the amount of nitrogen fixed in natural systems alone, meaning that human activity adds at least as much nitrogen to terrestrial ecosystems as do natural sources (Vitousek *et al.*, 1997). Therefore, we have essentially at least doubled the natural amount of nitrogen in our biosphere, resulting in accelerated soil acidification.



In New Zealand, 452,000 tonnes of nitrogen was applied to agricultural land in the form of nitrogen-based fertilisers in 2019 (Stats NZ, 2021). This was a 629% increase from 62,000 tonnes of nitrogen applied in 1991 (Stats NZ, 2021). The bulk of this nitrogen application came from the use of just over 600,000 tonnes of urea in 2019, versus just over 300,000 tonnes in 2002, whilst lesser amounts of other nitrogen-based fertilisers, such as diammonium phosphate and ammonium sulphate also contributed (Stats NZ, 2021).

The soil acidifying effect of nitrogen-based fertilisers is compounded by volatilisation of ammonia (NH_3) and other nitrous oxides, e.g. NO, N_2O , which occurs through volatilisation and denitrification, contributing to the formation of acid rain (Goulding, 2016) (Fig. 2).

Global anthropogenic input of nitrogen, largely of which is purposed for fertiliser (and industrial use), is projected to increase by approximately two thirds by 2050 (Reid *et al.*, 2005) (Fig. 4). This may now be an overestimate considering the increase in environmental awareness around the use of nitrogen fertiliser resulting in changes in legislation to reduce its application on agricultural soils (Ministry for the Environment, 2021). However, the bottom line is that the use of nitrogen fertiliser must reduce dramatically in order to mitigate the acidification of our soils, not to mention other environmental concerns.



Fig. 4. Trends of anthropogenic nitrogen inputs with projection to 2050. Inputs are largely from nitrogen manufactured for fertiliser and industrial use. The use of fertilisers (and industrial uses of N) and legumes in agroecosystems equates to natural rates of nitrogen fixation. Overall anthropogenic input is projected to increase by two thirds come the year 2050. One teragram equates to 1 million tonnes (Reid et al., 2005).

3. Why are we concerned about soil acidity?

Soil acidity has been observed to reduce the productivity of farmland (Boom & Dodd, 2021; Edmeades *et al.,* 1984; Gray & Morton, 2019; Morton, 2020; O'Connor & Hunt, 1996). Such a deleterious outcome is due to the underlying effects of soil acidity;

- Deterioration of soil structure and associated properties (e.g. aeration, water drainage and retention)
- Presence of elemental toxicities (i.e. aluminium, manganese)
- Reduced soil nutrient availability
- Hindered earthworm and microbial activity
- Changes in botanical composition; reduction in high fertility pasture species, e.g. ryegrass and especially white clover, leading to decreased pasture palatability.



4. Liming to overcome soil acidity

Limestone is mostly calcium carbonate, alongside varying proportions of sand, silt, clay, and other trace minerals (Sime, 2001). When limestone is applied to an acid soil (pH<7), it gradually dissolves in soil moisture, reducing acidity and releasing Ca^{2+} as an available nutrient for plant uptake. As a general rule relating to soils with an average cation exchange capacity (i.e. soils that aren't extremely coarse in texture – sand - or extremely fine – clay), one tonne of lime will raise soil pH by 0.1units, and thus 10 tonnes of lime will raise the pH by 1unit (McLaren & Cameron, 1996). The mechanisms of which lime ameliorates soil acidity are complex, however simplified examples are shown below (Albrecht, 2011; McLaren & Cameron, 1996; Sime, 2001):

When lime is dissolved in soil water, Ca²⁺ and hydrogen carbonate (HCO₃⁻) and hydroxide (OH⁻) ions are released/formed;

$$CaCO_3 + H_2O \rightarrow Ca^{2+} + HCO_3^- + OH^-(7)$$

and

Calcium carbonate dissociates upon interaction with H^+ on soil colloids, causing the release of H^+ and the formation of carbon dioxide and water;

$$CaCO_3 \rightarrow Ca^{2+} + H_2O + CO_2 \qquad (8)$$

then

From the above two reactions, Ca²⁺ displaces H⁺ on soil colloids;

(soil colloid)
$$H^+ + Ca^{2+} \rightarrow$$
 (soil colloid) $Ca^{2+} + 2H^+$ (dissociated) (9)

The H⁺ released by Ca²⁺ competing for the cation exchange site is then neutralised when it binds with HCO_3^- or OH⁻ anions – by-products of Eq. 7 - to form carbonic acid and water, respectively.

(soil colloid) $H^+ + HCO_3^- \rightarrow H_2CO_3 \rightarrow H_2O + CO_2$

or

(soil colloid) $H^+ + OH^- \rightarrow H_2O$

5. Different lime materials and their neutralising values

Ground limestone or "Ag Lime" (CaCO₃), and dolomite, a mixture of calcium and magnesium carbonates (CaCO3.MgCO3), are the most commonly used liming materials in agriculture, the former being the most commonly used in New Zealand (Havlin *et al.*, 2014; McLaren & Cameron, 1996). Very little fast-acting "quicklime" (CaO) or "slaked lime" (Ca(OH)₂) is used in agriculture, though the latter is commonly used in horticulture (McLaren & Cameron, 1996).

As outlined in McLaren & Cameron (1996), the speed at which Ag Lime in New Zealand reacts in soil to increase pH depends on the relative hardness of the original limestone rock; harder rocks will react slower, whilst softer rocks will react quicker. Most New Zealand limestone is considered 'moderately reactive'. Reaction speed is also dependent on the particle size of the lime; the finer the particle size, the faster the lime dissolves and reacts in the soil. New Zealand standards for approved Ag Lime require at least 50% to pass through a 0.5mm sieve, and that no more than 5% is retained on a 2mm sieve.

All liming materials are evaluated relative to their acid neutralising capacity compared with pure calcium carbonate (given a value of 100). This is termed its *calcium carbonate equivalent* (CCE) or *neutralising value* and is expressed as a percentage (%). For example, Ag Lime is typically 60-90% calcium carbonate equivalent (CCE); lower CCE values being due to greater levels of impurities, such as clay, and "slaked lime" has a CCE of up to 135% (Table 1). These values mean that, when quantities are equal, Ag Lime can neutralise 5-40% less than pure calcium carbonate, whilst "slaked lime" can neutralise up to 35% more.



Liming Material	CCE / Neutralising Value (%)
Pure calcium carbonate (CaCO ₃)	100
"Ag Lime" Calcium Carbonate (CaCO ₃)	65-95
Calcium Hydroxide/Hydrated Lime/Slaked Lime (Ca(OH) ₂)	120-135
Calcium Oxide/Burnt Lime/Quicklime (CaO)	150-179
Dolomite (<50% Mg) /Calcium magnesium carbonate (CaMg(CO ₃) ₂)	95-109
Gypsum (CaSO₄)	none

Table 1. Various liming materials and their CCE/neutralising value (%) (Havlin et al., 2014; McLaren & Cameron, 1996; Prasad & Power, 1997).

6. Liming improves pasture yield and palatability

It is well known that the application of lime significantly correlates with soil pH, i.e. the more lime that is applied, the higher the soil pH (less acidic) (Berenji *et al.*, 2017). Hence, studies investigating the effect of soil acidity on pasture yield typically use lime to increase the pH of the soils, in order to make comparison against an acidic 'control' soil. Therefore, results obtained in response to liming can be interpreted as results in response to increasing soil pH (reducing soil acidity).

Various lime trials within New Zealand consistently display improvements in pasture yields in response to lime application. Trials in Northland conducted on Hill Country pasture displayed average increases in pasture production of 16% on soils that were raised up to a pH of 6.3 in response to the addition of lime, of which had initial pH values ranging from 4.8-5.6 (O'Connor & Hunt, 1996). A trial in the western Waikato also displayed increased pasture production in response to lime rates ranging from 1.25 tonnes/ha to 10 tonnes/ha; results ranged from a 20% increase at 1.25t/ha to a 68% increase at 10t/ha by the fourth/last year of the trial (Boom & Dodd, 2021). Reviews of research on the effect of lime on New Zealand soils and pastures was conducted by Morton (2020) and Gray & Morton (2019) who highlighted significant increases in pasture production within numerous trials where more than one tonne/hectare of lime was applied to soils with an initial pH range of 5.2-5.6 (Bircham & Crouchley, 1977; Edmeades *et al.*, 1984; Morton *et al.*, 1998; O'Connor & Gray, 1984; Thomson, 1982; Wheeler, 1998). All trials were conducted over a time period of at least three years.

Soil acidity has been observed to negatively impact the function and yield of legumes, of which are prominent in New Zealand's pastoral farming systems (Bordeleau & Prévost, 1994; Goldson *et al.*, 2020; Mohammadi *et al.*, 2012). Soil acidity causes deleterious effects such as the inhibition of rhizobia to survive and their subsequent colonisation of legume roots (Coventry & Evans, 1989). Consequently, nodulation is prevented or inhibited resulting in the lack or absence of legume root nodules (Gibson, 1959). As a result, nitrogen fixation is impaired or does not occur. Since legumes provide nitrogen to other non-leguminous plant species, growth of both legumes and other pasture species is inhibited or prevented, thus reducing overall pasture yield (Andrew, 1976; Berenji *et al.*, 2015; Moreira & Fageria, 2010; Moreira *et al.*, 2011). Furthermore, elemental toxicities, which often occurs as a result of soil acidity, has a compounding effect on legumerhizobia symbiosis and function, legume growth, and subsequent yield (Jaiswal *et al.*, 2018).

Within the aforementioned New Zealand lime trials, white clover yield increased significantly on multiple accounts regardless of being mown or grazed (Edmeades *et al.*, 1984; Morton, 2020; Morton *et al.*, 2005; O'Connor *et al.*, 1981; Wheeler, 1998). Similarly, Boom & Dodd (2021) noted a significantly greater abundance of white clover (8% vs. 1-2%) in response to the application of 10 tonnes/ha of lime. O'connor *et al.* (1981) and Morton *et al.* (2005) noted that the increase in pasture yield was attributed to increased white clover yield, rather than changes in ryegrass yield, which may reflect the higher sensitivity of white clover to



calcium deficiency and/or elemental toxicities. In fact, it was suggested that the most likely mechanism behind these increases in white clover yields was through the amelioration of soil aluminium toxicity by liming (Morton *et al.,* 2005).

Results from studies investigating the effect of lime on yields of various arable crops are not as well documented or consistent as those within pastoral systems as some crops prefer slightly more acidic soil (e.g. potatoes) and others have greater tolerances of soil acidity (e.g. oats) (Holland *et al.*, 2019). However Boke & Fekadu (2014) and Holland *et al.* (2019) reported significant yield increases of arable crops such as barley, cereals, and winter oilseed rape in response to increased soil pH after lime application.

Limed pastures are typically more palatable to livestock due to increases in high fertility species such as ryegrass and white clover, at the expense of low fertility species such as browntop (Sime, 2001). Consequently, studies have shown more even grazing of limed pastures by livestock (Toxopeus, 1989). Additionally, Li *et al.* (2006) reported increased sheep liveweight gains of up to 34% and increased wool production of up to 28% due to both increased pasture productivity and improved pasture quality after lime application.

7. Liming improves soil structure and properties

Soil structure is expressed as the degree of stability of aggregates (Bronick & Lal, 2005). Soil aggregates are soil particles bound together: soil colloids (clay and OM), OM, and sand and silt particles covered in OM (McLaren & Cameron, 1996). Soil microbes feed on carbon by decomposing OM, subsequently excreting polysaccharide glues which bind these components together to form *micro*aggregates (<0.25mm) (Angers & Caron, 1998; Bardgett, 2005; Eyles *et al.*, 2015; McLaren & Cameron, 1996). Plant roots, root hairs, and fungal hyphae then enmesh and secrete polysaccharide 'glues' that hold these microaggregates together to form *larger macro*aggregates (>0.25mm) (Bronick & Lal., 2005). Consequently, *micro-* and *macro*pores are created. The negatively charged soil particles (clay and OM) attract positively charged nutrient ions and dipolar water molecules resulting in the ability of soil to retain plant available nutrients and water (McLaren & Cameron, 1996). Between aggregates, macropores allow for soil aeration and water drainage (Finch *et al.*, 2014). Smaller micropores store water within soil aggregates, protected from evapotranspiration yet plant available (Finch *et al.*, 2014; McLaren & Cameron, 1996).

Soil structure relates to the size, shape, and relative abundance of fine soil aggregates and large soil 'clods', whilst also considering soil porosity; their continuity, capacity to retain and transmit fluids (e.g. water) as well as organic/inorganic substances (e.g. nutrients), and ability to support vigorous root growth (Bronick & Lal, 2005). The relative abundance of soil aggregates and clods influences the abundance of micro- and macropores (Rai *et al.*, 2017).

A decline in soil structure is considered a form of soil degradation of which is related to land use and soil/crop management (Bronick & Lal, 2005). Soil in good condition will have a greater relative proportion of porous, fine aggregates, with few or no clods present, whereas poorly structured soil, typically compacted, will have a greater relative proportion of large clods, with few pores (Shepherd, 2009). Relative to poorly structured soils, good soil structure and porosity increases aeration, gaseous exchange, water infiltration, water and nutrient retention, and root penetration which are important for pasture growth (Bronick & Lal, 2005; Rai et al., 2017). Structural stability - the ability of a soil to resist structural degradation by internal (e.g. water flow) or external (wheel traffic, stock treading) forces - is also improved by good soil structure (Bölscher et al., 2021; Shepherd, 2009). Poor soil structure and porosity is likely to reduce pasture resilience to drought as the capacity to store water is limited by a lack of microaggregates (Finch et al., 2014). Conversely, in wet conditions, poor soils are more susceptible to waterlogging due to a lack of macroaggregates, resulting in anaerobic soil conditions which slow the activity of aerobic soil microbes and earthworms, thus reducing OM decomposition (Finch et al., 2014; Rai et al., 2017). This creates a negative feedback on soil aggregation which increases erosion, runoff, and reduces nutrient retention and therefore plant nutrient uptake, increasing production costs through fertiliser dependency (Shepherd, 2009). Furthermore, microbes in anaerobic conditions produce greenhouse gases, e.g. methane and nitrous oxide (McLaren & Cameron, 1996). Pasture production can reduce by 30-50% in spring, increase weed numbers, and be a catalyst for plant diseases (Shepherd, 2009). Overall, pasture growth is reduced when soil structure and porosity is poor, which correlates to reduced farm productivity and profitability (Finch et al., 2014).



Lime is thought to improve soil aggregation and stability, and therefore soil structure, through two main mechanisms (Bronick & Lal, 2005; Haynes & Naidu, 1998):

i. *Flocculation*: Ca²⁺ improves soil stability through cationic bridging with clay particles and OM. These negatively charged particles typically repel each other, resulting in their unstable, dispersed state. Flocculation is the term given to the mechanism of cationic bridging by Ca²⁺, of which brings soil particles (clay and OM) closer together to aid the formation of stable soil aggregates (Fig. 5).



Fig. 5. Ca²⁺ links negatively charged organic matter and soil colloids (clay), resulting in flocculation.

ii. **OM returns to the soil:** depending on farm management, increased yields as a result of liming increases OM returns to the soil as residues, of which is integral to soil aggregate formation and stability. However, researching regarding the long term effect of liming on soil OM and soil structure is scant.

Various studies have reported improvements in soil structure and associated soil properties in response to liming;

Within arable systems in Germany, Frank *et al.* (2019) and (2020) noted shifts in pore size distribution from fine pores towards narrow coarse pores and medium pores of which indicated positive structure formation via flocculation by Ca²⁺. Reduced soil bulk density was also reported. In turn, there was a positive relationship between plant available water, soil porosity, and soil pore continuity, and the addition of lime. Soil stability also significantly improved with lime application. These results occurred in just 6-12 months. Chan *et al.* (2007) in NSW, Australia, applied various lime rates to soils of a mixed cropping and sheep system, raising soil pH from 5.1 to 7.5 at the highest lime rate. They too reported reduced soil bulk density and increased soil stability with increasing lime rate due to increased flocculation. Furthermore, they revealed increases in OM of which resulted in increased macroaggregates and their stability. Also in NSW, Australia, Chan & Heenan (1998) applied 1.5t/ha of lime to trial soils of a cropping system with different cultivation methods (e.g. direct drill or cultivation), resulting in increased micro- and macroaggregate stability 18 months after application and remaining so 3 years later.

Jackson & Gillingham (1984) exhibited soil moisture increases just 8 months after lime application to hill country pastoral soils, and subsequent increases in dry matter production of up to 42%. Interestingly, a similar response was observed upon application of gypsum (CaSO₄), of which does not have the ability to neutralise soil as lime (CaCO₃) does. Therefore, this study reinforces that pH amelioration isn't solely involved in obtaining such results, and that calcium plays a critical role in promoting good soil structure, i.e. flocculation. Furthermore, results of water droplet disappearance tests (WDDT) – time taken (seconds) for a droplet of water to be absorbed by a soil sample – was dramatically lower in limed soil samples, with the time taken generally at least halved and the greatest result reduced to a quarter of the time (34 minutes to 8 minutes).

Frank *et al.* (2020) comment that farmers typically fertilise their farms regularly, yet the application of limestone is often minimal. This is due to a widespread lack of knowledge regarding the profound effects that liming has on increasing farm productivity through dramatic improvements in soil structure and porosity, and associated soil properties and functions.



8. Liming reduces elemental toxicities

In acid soils, typically <pH5, concentrations of aluminium, iron and manganese increase to levels that are toxic to plants. Iron and aluminium in the form of hydrous oxides of iron and short-range order aluminosilicate minerals hinder plant growth by reducing the availability of nutrients, especially phosphorous through its fixation/adsorption to these materials (McLaren & Cameron, 1996). Weathering processes that release soluble aluminium (Al³⁺) also release H⁺, both of which bind to cation exchange sites, further promoting acidic soil conditions (McLaren & Cameron, 1996). Al³⁺ toxicity causes deleterious effects on root growth and development and impairs nodule formation and nitrogenase enzymes in legumes, thus inhibiting nitrogen fixation (Berenji *et al.*, 2015; Berenji *et al.*, 2017; Bordeleau & Prévost, 1994; Edmeades *et al.*, 1983; Jaiswal *et al.*, 2018; Wood & Cooper, 1985). High concentrations of manganese also stunts plant growth, particularly in the roots, causing inefficient water and nutrient uptake, and reduces nodulation in legumes (El-Jaoual & Cox, 1998).

Liming is carried out to overcome elemental toxicities (Corbett *et al.*, 2021; Martini & Mutters, 1985a), particularly aluminium toxicity as manganese toxicity is relatively rare in New Zealand (McLaren & Cameron, 1996; Sime 2001). If agricultural land is left too long without lime, subsoil acidification will occur, resulting in aluminium toxicity at greater depths than the topsoil alone (Sime, 2001). This phenomena is far more difficult and expensive to remedy with the application of lime than addressing topsoil acidity, and is a particularly prevalent issue in the agricultural High Country areas of New Zealand where lime can only be spread by aircraft (Goulding, 2016; Sime, 2001). This method of application is commonly not economic for farmers, reducing or preventing the frequent application of lime. However, the long-term cost of not liming will be far greater for future generations as agricultural production declines.

9. Liming improves nutrient availability

If soil is too acid or too alkaline, nutrients that already exist in the soil and those that have been added will not be plant available. Figs. 6 and 7 display the influence of pH on the availability of 12 essential plant nutrients (McLaren & Cameron, 1996; Sime, 2001). The major nutrients (Ca, Mg, N, P, S, K, and Na) as well as trace elements Mo and B are most available in near neutral soils, whilst other trace elements (Fe, Mn, Cu, Zn) are more available in acidic soils.



Fig. 6. Relationship between soil pH and the relative availability of individual nutrients. This figure does not compare amounts of different nutrients, only amounts of <u>individual</u> nutrients relative to pH (McLaren & Cameron, 1996).



Acid		17	A	htly cid		Slig Alka	line			Strongly Alkaline
4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5 10.0
				N	litroge	en				
				Ph	ospho	rus				
				Pe	otassi	um		-0	1/120	BHIDTS
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12. 14		2010		å	Iron					
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	4.5		Acid	Acid A	Congly Slightly 4.5 5.0 5.5 6.0 6.5 Image: State of the sta	Acid 4.5 5.0 5.5 6.0 6.5 7.0 Nitroge Phospho Potassi Sulphu Calciu Magnesi Iron Mangan Boror Copper &	Acid Acid Acid Acid Acid Acid Acid Acid	Acid Alkaline 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 Nitrogen Phosphorus Potassium Sulphur Calcium Magnesium Iron Manganese Boron Copper & Zinc	Acid Slightly Acid Alkaline 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 Nitrogen Phosphorus Potassium Sulphur Calcium Magnesium Iron Manganese Boron Copper & Zinc	Acid Acid Alkaline 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 Nitrogen Phosphorus Potassium Sulphur Calcium Magnesium Iron Manganese Boron Copper & Zinc

Fig. 7. Relationship between soil pH and the relative availability of individual nutrients. Bar breadth represents the relative availability of the nutrient concerned at the corresponding pH. The pH for overall optimum nutrient availability is shown by the vertical green line at approximately pH6.3 (Sime, 2001).

As outlined in McLaren & Cameron (1996) and Havlin et al. (2014):

Nitrogen

Acid soils result in the retardation of the colonisation, nodulation, and nitrogen fixation by rhizobia in legume root nodules. Furthermore, acid soils cause reduced activity of nitrifying bacteria (of which also require an adequate supply of Ca²⁺) thus inhibiting nitrification, the conversion of NH₄⁺ to plant available NO₃⁻. In turn, nitrogen availability is lowest in soils of low pH (Figs. 6 & 7). Consequently, deficiency symptoms are displayed as yellowing leaves due to the collapse of chloroplasts required for photosynthesis, stunted growth, reduced tillering in cereals, and delayed maturity in fruit crops, all of which result in reduced yield. Liming, and a subsequent rise in pH, increases nitrogen availability by enhancing the activity of nitrogen-fixing rhizobia and nitrifying bacteria, of which can allow for facilitative transfer of nitrogen to non-leguminous plants, increasing overall yield (Andrew, 1976; Berenji *et al.,* 2015; Moreira & Fageria, 2010; Goulding, 2016; Moreira & Fageria, 2011; Žurovec *et al.,* 2021).

Phosphorous

Phosphorous deficiency is exhibited as stunted plants with limited root systems and thin stems. Fruit and seed formation is inhibited in horticultural crops, and tillering is reduced in cereals. Commonly, plants will display a redish-purple discolouration. If the soil pH is too acidic (<pH6), phosphorous fixation/adsorption mechanisms involving aluminium and iron dominate, rendering phosphorous unavailable to plants. Similarly, if soil is too alkaline (>pH7), phosphorous becomes fixed as calcium or magnesium phosphates. In New Zealand, a soil's capacity to 'fix' phosphorous is determined by a phosphate retention test, presented as a percentage; the higher the percentage, the greater the capacity of a soil to 'fix' phosphorous, of which tends to reflect the amount of iron and aluminium or calcium and magnesium in soils. Therefore, liming is critical in order to maintain a pH of 6.3-6.5 where phosphorous fixation mechanisms are at a minimum and plant availability of phosphorous is at a maximum (Figs. 6 & 7). Liming to increase pH and subsequent phosphorous availability has been termed a "phosphorous sparing effect" of which can take effect in various ways. For example, as pH increases, the presence of iron and aluminium compounds declines resulting in reduced phosphorous adsorption, rendering more plant available phosphorous (Corbett et al., 2021; Havlin et al., 2014; Martini & Mutters, 1985a; O'Connor et al., 2007). As another example displayed by O'Connor et al. (2007), lime increases the mineralisation of organic nitrogen in soil, thus increasing plant growth. In turn, their roots exploit a greater volume of soil allowing for greater uptake of aluminium- and iron-bound phosphorous. O'Connor et al. (2007) reported a phosphorous sparing effect equivalent to 50-60kg P/ha consistent over 3 years after 5t/ha of lime was applied to a pH5.8 soil in Northland. Phosphorous is important for numerous plant processes, however of particular note, insufficient levels of phosphorous result in stunted growth, and therefore reduced yield (Prasad & Power, 1997).



Sulphur

Sulphur is considered to be as essential as phosphorous due to similar amounts of it being required by plants. It is most available at pH6 and above (Fig. 7). Sulphur deficiency is typically exhibited as spindly and short plants with yellowish-green leaves, reduced nodulation in legumes, and delayed maturity of fruits regarding horticultural crops. In recent years, the use of sulphur-free nitrogen- and phosphorous-based fertilisers has renewed interest in this important nutrient. As lime increases soil pH, microbial activity also increases allowing for decomposition of OM and mineralisation of the sulphur within (Haynes and Swift, 1988). Mineralisation of sulphur is critical to maintaining its supply in New Zealand's soils as organic sulphur accounts for the major proportion of sulphur in most soils.

Potassium

The effect of liming on potassium availability is varied, neither significantly increasing or decreasing plant available potassium (Sime, 2001). According to Prasad & Power (1997), some state that liming reduces potassium availability as more is 'fixed' on clay minerals at a higher pH. However, it is thought that the reduction in elemental toxicities that correspond with a lower pH more than compensates for slight reductions in potassium availability. Furthermore, others state that the overall effect of liming is beneficial as it reduces potassium leaching. Maintaining ~pH6-7.5 by liming will provide a consistent level of potassium to plants (Fig. 7).

Calcium

Calcium is a significant constituent of lime. Its optimum availability is at ~pH7, preferring alkaline soils (Fig. 7). Calcium ensures efficient plant uptake of water and nutrients, carbohydrate storage in plant leaves, nodulation and nitrogen fixation in legumes, and is thought to encourage earthworm activity (Albrecht, 2011; Andrew & Norris, 1961). Thus lime has a dual role as a soil conditioner, reducing soil acidity, and as a calcium provision.

Magnesium

Regarding optimum pH for nutrient availability, magnesium follows a similar trend to calcium. Liming increases magnesium availability (Martini & Mutters, 1985b) requiring a pH of 6 to be reached to obtain optimum magnesium availability (Figs. 6 & 7). Deficiencies are not typically seen in plants, rather it is displayed in stock health as hypomagnesaemia, of which lactating cows are most at risk.

Micronutrients: Iron, Manganese, Boron, Copper, Zinc, & Molybdenum

Despite the term *micro*nutrients, being required in small quantities, their essentiality should not be overlooked. In general, all micronutrients become more available with increasing soil acidity, aside from molybdenum which becomes more available with increasing soil alkalinity. Maintaining a pH of 6.3-6.5 by liming is critical to promoting optimal availability of these micronutrients to plants (Fig. 7). Copper is required for photosynthesis, protein and carbohydrate metabolism, and nitrogen fixation. Boron is essential for the synthesis of new cells. Boron deficiency is widespread in New Zealand soils. At concentrations that don't allow manganese toxicity to dominate, manganese is important for photosynthesis, nitrogen uptake. Manganese deficiency is rare in New Zealand agriculture. Molybdenum is particularly important due to its presence in the enzymes that control nitrogen fixation and the conversion of nitrates to amino acids and proteins within the plant. Zinc is essential due to its presence in numerous enzymes, promotion of growth hormones, starch formation, and seed production. Iron is important for both plants and animals, found in haemoglobin and involved in chlorophyll synthesis in leaves.



10. Liming improves earthworm and microbial activity

Earthworms

Earthworm abundance is considered a bio-indicator of sustainability (Buckerfield *et al.*, 1997; Mele & Carter, 1999). Earthworms and their activities of burrowing and casting can improve soil aggregate stability, aeration, and water infiltration (Barret, 1948; Bölscher *et al.*, 2021; Bronick & Lal, 2005). Sharpley *et al.* (1979) reported that the presence of earthworms can halve the amount of runoff, thus reducing erosion. Earthworms also incorporate OM, lime, and fertilisers of which enhances soil nutrient availability (Baker *et al.*, 1999; Chan 2003; Haynes *et al.*, 1999). Furthermore, earthworm casts contain more OM and a higher concentration of nutrients than the surrounding soil such as calcium, phosphorous, magnesium, and potassium (Barrett, 1948; Ernst, 1958). Zhang & Schrader (1992) and Chan (2003) also found that earthworm cast and burrow wall materials had greater organic carbon than bulk soil. Ultimately, earthworms play a key role in building topsoil (Barrett, 1948). Liming increases earthworm abundance and activity by reducing soil acidity and providing calcium (Hirth *et al.*, 2009; Springett & Syers, 1984). Calcium in the earthworm diet is thought to encourage their activity; their calciferous glands secrete calcium-rich fluid which neutralises the organic and inorganic material they ingest of which is subsequently excreted as casts with a pH close to neutral (Barrett, 1948; Ernst, 1958; Haynes & Naidu, 1998; McLaren & Cameron, 1996; Piearce, 1972).

Over 10 years, Hirth *et al.* (2009) investigated the long term effects of lime on richness and abundance on native and exotic earthworms within a pastoral system in New South Wales, Australia. 3.7t/ha of lime was applied at the start of the trial and 6 years later in order to maintain a pH of 5.5 (from an initial pH of 4.1). Although there were minimal effects of lime on native species, there was a 3-fold increase in exotic species numbers m⁻² in limed soil compared to unlimed soil. The increase in earthworm numbers from 24/m² to 71/m² over 10 years concluded that liming increases earthworm numbers over the long-term. Furthermore, Springett & Syers (1984) reported increased cast production as a result of increased pH and calcium level upon lime application.

Microbial Activity

Liming promotes soil nutrient cycling, alleviates elemental toxicities, and decrease greenhouse gas emissions, and soil microbes (prokaryotes and fungi) are key players in these critical soil processes (Li *et al.,* 2021).

Liming has been shown to increase microbial biomass, soil respiration rate, soil enzyme activity, and mineralisation of nitrogen and sulphur, all of which are indicative of increased microbial numbers and activity (Badalucco *et al.*, 1992; Edmeades *et al.*, 1981; Haynes and Swift, 1988). Increased microbial activity can aid aggregate stability via the polysaccharide glues secreted by microbes, and enmenshment by fungal hyphae (Haynes & Naidu, 1998). Although Chan & Heenan (1998) reported an initial decrease in aggregate stability due to the promotive effect that liming has on carbon/OM mineralisation, a beneficial effect of lime was then reported after 18 months.

Sarathchandra & Edmeades (1984) conducted various experiments investigating the effect of lime on nitrogen mineralisation and microbial activity in soil. Results of a pot trial showed a 125% increase in g DM/pot due to increased mineralisation of organic N upon lime application. This increase in soil N availability due to liming was supported in their field study of which showed increased total soil N uptake by pasture in limed plots (5000kg/ha) compared to unlimed plots. This increase was equivalent to 50kg N/ha over a two year period. Their microbiological study highlighted increases in soil microbial biomass in response to the application of Ca(OH)₂. This increase was largely due to increased bacterial numbers, likely those that are involved in organic N mineralisation.

Furthermore, Žurovec *et al.* (2020) reported reductions in nitrous oxide (N₂O) emissions upon lime application to pH5.2 pastoral soils in a 12 month experiment in Ireland. Cumulative emissions in lowest pH soils were significantly higher than in the highest pH soils. Soil pH and N₂O emissions had a negative linear relationship, pH being a significant predictor of N₂O emissions (p<0.001). Such results are likely due to the synthesis of N₂O reductase (the enzyme required to convert N₂O to N₂) in denitrifying bacteria being hindered at low pH (Bergaust *et al.*, 2010; Bakken *et al.*, 2012). Another underlying mechanism was likely a shift in composition and abundance of denitrifying communities in response to liming (Zheng *et al.*, 2019). This is supported by Samad *et al.* (2016) who discovered a positive correlation between pH and gene abundance for enzymes that convert nitrite (NO₂⁻) and N₂O to N₂, and with community diversity. Žurovec *et al.* (2020) calculated that yield-scaled emissions of soils limed to a pH of 6.9 emitted 36% less N₂O/t DM compared to unlimed soils.



11. Lime as a calcium provision to soil/plants; New Zealand's context; are our soils really Ca sufficient?

A number of reports have acknowledged the dual purpose of liming: increasing soil pH (reducing acidity) and the provisioning of calcium (Andrew, 1976; Berenji *et al.*, 2017; Bordeleau & Prévost, 1994). However, it has been suggested that it is not soil acidity itself that causes deleterious effects on plant growth, but a lack of calcium (and other nutrients) (Albrecht, 2011, Albrecht & Davis, 1929; Albrecht & Smith, 1952). Therefore, the idea is entertained that soil acidity itself is an *indirect* hinderance of optimal plant growth and function, and that a lack of calcium *caused by* soil acidity, via leaching, is a direct cause. However, the role of H⁺ is acknowledged for its role in weathering minerals resulting in the formation of clay minerals, the release of nutrient ions that bind to them, and their subsequent availability to plant roots and microbes (McLaren & Cameron, 1996). Thus, it should be remembered that some soil acidity is essential for plant nutrition in order for these dynamics to occur, and that increasing soil acidity is the reciprocal of the real issue; declining soil fertility (Albrecht & Smith, 1952).

Soil pH is important for plant growth, however adequate soil nutrition to support such growth is crucial (Hackney *et al.*, 2019). Calcium is an essential nutrient for plant growth and functioning (Kinsey & Walters, 2013; Uchida & Hue, 2014). Amongst other roles, calcium influences carbohydrate accumulation in leaves, and plant uptake efficiency of water and every other soil nutrient (Havlin *et al.*, 2014; Kinsey & Walters, 2013). Legumes in particular require high concentrations of calcium (Ledgard & Steele, 1992; McLaren & Cameron, 1996). Calcium is required for the functioning of meristems, particularly the root tip (Sorokin and Sommer 1929), therefore calcium deficiency causes the growth of roots to cease which in turn prevents root curling and thus the formation of root nodules in legumes (Andrew & Norris, 1961; Sumner & Noble, 2003). At the level of the legume-rhizobia symbiosis, calcium deficiency negatively impacts attachment of rhizobia to root hairs, nodule initiation and development, and nodule function, i.e. nitrogen fixation (Ledgard & Steele, 1992; Lie, 1981; Mohammadi *et al.*, 2012). At the level of rhizobia alone, calcium deficiency affects rhizobia cell wall integrity, some of their enzymes, and their membrane transport systems (Hungria and Vargas, 2000).

Although various studies support the idea of lime having a dual purpose, its role in supplying calcium is often overlooked. However, some studies display this importance with a heavy focus on legumes due to their higher calcium requirement. Historically, Romans applied gypsum to their soils which provided calcium but did not remove soil acidity. In fact, the presence of sulphur made the soil more acid, however they were still able to grow crops regardless of such acidity (Albrecht, 2011). In the USA, leguminous soybean plants were treated with either calcium chloride (CaCl₂) or calcium hydroxide (Ca(OH)₂), the latter of which could neutralise soil acidity via its hydroxy ions (OH⁻) reacting with soil H⁺ to form water (H₂O). Both treatments resulted in effective nodulation and larger plants, indicating the importance of calcium for growth, rather than pH alone (Albrecht, 2011). Furthermore, on soils of pH5.4 soybeans were either treated with calcium chloride or left untreated. Total nodulation across all treated plants was 48 times higher than the total across untreated plants (Albrecht & Davis, 1929). As calcium chloride does not ameliorate acidity, this effect was due to the provisioning of calcium. Equal quantities of limestone were applied to two highly acid fields, failing to grow clover on the same farm. One field had a lower exchange/buffering capacity and therefore increased in soil pH upon the application of lime, however the other field's soil pH did not change at all due to its high exchange/buffering capacity. Regardless, both fields resulted in a dramatically improved clover yield, thus reiterating the importance of calcium as a plant nutrient (Albrecht & Smith, 1952). Albrecht & Smith (1952) drilled clover seeds with limestone in a soil of pH5. Using this method, only localised areas of soil where the seeds were planted had their acidity reduced. Regardless, legume root growth extended to areas that had not been ameliorated by liming, and nodulation was successful. This experiment indicated that having legume roots and rhizobia in contact with calcium allowed for successful growth and nodulation, regardless of surrounding soil acidity. Wood & Cooper (1985) exhibited calcium as a significant main driver of white clover yield, whereas pH had a weakly positive correlation with yield. Various studies have acknowledged that increases in white clover and lucerne yields and nodulation were congruent with increases in calcium content of the plants (Andrew & Norris, 1961; Grewal & Williams, 2003; Guo et al., 2010; Moreira et al., 2011). Within the aforementioned studies, the presence of soil acidity did not appear to hinder the productivity of legumes when supplied with calcium, thus exhibiting the importance of the nutritional value of calcium for legume growth and legume-rhizobia symbiosis formation.

Of course, limestone is essential for increasing soil pH to a level that does not allow for elemental toxicities to be present, typically at pH<5 (Follet *et al.*, 1981), in addition to its ability to provide calcium. Therefore, it is important to perceive the role of limestone as a product that ameliorates soil acidity *and* provides calcium. Both purposes are critical to plant growth. Plants can tolerate soil acidity (the presence of H⁺) if soil fertility is



sufficient; the plant root itself creates acidity by respiring carbon dioxide which binds with water in soil solution to create carbonic acid (Eq. 2) of which the plant uses to exchange hydrogen ions for nutrient cations from negatively charged clay and OM (Albrecht, 2011; McLaren & Cameron, 1996). However, the natural or anthropogenic factors that increase the acidity of soils will eventually give rise to elemental toxicities. It is important to realise that this occurrence is a by-product of increased soil acidity *created by* reduced soil fertility, hence the need to ameliorate it with limestone (and the addition of non-acidifying forms of nutrients). A pH of approximately 6.3-6.5 is considered optimal in terms of preventing elemental toxicities and allowing all nutrients to become available for plant uptake (Kinsey & Walters, 2013; McLaren & Cameron, 1996). Of course, different plant species may differ slightly in their ability to grow at varying pH values and calcium concentrations (Andrew, 1976) e.g. lucerne requires a higher pH than white clover to thrive.

In the context of New Zealand, it is claimed that our soils are generally not deficient in calcium (McLaren & Cameron, 1996). The amount of calcium present in soils depends on the parent material, from which the soil formed, and the amount of weathering that has occurred. New Zealand mineral soils generally contain between 0.1% and 5% calcium within the entire soil profile, whilst others that are derived from limestone or chalk can contain up to 20% calcium (McLaren & Cameron. 1996). However, it is important to note that unless the calcium contained within these parent materials converts into a plant-available form, they are essentially useless in terms of providing calcium for plant nutrition and ameliorating soil acidity (Kinsey & Walters, 2013). Exchangeable Ca²⁺ (on soil colloids) within New Zealand soils is typically between 1000 and 5000 kg/ha, of which is 1000 times higher than the Ca²⁺ present in soil solution (McLaren & Cameron, 1996). This allows for the maintenance of an equilibrium between soil cation exchange sites and soil solution. From these numbers, it is perceived that it is soil acidity alone that is of main concern in New Zealand.

However, variation in soil cation exchange capacity will influence the amount of calcium required to raise a soils' pH. Cation exchange capacity refers to a soils' total number of sites available for cation exchange (the exchange of positively charged nutrient ions between soil solution and cation exchange sites). These sites are located on clay surfaces and OM, within soil colloids (Manaaki Whenua Landcare Research, 2020; McLaren & Cameron, 1996).

In New Zealand, cation exchange capacities are measured as units of centimoles of charge per kilogram of soil (cmoles(+)/kg) in relation to the top 6cm of soil (Manaaki Whenua Landcare Research, 2020). New Zealand soil cation exchange capacities range from 1-70 centimoles(+)/kg of soil, with most soils between 12 and 40 centimoles(+)/kg of soil (Manaaki Whenua Landcare Research, 2020). Therefore, can it really be said that our soils aren't deficient in calcium when cation exchange capacities vary significantly all over the country? Or even more so, when the aforementioned natural and anthropogenic acidifying soil processes continue to occur? Or furthermore, when our current agricultural nutrient management typically focuses on inputs of nitrogen, phosphorous, and potassium (NPK) fertilisers (Bryant et al., 2019), despite the fundamental requirement for calcium by plants?

Conclusion

Natural soil acidification processes cannot be avoided, i.e. weathering via rainfall and plant-soil chemodynamics. However, anthropogenic activities that cause the acceleration of soil acidification, i.e. the abundant use of legumes in New Zealand's agricultural di-cultures alongside the use of soil-acidifying fertilisers, can be addressed in order to reduce acidification rates of our agricultural soils. The rate at which soils of an agroecosystem acidify is a function of soil properties, climate, and farming practice, therefore the rate of 'acidaddition' by various natural and anthropogenic factors must be matched by corrective actions (Sumner & Noble, 2003). The application of lime is common practice in most areas of New Zealand, with the exception of hard-to-reach places such as the New Zealand High Country. Lime ameliorates soil acidity, which must occur frequently and in sufficient amounts to prevent sub-soil acidity (aluminium toxicity) of which is far more difficult and expensive to remedy than topsoil acidity alone. Furthermore, liming improves soil structure and associated properties (e.g. aeration, water drainage and retention), increases the availability of nutrients already present in the soil or that have been added (e.g. from fertilisers), promotes earthworm and microbial activity, and increases pasture palatability, all of which can result in improved productivity. Additionally, it has been implied that the application of lime serves as a calcium provision of which is essential to the legumes prominent in our pastoral systems, thus lime may be more relevant to New Zealand soils than initially thought.



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