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Optimising the Use of Soil Alkalising Agents to Enhance Crop Yields

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In collaboration with

Silverwoods Waste Management Ltd

Thesis submitted for the degree of Ph.D at the University of Lancaster

July 2023

DECLARATION

I Declare that this thesis is my own work and has not been submitted in substantially the same form for the award of a higher degree elsewhere.

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Abstract

The pressures on our nutrient resources from intensive agricultural practices are increasing the need for optimised fertiliser use. Alternative nutrient sources derived from industrial waste products can recycle nutrients back into the food system, promoting a circular approach to nutrient management and reducing fertiliser inputs. By products from cement manufacturing such as cement by-pass dust (CBD) and cement kiln dust (CKD) contain considerable amounts of K and are highly alkaline, making them a suitable fertiliser and alkalising agent. Analysis of existing soil pH and K indices found the CBD/CKD produced by four plants supplies enough K to meet the demands of 7% of grassland or 5% of arable land across England and Wales. However, the practice of treating CBD and CKD as liming agents was significantly oversupplying K. A field trial found that CBD and CKD applied at liming rates (5 t ha^{-1}) to a ryegrass (*Lolium perenne* L.) pasture, were as effective as lime and K fertiliser at increasing biomass production, K availability and uptake and soil pH. However, a Partial Nutrient Balance assessment revealed that these rates would lead to build up of soil K and risk leaching. A mesocosm experiment with ryegrass and white clover (*Trifolium repens* L.) demonstrated that intercropping the two species enhances growth and P uptake in limed pastures and improve the efficiency of applied P. Finally, a pot barrier experiment discovered that the facilitative and competitive effects of intercropping ryegrass and clover required direct root interaction. This research identified aspects of current regulatory practice in Great Britain that are leading to inefficiencies in CBD and CKD application and demonstrated that the use of intercropping can increase P efficiency in limed soils. It has also contributed to the understanding of the level of interaction between white clover and perennial ryegrass in intercropped systems.

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LIST OF ABBREVIATIONS

Abbreviation	Meaning	Page
AHDB	Agriculture and Horticulture Development Board	22
AMF	Arbuscular mycorrhizal fungi	39
ANOVA	Analysis of Variance	50
APase	Alkaline phosphatase	112
Ca-P	Calcium Phosphate	111
CBD	Cement by-pass dust	30
CEC	Cation Exchange Capacity	16
CKD	Cement kiln dust	30
GB	Great Britain	76
LER	Land equivalent ratio	14
PNB	Partial nutrient balance	84
PTE	Potentially toxic elements	76
SNF	Symbiotic nitrogen fixation	131

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CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

The global population is currently over 8 billion, and with annual increases of 1.1% it is estimated to reach 9.7 billion by 2050 (United Nations, 2022). The increasing wealth of the earth's population is resulting in a dietary shift towards meat and dairy products which require higher nutrient inputs compared to other foods (Kopittke *et al*., 2019). To meet the dietary requirements of this expanding population, a considerable increase in crop production will be required (Lenaerts *et al*., 2019). Until now, food production has kept up with demand through intensification of agriculture via advances in breeding improved crop varieties and intensive use of fertilisers (especially nitrogen), pesticides and irrigation (McKenzie and Williams, 2015). Excessive or inappropriate use of fertilisers pollutes watercourses, depletes finite resources such as phosphorus and accelerates greenhouse gas emissions (Udeigwe *et al.*, 2015). These environmental consequences are clearly not sustainable either ecologically or economically and improving crop production sustainably to meet future demand is a considerable challenge for both the agricultural and scientific sectors. Therefore, developing land practices that optimise plant nutrition are important factors to consider for increasing the sustainability of crop production.

The aim of this literature review is to examine the importance of mineral nutrition in regulating plant growth and thus crop yields. Additionally, fertiliser use and the issues surrounding its use will be examined alongside the role of soil pH in managing nutrient availability and the potential for optimising fertiliser use. This will include investigating the use of lime and alternative alkalising agents made from industrial by-products to ameliorate soil acidity and improve nutrient availability. Research into the agronomic viability of using alternative alkalising agents will be addressed and opportunities for further research will be identified.

The Importance of Plant Nutrition

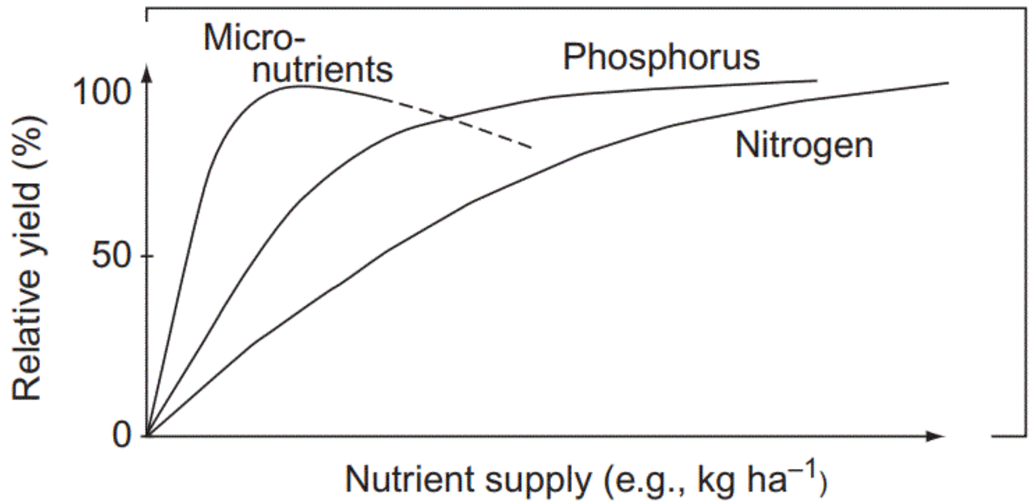
Plants require 14 mineral elements for optimal growth. Since plant growth is limited by the resource that is the least available (Liebig's Law of the Minimum (Tang and Riley, 2021)), deficiency in just one nutrient will have a negative influence (Paris, 1992). Adequate Plant nutrition is important for providing key components for biological processes and is essential for proper plant growth and development. These nutrients and their role in plant functions are summarised in Table 1.1.

The Growth Implications of Nutrient Deficiency

Plant growth responds positively to nutrient supply in a curvilinear fashion (Figure 1.1), with decreased nutrient availability typically increasing root-to-shoot ratio. More biomass is partitioned to roots to allow greater soil exploration and nutrient acquisition (Borch *et al.*, 1999; Reymond *et al.*, 2006; Péret *et al.*, 2011). Shoot biomass is limited by stronger sink competition of the roots, allowing the plant to maintain root growth under limiting conditions (Ben Brahim *et al.*, 1996). This is a common response when plants experience N and P deficiency, however deficiencies in other nutrients such as K, Ca and Fe do not elicit this response (Ericsson, 1995; Marschner, Kirkby and Cakmak, 1996; Guo *et al.*, 2015). These adaptations allow plants to survive when nutrients are scarce, but this is undesirable from an agronomic perspective as it reduces shoot growth and therefore yield.

Table 1.1: The nutrients essential for optimal plant growth and their role in maintaining physiological functions. Adapted from: Schachtman, Reid and Ayling (1998), de Groot (2003), Miller and Cramer (2005) and Marschner and Marschner (2012).

Nutrient	Function
	Macronutrients
Nitrogen (N)	Component of proteins, nucleic acids, chlorophyll, co-enzymes, phytohormones and secondary metabolites. Needed for functioning of photosynthetic machinery.
Phosphorus (P)	Constituent of nucleic acids, phospholipids, ATP, NADPH. Needed for energy and carbohydrate transfer and controlling enzyme reactions.
Potassium (K)	Required for osmoregulation and therefore cell extension, stomatal regulation and solute movement through the plant.
Calcium (Ca)	Acts as a signal in response to environmental stimuli. Needed for cell wall and membrane stabilization as well as osmoregulation.
Sulphur (S)	Required for synthesis of enzymes, co-enzymes and secondary compounds.
Magnesium (Mg)	Component of chlorophyll and required for protein synthesis and photosynthesis.
	Micronutrients
Iron (Fe)	Needed for redox systems in cells and enzymes.
Boron (B)	Maintains cell wall and membrane integrity.
Chlorine (Cl)	Required for osmoregulation and, stomatal regulation.
Manganese (Mn)	Activator of enzymes and needed for lignin synthesis.
Zinc (Zn)	Required for membrane integrity, protein and phytohormone synthesis.
Copper (Cu)	Activator of enzymes and needed for lignin synthesis.
Molybdenum (Mo)	Component of nitrogenase and nitrate reductase enzymes. Needed for N_2 fixation and N metabolism.
Nickel (Ni)	Needed for enzyme synthesis (urease) and N metabolism.



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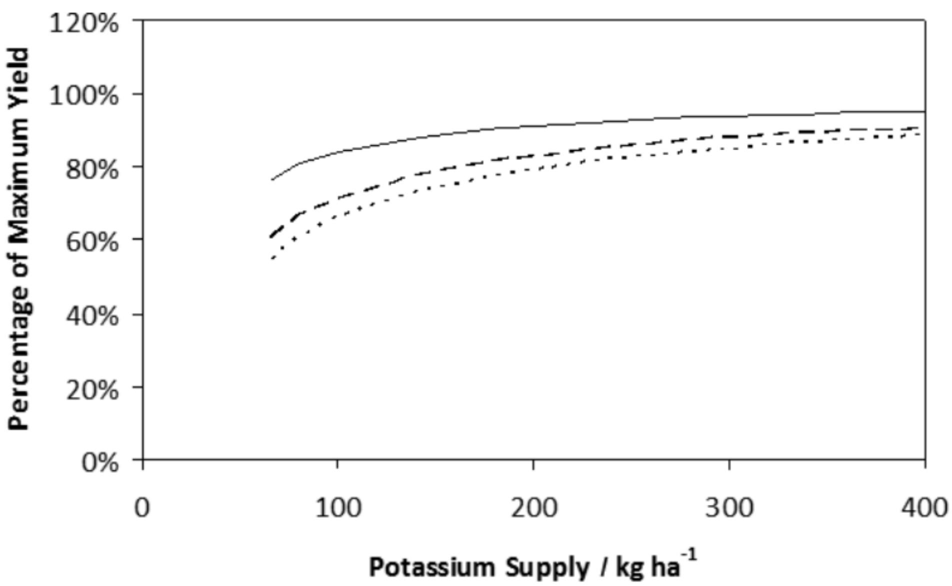

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Figure 1.1: a) Yield response to increasing supply of nitrogen, phosphorus, and micronutrients. Adapted from Marschner and Marschner (2012).
b) Yield response to increasing supply in spring wheat (solid line), broad bean (dashed line),and potato (dotted line) (White, 2013)

Root Responses to Nutrient Deficiency

Plants respond to changes in nutrient availability by adjusting their root architecture to maximise total absorptive surface of the root system (López-Bucio, Cruz-Ramírez and Herrera-Estrella, 2003). Decreased availability of local N and P supply causes pronounced lateral root proliferation in the upper layers of the soil profile, where nutrients are concentrated (Hodge, 2004). A shallow, sometimes highly branched root system facilitates nutrient acquisition; however, this effect varies depending on the deficient nutrient (Gruber *et al.,* 2013). For example, potassium availability can have no influence on localised root proliferation in barley (Drew, 1975) and rice (Robinson, 1994), whereas nitrogen and phosphorus deficiency stimulate primary and lateral root elongation nutrient (Gruber *et al.,* 2013).

Different species vary in their root system plasticity and therefore their ability to acquire nutrients at different soil depths (Hodge, 2004). Phytohormones, including auxin, cytokinin and ethylene mediate morphological changes to the root system induced by variations in nutrient supply by regulating lateral root proliferation, emergence, and elongation (Marchant *et al*., 2002; Tian, De Smet and Ding, 2014).

Turgor Mediated Leaf Growth Inhibition

Deficiency in magnesium, nitrogen, phosphorus, potassium and zinc can inhibit leaf growth by reducing leaf expansion, elongation rate and final area, impeding the plant's capacity to intercept photosynthetically active radiation (PAR) and produce biomass (Fischer and Bremer, 1993; Cakmak, Hengeler and Marschner, 1994; Rodríguez, Keltjens and Goudriaan, 1998; Plénet *et al*., 2000; Zhao *et al*., 2005; Seepaul et al., 2019). Limited carbohydrate availability does not appear to decrease leaf expansion as short periods of stress can cause reductions in leaf area long after the photosynthetic rate recovers (Guidi *et al*., 1997; Tardieu, Granier and Muller, 1999). Instead, starch accumulation is favoured over assimilate export from the leaves, reducing growth (Qiu and Israel, 1994).

Decreases in root hydraulic conductance can inhibit leaf growth by lowering leaf cell turgor (Clarkson *et al*., 2000). Leaf turgor reductions have reduced leaf growth by up to 75% in corn (*Zea mays*), soybean (*Glycine max*) and sunflower (*Helianthus annuus*) by limiting cell enlargement and subsequently, the leaf expansion rate (Boyer, 1970; Matthews, van Volkenburgh and Boyer, 1984; Ehlert *et al.*, 2009). Radin and Eidenbock (1984) proposed that decreased root hydraulic conductance limits growth of phosphorus deficient cotton plants by restricting leaf expansion; however, this response does not appear to be consistent in plants subject to nitrogen deficiency.

Increasing application of N increases leaf turgor pressure in creeping bentgrass (*Agrostis palustris* Huds.) subject to water-stress, suggesting that N supply may mediate leaf expansion (Saneoka *et al.*, 2004). Withdrawing nitrate from the nutrient solution of barley and tomato decreased leaf elongation, coincident with a decline in root hydraulic conductance (Chapin, Walter and Clarkson 1988). However, leaf water content and water potential were not affected, suggesting that in these species leaf elongation was not mediated by a reduction in leaf turgor. Additionally, Palmer *et al*. (1996) found leaf turgor pressure did not decline with nitrate availability in sunflower and changes in cell wall properties may have caused reduced cell expansion. In dicotyledonous plants, the growing leaf is exposed to the air and therefore subject to transpiration and evaporation, making these plants more sensitive to N stress than monocotyledonous plants such as cereals where expanding cells are enclosed in surrounding leaf sheaths (Radin, 1983). The extent that N deficiency decreases leaf growth also depends on what stage it occurs during leaf development with N deficiency restricting cell division and leaf size in younger leaves rather than changes in turgor (Roggatz *et al.*, 1999). Therefore, the effects of N deficiency and turgor mediated growth restriction depends on both crop species and the development stage in which N deficiency occurs.

Stomatal Limitation of Photosynthesis

Low nutrient availability can limit plant growth through reducing photosynthesis, with a number of mechanisms being proposed. Stomatal limitation of gas exchange has been associated with growth reductions of nutrient deficient plants (Zhao *et al*., 2005; He *et al*., 2010; Rothwell, Elphinstone and Dodd, 2015), with root hormonal signals suggested to mediate this response (Guidi *et al*., 1997). I In *P. sativum*, leaf water status was not always associated with decrease stomatal conductance (g_s) and that the phytohormone ABA was mediating stomatal closure rather than a hydraulic signal (Rothwell, Elphinstone, and Dodd 2015). However, stomatal response can vary depending on the type and severity of nutrient deficiency. Zhao, Oosterhuis and Bednarz (2001) found that lower g_s was the first factor in reducing photosynthetic rate under mild potassium deficiency but that under more severe deficiency, biochemical factors such as decreased chlorophyll content were more limiting. Experiments with ABA deficient tomato mutant *flacca* imply that ABA mediates stomatal response in the short term rather than regulating a centralised response to low resources (Coleman and Schneider, 1996). Furthermore, work offering alternative explanations such as mesophyll limitation of photosynthesis contests the importance of stomatal limitation of photosynthesis under nutrient stress.

Mesophyll activity may limit photosynthesis more than stomatal restrictions (Ciompi *et al*., 1996; Zhao, Oosterhuis and Bednarz, 2001; Huang *et al*., 2004). Decreased photosynthetic CO_2 fixation with declining P leaf concentrations was associated with increased mesophyll resistance (Singh *et al*., 2013). Causes of this mesophyll resistance may be due to starch accumulation resulting from reduced leaf expansion, which causes a decrease in CO_2 conductance in the mesophyll (Guidi *et al*., 1997); structural changes such as decreases in protein and pigment content (Jacob and Lawlor, 1991) and restrictions to the carboxylation process (Terry and Ulrich, 1973). This demonstrates that a number of interacting mechanisms may be involved in limiting photosynthesis under nutrient stress. Evidently, this is a complex issue, however Loustau *et al.* (1999) offer a possible explanation for these contradictions in that impaired nutrition does not directly affect stomatal conductance but rather the g_s values reflect a feedback adjustment to photosynthesis.

Nutrient deficiency can also decrease photosynthetic rate through non-stomatal means as plant nutrients are required for biochemical processes associated with photosynthesis. Decreases in leaf concentrations of photosynthetic pigments such as chlorophyll (Jacob and Lawlor, 1991; Oosterhuis and Bednarz, 2001; Huang et al., 2004) may be partially compensated by increasing chlorophyll efficiency, yet reductions in leaf area and photosynthetic rate still limit growth (Ciompi *et al*., 1996; Zhao *et al*., 2005). Furthermore, nutrient deficiency is associated with increased susceptibility to photosystem damage, limiting formation of ATP and NADPH and changing the activity and regeneration of Calvin cycle enzymes such as RuBisco (Ben Brahim *et al*., 1996; Ciompi *et al*, 1996; Lu and Zhang, 2000; de Groot, 2003; Huang *et al*., 2004; Zhao *et al*., 2005; Fleisher *et al*., 2012). However, the extent of which deficiency impedes photosynthetic processes can vary between species (Chaudhary *et al*., 2008) and cultivars of the same species (Davies, Jr. *et al*., 1999) subject to the same level of P deficiency.

Evidently, the interruption of vital plant process by nutrient deficiency means that plant nutrition is an integral part of crop production. However, availability of these nutrients can be a major constraint to productivity, especially in regions where lack of infrastructure and fertiliser availability limit their use (Horst *et al*., 2001; Vance, 2001; Uhde-Stone and Allan, 2003). Growth responses to nutrient deficiency involve complex interactions between different physiological processes that are not fully understood. Conflicting reports and variation in regulatory mechanisms of growth between plant genera, developmental stage, nutrient type and nutrient availability mean that predicting plant response to nutrient deficiency is difficult. More work assessing the role of pytohormones may provide explanations for conflicting evidence about the importance of their roles in mediating response to different nutrient deficiencies and identify plant traits to exploit and improve performance in nutritionally poor soils. Additionally, selecting species that are more tolerant to certain nutrient deficiencies could reduce fertiliser use and its associated problems, which will be discussed next.

Global Impact of Dwindling Nutrient Resources

Improved plant nutrition has been the cornerstone of modern crop production, which has become dependent on a sufficient supply of fertilisers. Without nitrogen fertilisers, global food production would not meet the demands of half the world's current population (Ladha *et al*., 2016) and 90% of global phosphorus demand is for food production (Cordell, Drangert and White, 2009). Nitrogen and phosphorus are the most energy intensive to produce and are more critically limiting elements for plant growth compared to other nutrients (López-Bucio, Cruz-Ramírez and Herrera-Estrella, 2003; Dawson and Hilton, 2011). There are a number of vulnerabilities in current crop production systems and in many cases yield is compromised unless regular fertiliser inputs are used. Poor plant nutrition is partly responsible for yield decline seen in monoculture systems (Bennett *et al*., 2011), which could be exacerbated by climate change in the future (St.Clair and Lynch, 2010). Additionally, modern crop varieties are selected based on homogenous, high fertility systems and are not adapted for efficient nutrient acquisition (Wissuwa, Mazzola and Picard, 2008). However, intensification of agricultural systems and mismanagement of nutrient resources has resulted in some regions having a nutrient surplus whereas others are experiencing deficits and declining yields (Sheldrick, Syers and Lingard, 2002; Cordell, Drangert and White, 2009; Haygarth *et al*., 2014).

The global imbalance of nutrient supply and demand has consequences that affect both developing and developed countries. For example, demand for rock phosphate (an inexpensive and non-renewable source of phosphorus) is likely to continue increasing due to development of new agricultural technologies and expansion of agricultural land (Anlauf, 2022). Just six countries control 90% of the world's phosphate rock reserves and this concentration of the market can lead to restrictions in supply and dramatic price increases (Cordell and White, 2014; Anlauf, 2022). This is a particular problem for developing countries with nutrient-poor soils and limited capital to invest in fertiliser use. As human health is dependent on the phytoavailability of elements essential to human nutrition (Oliver and Gregory, 2014), poor soil fertility affects the nutritional health of large portions of the global population (Jones *et al*., 2013). Nutrient deficiency is further aggravated by the increasing use of modern crop cultivars, which provide sufficient calories and proteins but are lacking in essential micronutrients (Fageria, Baligar and Clark, 2002; Welch and Graham, 2004).

Implications of Current Fertiliser Use

In contrast, developed nations are facing challenges created by excessive use of fertilisers. In Great Britain fertiliser use has fallen over the last three decades (Figure 1.2), however, a large portion of cropland is still routinely treated with N (90%), P (49%), K, (50%) (DEFRA, 2018b). Applying quantities of fertiliser greater than that required for optimal plant growth (excessive) or use of fertiliser on soils that already supply adequate nutrients (inappropriate); in particular, nitrogen and phosphorus can cause considerable environmental damage. Nutrient run-off caused by the overloading of soil contributes to changes in soil pH (through nitrification of ammonia and ammonium), groundwater pollution, eutrophication and hypoxia of lakes and coastlines (Vitousek *et al*., 1997; Graham and Vance, 2000; Vance, 2001; Miller and Cramer, 2005).

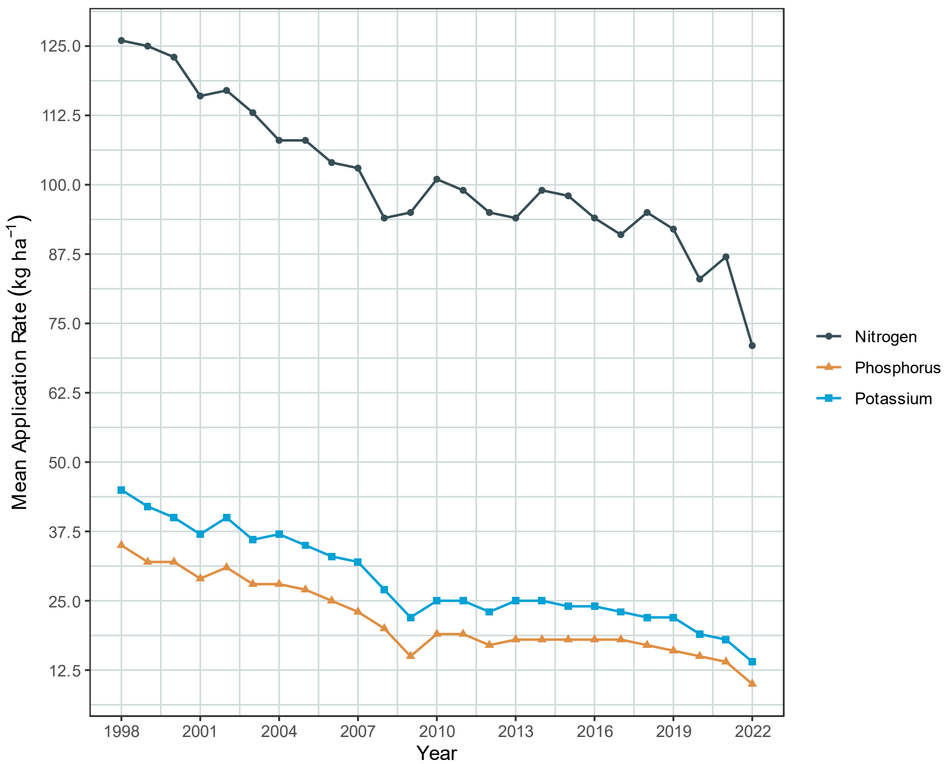


Figure 1.2: The decline in fertiliser application rate on all agricultural land in Great Britain from 1998-2020. Data sourced from DEFRA (2023).

Furthermore, nitrogen fertiliser relies on the combustion of fossil fuels during fixation of atmospheric nitrogen into ammonia (Socolow, 1999). This not only uses fossil fuel reserves, which are becoming limited, but also contributes to climate change through the emission of greenhouse gasses such as CO_2. Clearly, managing nutrient availability is essential for the continued sustainability of food production.

The adoption of organic agricultural practices may mitigate the problems facing traditional nutrient management. Proponents of organic agriculture argue that the use of legumes in an organic rotation can replace the amount of N fertiliser currently in use (Badgley *et al.*, 2007) and reduce nutrient runoff and N_2O emissions (Scialabba and Müller-Lindenlauf, 2010). However, the ability of organic systems to provide food for an expanding population has been questioned, as yields are often lower than conventional systems (Lotter, 2003; de

Ponti, Rijk and van Ittersum, 2012; Seufert, Ramankutty and Foley, 2012). As global food security depends on increasing crop yields, it is debatable whether organic agriculture can achieve this (Godfray *et al*., 2010; Foley *et al*., 2011).

Improving Nutrient Availability Without Additional Inputs

The pressures on crop production created by poor nutrient management threaten global food security and environmental stability. To reduce the impacts of fertiliser use it is important that nutrient use efficiency (NUE) be optimised, especially if increases in crop production will be required to feed an increasing population. NUE is the ability of a plant genotype to acquire nutrients and use them to accumulate biomass or usable plant material (e.g., grain). Increasing nutrient supply beyond the level of deficiency increases growth rate and yield before reaching a threshold where increasing supply diminishes growth (Figure 1). Because of this there has been increased interest in cropping systems that increase productivity and nutrient use efficiency without relying on further inputs. Different strategies involving careful crop selection and planting multiple species at once or in rotation are one way of achieving this. These strategies include use of cover crops, rotation cropping and intercropping.

Cover crops are plants that are grown after the primary crop is harvested and are popular in low or no-tillage systems (Abdalla *et al*., 2019; Osipitan *et al*., 2019). They confer a number of benefits through providing surface cover and increasing plant diversity. For example, cover crops suppress weed growth in between primary cropping through competition for nutrients, water and light (Osipitan *et a*l., 2019). By using cover crops as a mulch or green manure they can improve soil quality between periods of normal crop production (Adetunji et al., 2020). This can also reduce NO_3 leaching reduced by adding a cover crop to withdraw N from the soil that can be incorporated later (Abdalla et al., 2019). Soil quality can be further improved by reducing compaction and erosion as well as improving microbiome diversity, structural and hydraulic properties and temperature (Blanco-Canqui *et al*., 2015).

Rotation cropping involves growing a series of cash crops sequentially over time (Zhao et al., 2020). Again, plant species heterogeneity in these systems provides benefits. The diversity in crop residues left behind after harvest promotes soil microbial biomass and diversity by creating favourable niches for different functional microbe species (Pervaiz et al., 2020; Yang et al., 2020). Furthermore, water use efficiency can be improved through reducing soil evaporation and runoff, soil structure can be improved through increasing resistance to erosion and weed dominance can be reduced by reducing the weed seedbank (Yu et al., 2022). These different benefits can result in average yield increases of 20%, however this can vary greatly between regions. However, under-sowing with cover crops in spring can lead to competition for nutrients, water and light with the primary crop and therefore reduce yield if not planned correctly (Abdalla et al., 2019).

Intercropping is an ancient practice that involves planting two or more crop species together at the same time (Dai *et a*l., 2019; Maitra *et al*., 2021). In some regions (such as Latin America, Africa and India) it is still the dominant form of agriculture. Intercropping can be divided in to three strategies: mixed intercropping (two or more crops grown simultaneously), relay intercropping (growing crops sequentially where additional crops are added before the first is mature) and strip intercropping (different crops grown simultaneously in strips) (Booker *et al*., 2015). Combinations of cereals or grasses and legumes are widely used for intercropping systems (Demie et al., 2022) and species selection involves combining crops that have temporal, morphological or nutritional complementarity (Mamine and Farès, 2020). This allows for temporal and spatial exploitation of available resources and a reduction in interspecies competition (Gitari et al., 2020).

The benefits of intercropping systems are numerous and wide ranging, the foremost of which is the saving of land. This is quantified by the Land Equivalent Ratio (LER), defined as the relative land area required to produce, from sole crops, the same yields as are achieved by intercropping (Oyejola and Mead, 1982). Land area and fertiliser equivalent ratios (the ratio of the fertilizer amounts used in sole cropping to the fertilizer amounts used under intercropping to produce equal amounts of yield) often exceed 1.0 for intercropped systems, which implies that they save both land and nutrient resources compared to monocropping (Li *et al*., 2020). This due to the propensity of intercrop systems to overyield (by 2.2% on average) compared to a monocrop system (Bybee-Finley and Ryan, 2018; Gitari et al., 2020). Intercropping has also been proposed to promote biodiversity and delivery of ecosystems services such as pollination, pest control, soil quality, nutrient cycling and reduce soil erosion (Tscharntke et al., 2021; Scheper et al., 2023). As agriculture is considered the main cause of global biodiversity decline (Tscharntke et al., 2021), intercropping therefore offers a route to mitigate some of the vulnerabilities cause by our increasing reliance on intensive agricultural practices and monocropping (Mamine and Farès, 2020; Demie et al., 2022). Additionally, as multiple crops are grown at once, intercropping provides against crop failure and is more economically sustainable, especially for smallholder farmers in regions where use of resources such as fertilisers and pesticides is constrained (Gitari et al., 2020; Demie et al., 2022). Furthermore, such systems have improved nutrient resource use efficiency compared to monocultures (Carton et al., 2020) due to their lower need for fertiliser and pesticides (Demie et al., 2022).

The mechanisms behind the overyielding in intercropping are ascribed to complimentary use of resources such as soil nutrients, light and water as well as facilitative interactions between plant species promoting resource use (Li et al., 2014; Gitari et al., 2020). For example, adding n fixing legume species to cereal crops can reduce N_2O fluxes derived from fertiliser use and leave significant amounts of N in the soil after harvest (Kihara *et al.*, 2010; Demie et al., 2022). Furthermore, specific legume species are known for their ability to chemically alter P speciation in the rhizosphere and mobilize sparingly soluble P through rhizosphere acidification and root exudation (Pypers et al., 2023). This promotes P availability, P-use efficiency as well as grain protein content and forage quality (Zhang *et al.,* 2016; Mokolopi, 2019; Mamine and Farès, 2020). As a result, adding legumes to cropping systems can reduce both N and P fertiliser inputs. For these reasons grass-legume intercrops are a popular choice in pastures and forage production, where forage quality can be maintained for a longer duration (Bybee-Finley and Ryan, 2018).

There are however barriers to wider adoption of intercropping despite its benefits. Higher yield variability in legume species such as white lupin has prevented adoption in European systems that require reliable output (Carton et al., 2020). Intercropping is also not desirable in larger scale systems that require a standardised scalable crop the requires mechanised management (Booker et al., 2015). This is due to the requirement for trial and error to create tailored management and optimisation for each site (Huss *et al*., 2022). Furthermore, yield response to intercropped systems is highly context dependent and do not guarantee increased productivity, making some farmers reluctant to adopt them (Tamburini et al., 2020). However, strategic crop selection can maximise the agricultural and ecological benefits whilst reducing the complexity of the system and reduce the inconveniences of such practices (Bybee-Finley and Ryan, 2018). Therefore, adopting strategies such as Intercropping with N fixing and P mobilising species could be used to address global nutrient imbalances by reducing fertiliser load, improving NUE (Menezes-Blackburn *et al.,* 2018) and mitigate the decline in yields observed by modern monoculture systems mentioned previously (Bennett *et al*., 2011). However, other factors, such as soil pH, influence nutrient availability (Figure 3), and through maintaining an optimal soil pH, it is possible to increase nutrient availability and lower fertiliser rates should be possible.

1.2 Factors Affecting Nutrient Uptake

Numerous factors influence nutrient availability, from soil pH to the forms of the nutrient that are present in the soil. Plants take up nitrogen as nitrate (NO_3^-) and ammonium (NH_4^+). Potassium is taken up as potassium ions (K^+); and phosphorus is taken up in the orthophosphate (Pi) forms $H_2PO_4^-$ and HPO_4^{2-}, which occur in soil solutions at very low concentrations (Schachtman, Reid and Ayling, 1998; Vance, Uhde-Stone and Allan, 2003; Amtman *et al*., 2005; Miller and Cramer, 2005; Argyropoulou *et al*., 2015). Soil pH influences the availability and forms of nutrients in the soil. For example, between pH 6 and 7 plant uptake of phosphorus prefers $H_2PO_4^-$ over HPO_4^{2-}, illustrating the importance of managing soil pH for maximising nutrient availability (Schachtman, Reid and Ayling, 1998; Vance, Uhde-Stone and Allan, 2003). As soil pH decreases below 5.5, the availability of iron (Fe) and aluminium (Al) increases, whereas above pH 6.5calcium availability increases. This affects phosphorus availability as calcium carbonate and Fe and Al oxides react with phosphorus, forming insoluble compounds that render it unavailable.

A soil pH of <6.5 can increase the availability of nutrients such as B, Cu, Fe, Mn and Zn (Figure 1.3) and conversely, they can remain unavailable in alkaline soils (Foth, 1990, Sumner and Yamada, 2000). On the other hand, a soil pH of <6 is associated with decreasing availability of P, K, Ca, Mg and Mo, resulting in deficiency. Nutrient availability is further influenced by the soil ion exchange capacity, chemical properties as well as plant and microbial activity (Horst *et al*., 2001; Vance, 2001; Vance, Uhde-Stone and Allan, 2003). K for example is relatively abundant in soils compared to P, however most of this K is held in non-exchangeable forms in many mineral soils and is thus not available to plants (Schmidt *et al.*, 2022). The plant available form of K exists in soil solution as the positively charged cation K^+ and is released into the soil solution through diffusion of exchangeable-K held on negatively charged surfaces of clay minerals and soil organic matter (Paul *et al*., 2024). Consequently, the behaviour of K in soils is governed by the cation exchange capacity (CEC) of soils (Brady and Weil, 2008). This is defined as total amount of exchangeable positively charged ions (cations) such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Al^{3+}, Fe^{2+}, H^+ that can adsorb to a soil's surfaces at a given pH (Solly *et al.*, 2020). As the negative charge of soils surfaces increases with increased pH, adsorption of cations such as K^+ is increased, thus reducing the amount of K^+ diffused into solution, where it is more vulnerable to loss through processes such as leaching (Brady and Weil, 2008). An increase in pH also reduces the presence of Al^{3+} at cation exchange sites that would otherwise displace K^+ to the soil solution (Brady and Weil, 2008). Therefore, maintaining higher soil pH reduces K losses that would otherwise require further fertilisation to correct.

As the availability of nutrients depends on different factors, it is often present in forms that are unavailable to plants and recovery from soils can be low. This is a problem for modern agriculture as without fertiliser, few soils could support the demand of modern crop species that exhibit high growth rates (Schachtman, Reid and Ayling, 1998). Again, this highlights the need to optimise nutrient management to address the issues associated with increasing pressures on food production.

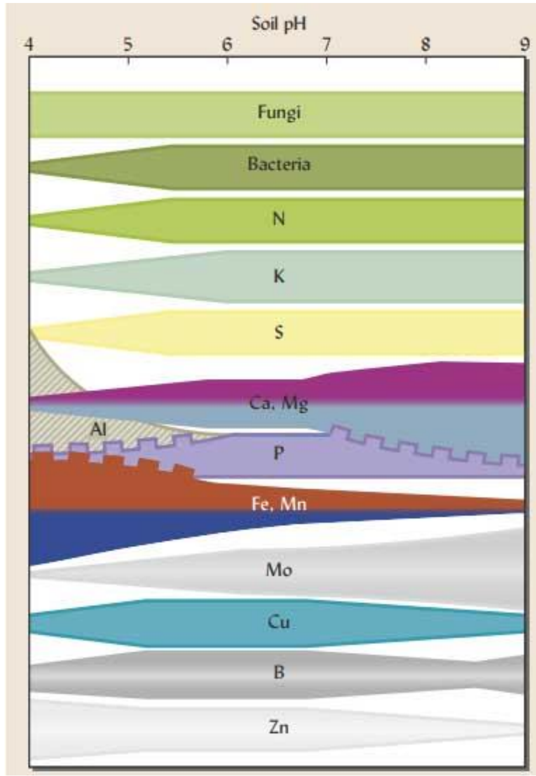


Figure 1.3: The relationship between soil pH and nutrient availability in mineral spoils. Adapted from Brady and Weil (2017).

Problems Associated with Soil Acidification

Soil acidification can be a major limitation to plant growth in agricultural systems, and if not managed it can require considerable investments in time and money to rectify (Haynes and Mokolobate, 2001). Soil acidification results from the release of hydrogen ions (H^+) into the soil solution, often caused in areas where rainfall exceeds evapotranspiration as part of natural processes involving the oxidation of metal-sulfides such as pyrite (Bolan, Adriano and Curtin, 2003). Other causes are plant acidification of the rhizosphere via exudation of organic acids to facilitate nutrient uptake (Bolan, Hedley and White, 1991) and decomposition of organic matter by microorganisms (van Breemen, Mulder and Driscoll, 1983). In natural ecosystems, acid drainage (the drainage of acid water due to rock weathering) can also contribute to soil acidification, which is influenced by human activity. For example, oxidation of pyrite increases acid drainage and land disturbance caused by activities such as agriculture that expose it the atmosphere further encourage this process (Bolan, Adriano and Curtin, 2003).

Intensive agricultural practices, especially the use of nitrogenous fertilisers, are a major cause of acidity in managed land. Ammonia-based nitrogen fertilisers are a problem due to their high application rates for cereal crops, especially in the United States and China (Haynes and Mokolobate, 2001; Brown *et al*., 2008; Liu *et al*., 2011). Nitrogen fertiliser produces an abundance of H^+ through NO^{3-} leaching and nitrification, which lowers soil pH (Bolan, Adriano and Curtin, 2003). This is partly counteracted by the plant uptake of NO_3^- ions that release OH^- into the rhizosphere (Bolan, Adriano and Curtin, 2003). Furthermore, the removal of base cations (Ca, K, and Mg) from the soil via crop offtake can lower pH (Lukin and Epplin, 2003). Some soils are more susceptible to acidification than others, with the soil buffering capacity (the ability of the ions associated with the solid soil component to resist changes to soil solution pH) being influenced by organic matter content and the soil's texture (Brady and Weil, 2008). This is evident in highly weathered soils, where a lower cation exchange capacity (CEC) reduces the soil's ability to buffer against changes in pH (Goulding, 2016).

Low Soil PH and Plant Growth

Although soil pH does not affect plant growth *per se* (Sumner and Yamada, 2002), soil acidity can limit plant growth in numerous ways. For example, Al and manganese Mn toxicity are commonly encountered in acid soils because these elements are more available in the soil solution at a low pH, (Brown *et al* ., 2008) (Figure 1.3). Under acid soil conditions (<pH.5.5) Al^{3+} and Mn^{2+} become soluble due to dissolution of clay minerals, gibbsite and manganese

oxide (MnO_2) (Haynes and Mokolobate, 2001; Sumner and Yamada, 2002; Lukin and Epplin, 2003). When experiencing Al toxicity, plant growth is similar to low phosphorus (P) availability in non-acid soils, with a negative impact on root growth, nutrient uptake and biomass accumulation (Sierra *et al*., 2003). Al toxicity dsamages and inhibits growth of both the main axis and lateral roots. This reduced root growth leads to inefficient soil exploration, commonly resulting in nutrient and water deficits (Haynes and Mokolobate, 2001). Additionally, Al toxicity interferes with the active ion uptake by blocking ion channels across the plasma membrane of the root cells (Kochian, 1995) and consequently, reductions in Calcium (Ca) and P uptake are often observed and P deficiency symptoms are common (Haynes and Mokolobate, 2001).

Managing Soil Acidity in Agriculture

The most common method of moderating the effects of soil acidity in agriculture is the application of lime. Currently, there are numerous materials that can be used, each with varying ability to neutralise acidity, including: calcium carbonate ($CaCO_3$), burnt lime (CaO), calcium hydroxide ($Ca (OH)_2$) and dolomite ($CaMg (CO_3)_2$) (Bolan, Adriano and Curtin, 2003). In the UK, ground limestone ($CaCO_3$) makes up 70% of the liming material used (Goulding, 2016). Liming influences soil pH by hydrolysis of the basic cations present in the material (Ca or Mg), which produces OH^- ions that in turn neutralize the H^+ ions present in the soil (Bolan, Adriano and Curtin, 2003). The amount of liming agent required to raise soil pH to a desired level depends on the initial pH of the soil, the Neutralising Value (NV) of the liming material and the buffering capacity of the soil (Bolan, Adriano and Curtin, 2003; Goulding, 2016). The Neutralising Value is a measure off the efficiency of a liming material relative to calcium carbonate ($CaCO_3$), which is usually expressed as a weight percentage of pure $CaCO_3$ (Bolan, Adriano and Curtin, 2003) or as percentage of calcium oxide (CaO) equivalent (Aglime.org.uk, 2018). However, the efficacy of a liming material also depends on its particle size and hardness, which influence its rate of dissolution within the soil (Goulding, 2016).

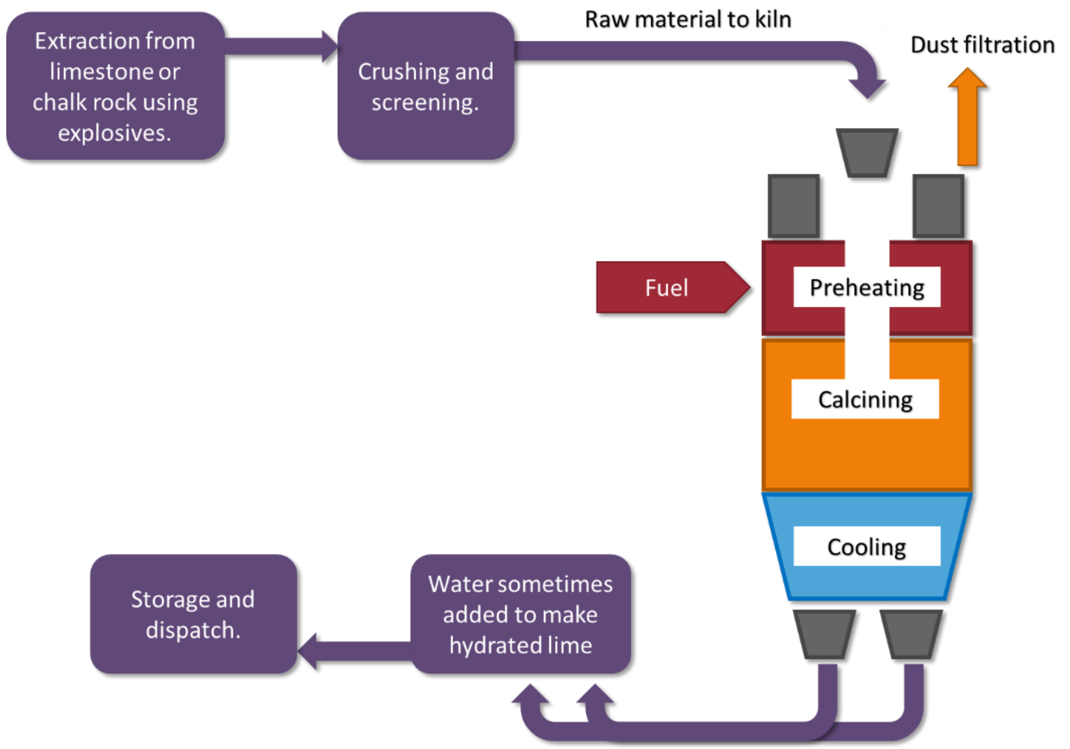


Figure 1.4: The production process of agricultural lime. The lime is extracted from limestone or chalk rock before being screened and heated in a kiln. Water is sometimes added before storage to make hydrated lime. Adapted from Britishlime.org (2018).

Benefits of Lime Application

Although raising soil pH can effectively mitigate the crop production issues associated with soil acidity, advice on which pH range is 'ideal' varies. The Nutrient Management Guide (RB209) for liming applications in England and Wales advises that mineral soils are limed to maintain a soil pH of between 6.0 and 6.5 depending on soil type or cropping system (AHDB 2023b). Traditional advice suggests liming to a pH of 6.5 - 7.0 depending on the crop (Sumner and Yamada 2002) whereas others observe that most plants will grow well at a pH as low as 5.5 (Bolan, Adriano and Curtin, 2003). Clearly, there is no universal ideal soil pH for all crops, and a number of factors will determine the target pH. For example, in two UK soils Bolton (1970) observed that optimum pH depended on the type of crop, with spring bean yield optimised at pH 6.8 and spring barley between 6.5 and 7.5. These variations in response were not due to the soil pH *per se*, but rather due to decreases in exchangeable Al resulting from lime application. This would otherwise immobilise phosphorus in the soil, resulting in deficiency, which was tolerated less by some barley varieties. However, other research suggests that current recommendations can lead to liming at rates that are much higher than needed for successful crop growth (Sumner and Yamada, 2002).

The application of lime and its influence on plant growth have been studied extensively, with plant responses being generally positive. However, plant species, soil texture, application rates, methods and opinions on the subject vary. Liming from pH 5 to 6.3 increased yields of field pea (*Pisum sativum* L.) (Arshad and Gill, 1996) and wheat by decreasing Al toxicity and increasing availability of phosphorus. Increased yield of wheat, barley and faba beans was attributed to an increase in soil pH (from 5.1 to 5.5) and a reduction in exchangeable Al^{3+} and Mn^{4+} (Osundwa *et al*., 2013). However, the authors do recognise that liming may not always result improvements in yield and that any liming strategy should take crop species and sensitivity to Al and Mn, soil type and relative grain yields. This is reflected in the findings collated in Figure 1.5, where in some cases lime application reduced yield. The presence of P and organic matter in the upper soil layers of un-limed plots may improve yield through precipitation of toxic levels of Al (Caires *et al*., 2005), negating the need for lime. Despite the discrepancies observed in the yield data, liming is still considered to an important component of crop production due to its positive influences on soil properties and plant growth.

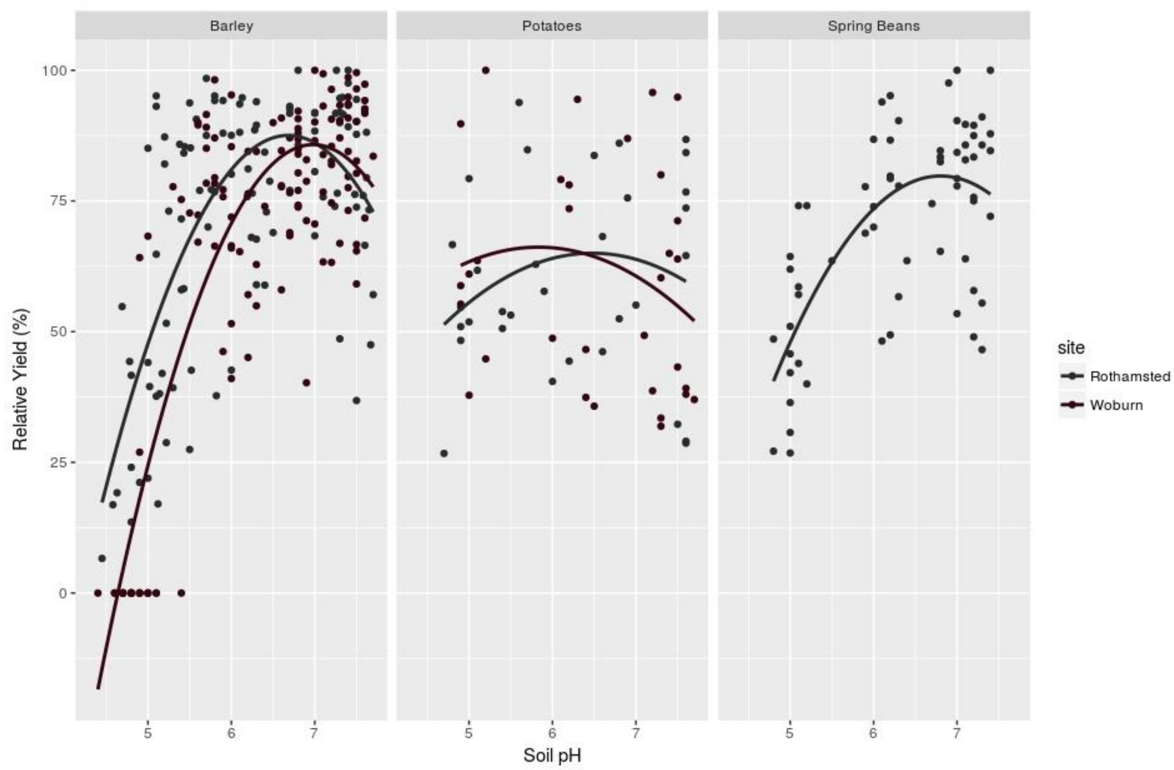


Figure 1.5: Relative yield response of three different crops to soil pH across two UK sites: Rothamsted (flinty silty clay loam, Batcombe-Carstens Series) and Woburn (sandy loam, Cottenham Series). The point of yield depression differs between crops and between the same crop grown in different soils. Data obtained from Rothamsted Research Archive (Rothamsted, 2018).

Liming Effects on Nutrient Availability

Although reports conflict about the influence of soil pH on nutrient availability, liming typically mobilises plant nutrients (Bolan, Adriano and Curtin, 2003). Liming increases available Ca, Mg and K by increasing supply of Ca^{2+}, Mg^{2+} and K^{+} and alleviates N and S deficiency through increased mineralisation of organic matter (Williams, 1967; Wilmot, Ellsworth and Tyree, 1996; Curtin, Campbell and Jalil, 1998). Increasing soil pH promotes nitrification through rapid conversion of ammonium to nitrate, promoting availability (Ste-Marie and Paré, 1999; Hachiya and Sakakibara, 2016). However, this process can be so rapid that it results in inefficient crop use of N, nitrate leaching, groundwater contamination (Sumner and Yamada, 2002) and increased N_2O emissions (Stevens, Laughlin and Malone, 1998; Mørkved, Dörsch and Bakken, 2007). Additionally, solubility of the trace elements Cu, Fe, Mn and Zn decreases as pH is increased, leading to deficiencies in these elements as pH approaches neutral (Brady and Weil, 2008). Therefore, it can be argued that maintaining a pH that improves nutrient availability whilst lowering the potential for groundwater contamination should be the aim of any nutrient management practice.

In highly acidic tropical soils, liming reduced P sorption by reducing levels of exchangeable Al^{3+}, Fe^{3+} and Mn^{4+}, which increased available P and improved P fertiliser recovery needed for high grain yield (Kisinyo *et al*. 2013). Plots that applied lime and P fertilizer had higher available P than when either was applied alone; allowing combined lime and P application to be repeated after every two cropping seasons as opposed to after every season. Osundwa *et al*. (2013) also found that lime application (at all levels) increased the availability of both native soil P and of P fertiliser. This strongly correlated with wheat yield in some of the plots studied. However, as both studies focused on tropical soils, the findings may not represent edaphic conditions found in other regions and it is unclear whether this is applicable to British agriculture.

Influence of Liming on Soil Microbial Activity

Liming can indirectly influence nutrient availability by stimulating microbial activity, which increases mineralisation of soil organic N, S and P (Haynes, 1984). Soil pH positively correlated with microbial biomass and respiration (Aciego *et al*., 2008). Microbial biomass increased directly through a reduction of exchangeable Al and therefore toxicity, and indirectly by increasing inputs of plant-derived substrates such as roots and root exudates. However, this study was focused on a single soil type (a flinty, silty clay loam), which may not be representative of all soils, growing conditions and land management practices, especially as it had not received any other soil amendments for years prior to the experiment.

Johnson, Leake and Read (2005) found that microbial communities are sensitive to short-term applications of lime (annual application over two years). In their study, liming increased arbuscular mycorrhizal fungal colonisation of *Agrostis capillaris* roots but significantly decreased overall microbial biomass carbon. This suggests that liming may alter the diversity of the microbial community, which may in turn influence nutrient availability.

Liming Effects on Soil Physical Properties

In addition to increasing nutrient ability and alleviating toxicity, liming improves soil structure and hydraulic conductivity, which indirectly influences plant growth (Valzano, Murphy and Greene, 2001). Liming increases the Ca concentration in the soil solution and in turn influences flocculation and dispersion of soil colloids, helping form soil aggregates and therefore improving soil structure (Bolan, Adriano and Curtin, 2003; Bennett *et al*., 2014; Goulding, 2016). This facilitates root exploration and improves infiltration of water into the soil profile, thus increasing water supply to the plant (Haynes and Naidu, 1998; Sumner and Yamada, 2002). However, contradictory reports suggest that the influence of lime on soil physical properties may change over time, with short term effects concentrating on dispersion of soil colloids and long-term effects favouring aggregate formation due to the cementing effects of $CaCO_3$ and precipitated hydroxy- Al polymers (Grant, 1992; Haynes and Naidu, 1998).

Negative Aspects of Using Lime

As mentioned previously, opinions differ as to which pH range is optimal for nutrient availability (Sumner and Yamada, 2002; Goulding, 2016) and this is reflected in findings on the influence of liming on P availability and plant growth. Sumner, Farina and Hurst (1978) observed that liming to neutrality can decrease yield, which the authors attributed to lower Mg uptake as there was less soil exchangeable Mg. Interestingly, the authors found that initially, exchangeable Mg increases with pH but then begins to decrease above pH 6 and they conclude that highly weathered soils 'fix' Mg and render it unavailable to plants. It was also noted that root uptake of P is sometimes depressed when Mg is limiting as it is required for activating phosphate transfer enzyme systems. Carran (1991) found similar responses to lime application, with clover (*Trifolium repens* and *Trifolium subterranneum*) yield decreased by 40%. However, no evidence of Mg fixation at pH 6.8 was found. Instead, it was thought that increasing pH to 5.4-5.8 resulted in Ca:Mg ratios in excess of 75:25, which proved damaging to growth. Similarly, Sumner and Yamada (2002) and Haynes (1982) report that liming can increase, decrease and cause no changes in phosphate availability in highly weathered soils.

Rothwell and Dodd (2014) found that liming a low-pH sandy-loam to UK recommended levels (AHDB, 2023b) decreased stomatal conductance, leaf area and photosynthesis in legume crops. It was originally thought that the lime increased the concentration of calcium ions (Ca^{2+}) in the soil making them more available to plants, which in turn elevated the levels of Ca^{2+} in the xylem sap, limiting gas exchange through promoting stomatal closure. However, the results indicated that xylem Ca++ concentrations were insufficiently elevated to have an anti-transpirant effect. Further experiments found that liming to ~pH 6.2 decreased xylem sap and tissue concentrations of P in *P. vulgaris* and *P. sativum* and caused yield reductions in *V. faba* (Rothwell, Elphinstone and Dodd, 2015). Furthermore, the negative effects of lime were partially reversed by application of superphosphate at 200kg ha^{-1}, which suggests that liming was rendering P unavailable to the plants. Similarly, liming decreased biomass when pH levels were between 6.3 and 6.5, but corn and alfalfa yields were increased two to twenty times when extreme rates of phosphorus fertiliser (64 tons/ha $^{-1}$) were applied (Bartlett and Picarelli 1973). Additionally, He et al. (2010) found that *Camellia oleifera* (Abel.) had higher root and shoot dry weight with combined lime and P application (P_2O_5 at 100 mg kg^{-1} and lime at 0.8 g kg^{-1}) compared to applications of either treatment on its own, suggesting a more general response.

Several factors can govern the interaction between pH and phosphorus availability. P speciation and distribution in the soil solution is determined by pH, however the mobility of inorganic P in most soils can still be unpredictable, which may partially explain conflicting reports on the influence of lime on P availability (Hinsinger, 2001). An increase in pH results in increased proportion of divalent phosphate ion (HPO_4^{2-}) and this change in speciation promotes adsorption to soil colloids (Bolan *et al*., 2003). Additionally, pH determines the type of precipitation mineral formed by P and the metal cations present in the soil (Hinsinger, 2001). As pH increases towards pH7, P precipitates with Ca to form P-Ca phosphates, which decreases P solubility and therefore plant availability (Hinsinger, 2001; Bolan *et al*., 2003). However, Haynes (1984) observes that this reaction can occur even at pH 6, which may also explain why research has found that liming can reduce P availability. This was further explored by Curtin and Syeres (2001), who found that for every unit increase in pH, the Olsen phosphorus (estimate of plant available P in the soil) values decreased by 2 to 5 mg kg $^{-1}$.

Highly Weathered Soils May Explain Why Reports Conflict

Soil type may also influence the interaction between pH and phosphorus availability. Haynes (1984) suggests that the decrease in phosphate adsorption in response to increasing pH may be a quirk of highly weathered soils and Hinsinger (2001) notes that the mineralogy and geochemistry of these soils favours retention of P ions onto the solid constituents of the soil and so low levels of P ions are retained in the soil solution. Furthermore, Haynes (1984) found that soil drying might also influence phosphate adsorption. Their experiments showed that when an acid soil (pH 4.2), high in exchangeable Al was incubated with lime, the moist soil the reacted with phosphate and increased phosphate adsorption, but if the limed soil was air dried before the reaction with phosphate, then liming decreased adsorption. It was concluded that drying significantly alters the surface characteristics of limed soil. Therefore, in regions where this phenomenon occurs, the timing of irrigation may be an important factor in nutrient management. Moreover, soil phosphate adsorption capacity can be greater immediately after liming but with diminish with time (Haynes, 1984).

Environmental Concerns

The production of lime is also problematic for the environment as it releases pollutants such as: sulphur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), nitrous oxide (N_2O), particulate matter and volatile organic compounds including methane (CH_4) (EEA, 2016). This does not include the greenhouse gasses released by the combustion of fuels during the manufacturing process that also contribute to pollution. In the United States approximately 30 Tg of lime are spread every year and it is thought that global lime use may triple in the next 50 years (Hamilton *et al*., 2007) through increasing conversion of natural ecosystems to cropland (Tilman, 2001). Robertson (2000) considered that CO_2 contributions from liming are comparable to other agricultural inputs in terms of potential global warming impact. However, lime may also act as a net sink for atmospheric CO_2 through carbonic acid weathering of the material caused by CO_2 emitted from root and microbial respiration (Hamilton *et al*., 2007). Although this may sound promising, a limited number of crop and soil types were used in this study, and it is difficult to say whether this would be relevant to all agricultural systems. Furthermore, it is unclear how much this would offset the carbon emitted by the production of lime considering the scale of its use globally. It is unsurprising then, that there has been a considerable amount of research focusing on finding more sustainable and accessible alternatives to agricultural lime. Many of these are developed from waste products from industrial processes and therefore present an opportunity to improve the sustainability of both agriculture and the industries from which they arise.

1.3 Soil amendments and lime alternatives.

Although liming is common practice in many parts of the world, there are issues with its use that may prevent adoption of the practice or raise questions about the sustainability of the practice. The cost of using and transporting lime can be prohibitive especially in developing countries or in areas far from lime deposits (Dann, Dear and Cunningham, 1989; Yuan and Xu, 2010; Arshad et al., 2012). This presents further issues for farmers choosing to forego liming, who may see reductions in yield and profit from their crop. Therefore, finding a cost-effective replacement could improve crop production for many smallholder farmers. A number of alternatives derived from industrial waste have been investigated. These materials include biochar, wood ash, fly ash, and sewage ash as well as sewage sludge. The alkalinity of these products makes them suitable for ameliorating soil acidity (Dann, Dear and Cunningham, 1989; Hass et al., 2012). Although their application improved plant growth and nutrient availability (Rosen, Olson and Bierman, 1994; Chan et al., 2007; Arshad et al., 2012; Schulz and Glaser, 2012), it is uncertain whether they are as effective over the long-term. Additionally, different production processes and materials used for combustion means that these waste products can vary in their chemical composition, and it is difficult to make general statements on their nutrient content and potentially toxic element (PTE) content (Rosen, Olson and Bierman, 1994; Demeyer, Voundi Nkana and Verloo, 2001; Ferreira, Ribeiro and Ottosen, 2003; Pandey and Singh, 2010). It is also worth considering that incubation experiments such as those carried out by Whalen et al. (2000) use application rates that could be considered excessive for use within the field and caution should be applied when making decisions based on these results in order to avoid compromising environmental and soil quality. Therefore, further work should ascertain whether these industrial by-products could serve as an effective replacement for lime.

Cement Bypass Dust and Cement Kiln Dust

Cement Bypass Dust (CBD) and Cement Kiln Dust (CKD) are by-products of the Portland cement production process that are recognised for their potential as an amendment for acid soils. Most cement in the United Kingdom is produced using the dry process, using raw material such as limestone, chalk or marlstone combined with shale, clay, slate, blast furnace slag, silica sand, and iron ore (cement.org, 2017). The material is fired at high temperatures in steel rotary kilns (MPA, 2016). Dust particles formed in the kiln are captured by exhaust gasses and then collected through cyclones, baghouses or electrostatic precipitators (Adaska and Taubert, 2008). The site of the dust collection determines its chemical composition and is referred to as either kiln dust or bypass dust (Figure 1.6). This means that CKD and CBD consist of partially calcined kiln feed, clinker dust and ash and as such they are typically composed of calcium carbonate ($CaCO_3$), silicon dioxide (SiO_2), calcium oxide (CaO), potassium sulphate (K_2SO_4), calcium sulphate ($CaSO_4$) and aluminium oxide (Al_2O_3) (Adaska and Taubert, 2008). The high $CaCO_3$ and K_2SO_4 content of CKD suggests that it has a potential as both a lime and potassium fertiliser replacement and both CBD and CKD are currently used in many countries as a soil ameliorant (Bhatty, 1995; Adaska and Taubert, 2008; Lalande, Gagnon and Royer, 2009). However, relatively little research has examined the agronomic benefits of these materials and furthermore CKD can vary considerably in its chemical and mineral composition and comparisons cannot be made between the dusts produced from each plant.

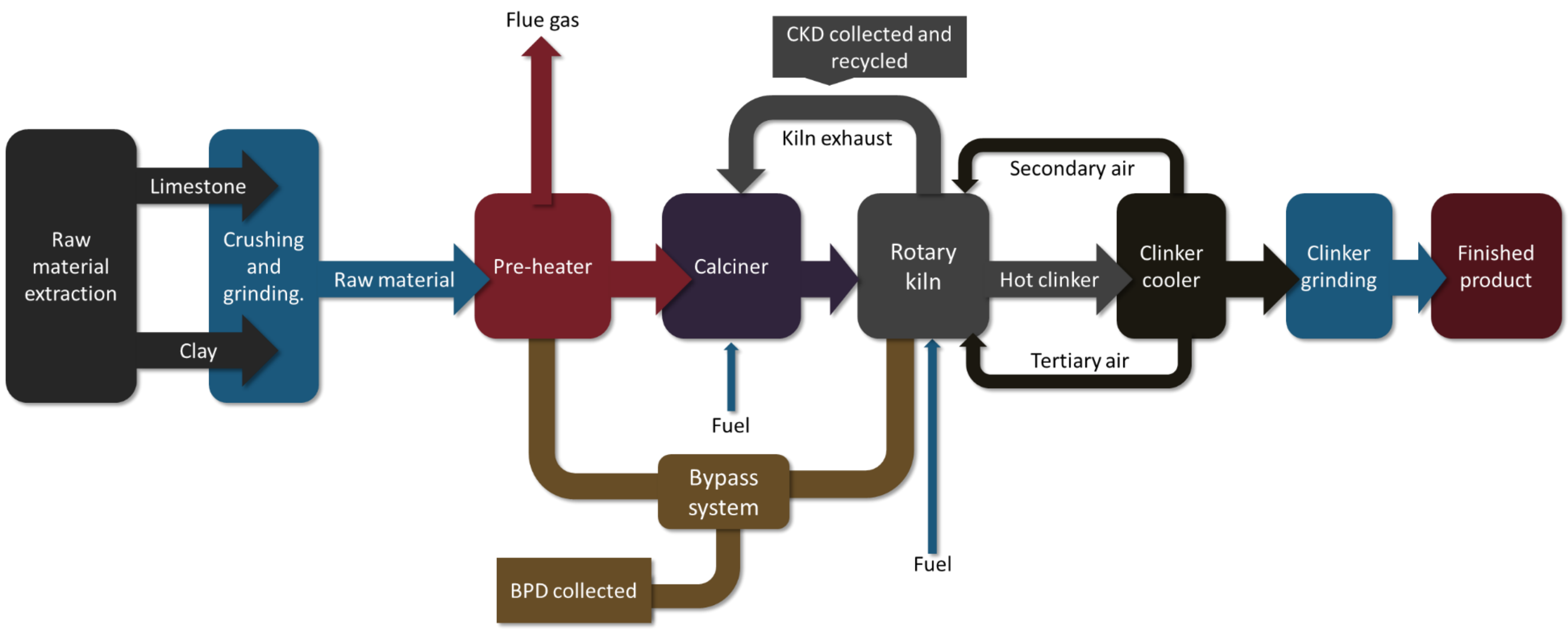


Figure 1.6: The process for producing Portland cement including the collection of cement kiln dust (CKD) and bypass dust (CBD). The site of collection determines the chemical composition of the dust collected. CKD is collected from exhaust gasses from the kiln and often recycled back into the kiln to supplement the raw feed. CBD is extracted from a bypass system between the preheater and the kiln inlet to avoid build-up of volatile species with the kiln. This would produce a clinker product that is too alkaline for use. Adapted from Afkhami *et al*. (2015).

Effect of CBD and CKD on Crop Growth and Soil Properties

Research suggests that CKD/CBD application can increase plant growth by improving soil pH and nutrient availability. When applied at equivalent rates to the K fertilisers (synthetic K fertiliser, KCl and K_2SO_4), CKD increased yields in potato (8%), barley (16.6%) and alfalfa (14%) averaged across 11 different soil types compared to control (Van Lierop, Tran and Morissette, 1982). There was no difference in yield between CKD and the fertiliser treatments, suggesting that it is equally effective as K fertiliser. These results also suggest that that the effects of CKD are not limited to a specific soil type. However, the effect of the lime can vary depending on the soil type, site and year and in some cases can increase yield compared to CKD (Lafond and Simard 1999).

Saralabai and Vivekanandan (1992) found that CKD application increased relative growth rate (7.4-fold), leaf area index (2.8-fold) and net assimilation rate (99%) of three legume species compared to an untreated control. CKD treatment increased leaf tissue concentrations of Cu, Fe, K, Ca, Mn, Mg, Pb and Zn, which were considered to stimulate growth. CKD increased forage yield in grasses (P. pratense L., E. repens L., F. pratensis Huds.) by 3% compared to control and 11% compared to lime applied at an equivalent rate in the first year after application and by 38% and 25% in the second year respectively (Rodd et al., 2010). Lime produced lower yield compared to the control and CKD treatments, possibly due to decreases in soil extractable K and Mg (Rodd et al., 2010). The yield responses to CKD were ascribed to increased soil pH and increased tissue concentrations of K and Ca. CKD application decreased forage N, P, Mg and Zn concentrations independent of any dilution effect from increased yield. The depressions in P and Mg concentrations were thought to be due to interactions with the Ca and K present in the material (Rodd *et al*., 2010).

Although CKD has a lower neutralising value compared to lime, it reacts quicker and can have a greater influence on soil pH. Rodd *et al*. (2004) found that CKD application changed soil pH at 12-15cm soil depth by 0.41 units compared to lime which increased pH by 0.12. These differences were attributed to the fineness of the CKD and its greater CaO content, which is more reactive than calcium carbonate. However, other research has found that crushed limestone reacted similar to CKD (Carol, Erickson and Whittaker, 1964). When CKD was applied at the same rate as agricultural lime, both materials increased soil pH to a similar degree (0.8) (Dann, Dear and Cunningham (1989). However, superfine lime was more effective, increasing soil pH by 1.3, though herbage yield of forage crops increased similarly between the three treatments. Lalande, Gagnon and Royer (2009) found that CKD increased soil pH to a similar degree to lime at the 0-20 cm depth when applied at the same rate across two contrasting soils (sandy loam and silty clay). These findings indicate that CBD and CKD may be effective substitutes for lime, however the variability in alkalising effect evidenced by this literature means that extrapolating the alkalising effects of the products to those produced in Great Britain is difficult. It is likely that the CBD and CKD produced in Great Britain vary in chemical composition than those studied previously (van Lierop, Tran and Morissette, 1982) and therefore more experimentation is needed to determine their alkalising effects on British soils.

CKD application may also increase the availability of certain soil nutrients. Soil extractable K was significantly increased compared to lime, but lime increases extractable P more than CKD (Lalande, Gagnon and Royer, 2009). It was as effective as coarse lime at increasing soil extractable K and Mg when applied at the same rate (Lafond and Simard 1999), correlating with increased potato yield. Similarily, plant K and Mg uptake increased with the CKD application, suggesting that CKD may be an effective source of K and Ca for potato production.

Generally, CKD has positive effects on plant growth, by reducing soil acidity and supplying some of the elements needed for plant growth. Therefore, its wider adoption could reduce fertiliser use. Although this is encouraging, no work has been published to assess its performance on UK soils. The UK has 10 cement kilns currently in operation (MPA Cement, 2023a), suggesting a plentiful supply if CKD is beneficial to UK agriculture. Therefore, more work is needed to assess the agricultural suitability of CKD to make use of this resource.

Advantages of Using Alternative Alkalising Agents

There may also be non-agronomic benefits of using waste products as a replacement for agricultural lime. Firstly, using alkalising waste products would reduce the amount of lime being used and therefore limestone being mined, lessening environmental impact and land degradation. The nutrients provided by some of these products could also reduce the number of fertilisers required for adequate plant nutrition, therefore reducing environmental impact and saving money (Mittra *et al*., 2005; Singh and Agrawal, 2008). Additionally, the cost and availability of materials prevents some farmers, especially those in developing countries, from liming their fields (Dann, Dear and Cunningham, 1989; Yuan and Xu, 2010; Arshad *et al*., 2012). Using an alkalising by-product such as CKD/CBD may provide a cost effective, more easily available alternative. However, this may only be applicable to farms situated within regions where cement plants operate, and transport costs may still be prohibitive to resource-poor farmers. In this case, other locally available alternatives such as biochar and wood ash may be more suitable.

Reusing industrial by-products such as CKD or wood ash as soil amendments would decrease the volume of these wastes being sent to landfill, therefore reducing the environmental impact of disposing of these products and avoiding the often-considerable fees associated with their disposal (Etiengi, Campbell and Mahler, 1991; Arshad *et al*., 2012). For example, although many modern cement plants can re-use CKD and CBD as raw feed, approximately 3.35 million tonnes are landfilled in North America each year, incurring financial losses for the industry (Bhatty, 1995; Rodd *et al*., 2010). However, the cement industry has recently focused on sustainability and in the United Kingdom it has ensured that 0% of production waste is sent to landfill through recycling the material back into the kiln and alternative methods such as spreading to land (Table 1.2) (MPA Cement, 2023b). In 2021, 31,095 tonnes of process waste were recovered off-site, indicating that there is a market for novel methods of disposing of these wastes, which would benefit both the producers of the waste and for growers who may require a cheaper alternative to lime.

Table 1.2: Cement production and waste (including CBD/CKD) management in the United Kingdom 2010 – 2021. Adapted from Mineral Products Association, (MPA Cement 2017, 2023b, 2023c).

Year	Cement Production	Total waste and by- products used as fuel and raw materials	Process waste recovered on-site	Process waste recovered off-site	Process waste sent to landfill
			(tonnes)		
2010	7,883,000	1,528,315	11,379	36,945	14,021
2011	8,529,000	2,481,106	9,195	47,796	4,631
2012	7,952,000	1,811,200	2,819	57,471	0
2013	8,203,000	1,452,553	10,390	47,238	0
2014	8,598,000	1,612,581	1,513	33,988	0
2015	9,235,000	1,619,766	11,009	35,103	0
2016	8,056,000	1,454,354	4,086	49,238	0
2017	7,824,000	1,549,393	2,270	43,273	0
2018	7,734,000	1,414,195	1,401	41,186	0
2019	7,830,000	1,329,517	1,126	43,624	0
2020	6,941,000	1,224,967	864	37,192	0
2021	9,008,000	1,292,639	1,152	31,095	0

Disadvantages of Using Alternative Alkalising Agents

One of the main disadvantages of using waste products is the inconsistency of the material produced. With CKD for example, the composition of the dust produced depends on the type of raw material used (e.g., limestone or chalk), processing and kiln operations at each cement plant (Bhatty, 1995; Adaska and Taubert, 2008). Thus, dust produced from each plant can vary markedly in its neutralising capacity, K and Ca content, particle size distribution, chemical, mineralogical, and physical composition (van Lierop, Tran and Morissette, 1982). Therefore, the findings of previous experiments may not be reproducible and the effects of individual batches of CKD on plant growth cannot be predicted with any certainty. This lack of quality assurance may limit more widespread adoption of the product as each batch of CKD would need characterising before use.

Concerns have been raised about the safety of applying CKD/CBD to agricultural land due to the concentrations of PTEs (such as arsenic (As), cadmium (Cd), lead (Pb), mecury (Hg) and nickel (Ni)) found in the material, which could cause harm if they enter the food chain (EPA, 1993). However, Bhatty (1995) argues that at the application rates used to ameliorate soil acidity, concentrations of these metals are well below the permissible land application levels in North America. Two applications of 2 t ha $^{-1}$ of CKD increased levels of extractable Chromium (Cr) soil content by 17%, though this did not affect heavy metal tuber uptake in two different soils and values were comparable to those from commercially available fertilizer and lime (Lafond & Simard 1999). This implies that although CKD application increased soil content of PTEs, they may not be bioavailable. In the UK, application of soil amendments (including CKD) containing PTEs is regulated by the Sludge (Use in Agriculture) Regulations 1989, which sets limits for yearly application rates and soil concentrations of these elements giving clear guidelines on permissible maximum application rates for CBD and CKD. Considering this evidence, the issues with CBD/CKD use as an agricultural amendment are not insurmountable and CBD/CKD has the potential to be alternative to agricultural lime. However, as few experiments have studied the agricultural benefits of using CKD/CBD, further work is needed to assess its viability as a soil amendment compared to conventional methods such as fertilisers and lime application.

1.4 Concluding Remarks

Managing soil acidity has a vital role in enhancing crop nutrition, which is becoming increasingly relevant due to the need to increase crop production to keep up with demand. Concerns surrounding the application of synthetic fertilisers means that their extensive use may no longer be an appropriate solution, and finding alternative methods of optimising nutrient availability is critical to addressing the sustainability challenges facing future crop production. Maintaining a pH that optimises nutrient availability may allow reduced fertiliser inputs, lessening their impact on the environment (e.g., nutrient run-off and pollution).

However, evidence suggests that crop and soil responses to agricultural lime application are not uniform and that in some situations, recommended liming rates may decrease yields (Sumner and Yamada, 2002; Rothwell, Elphinstone and Dodd, 2015) as a result of inefficient nutrient use and reduced nutrient availability (Haynes, 1984; Hinsinger, 2001; Sumner and Yamada, 2002; Bolan et al., 2003). Furthermore, gaps in the experimental data indicate that the mechanisms behind these responses are not fully understood. It is not clear if yield is limited solely by lack of soil extractable nutrients, or whether other factors influence growth.

Increased evaluation of alternative alkalising materials as a lime replacement implies that optimal rates need to be determined based on their individual composition. However, relatively little research has assessed the agronomic performance of CKD/CBD compared to conventional lime and fertiliser practice and determining their efficacy will require further examination of soil and plant responses to their application.

In Great Britain 65% of agricultural land is devoted to permanent grassland and beef lamb and dairy products currently contribute £6.9 billion to the British economy (Higgins *et al*., 2019; DEFRA, 2022). Livestock farming also provides numerous ecosystem services including but not limited to stabilising soils, cycling nutrients, carbon storage, habitat provision and rural income (Norton *et al*., 2022). However, the sector is coming under increasing scrutiny and sustainable livestock farming needs to develop more efficient nutrient management practices (Higgins *et al*., 2019; van der Linden *et al*., 2020). As CBD and CKD are currently being used as part of a sustainable nutrient management strategy in Great Britain, the aim of this thesis is to optimise the use of soil alkalising agents by determining the effect of differing rates CKD, CBD and agricultural lime on plant responses and soil properties on two crops typically used for grazing in Great Britain (white clover (*Trifolium repens* L.) and perennial ryegrass (*Lolium perenne* L.)).

White clover is one of the most important legumes in British farming and is often grown with perennial ryegrass in long term pastures to increase N availability, yield of companion grasses and to increase the nutritional value of livestock forage (Harris and Ratnieks, 2021). Chapter 2 analyses the efficacy of current CBD/CKD application practice by assessing whether treating CBD/CKD as a liming agent or K fertiliser is the more efficient practice and tests the hypothesis that applying CBD at rates designed to correct soil K deficiency rather than rates to correct soil pH is a more agronomically and economically efficient use of the product. Chapter 3 performs an agronomic comparison of one source of CBD and one source of CKD, agricultural lime and K fertiliser on a ryegrass-based pasture over the course of two growing seasons. The chapter tests two hypotheses: that CBD, CKD application will be comparable to lime + K fertiliser in terms of improving plant growth, increasing soil pH, soil nutrient availability (K and P) and nutrient uptake (Ca, Mg, K and P) compared to a control; and CBD and CKD will increase plant tissue concentration of PTEs compared to lime and K fertiliser. This is to provide insight in to whether CBD and CKD application at liming rates is efficient in the use of K and whether they are as effective as traditional sources of lime and K.

Although nutrient availability and yield responses to liming can be positive, this can vary with plant species and increasing soil pH above 6 can decrease P availability, uptake, and growth, especially in legumes (Figure 1.5) (Haynes, 1982; Sumner and Yamada, 2002; Rothwell, Elphinstone and Dodd, 2015). Therefore, CBD/CKD application could decrease P availability, uptake and growth in mixed ryegrass and legume pastures. To address this Chapter 4 compares the responses of perennial ryegrass and white clover grown across two cropping methods to lime and P fertiliser application over two growing seasons in a mesocosm pot experiment. The mesocosm pots allowed for greater control over the plant's environment and ease of access for harvest and soil analysis. Four hypotheses are tested: lime application will increase soil P availability and P uptake in both crops; intercropping ryegrass with clover will increase biomass production and P uptake in ryegrass; and P application + intercropping will improve P uptake in ryegrass more than if no P was added.

Finally, Chapter 5 examines the importance of root interaction between the two species to the facilitative and competitive effects seen in the intercropping mesocosm by testing three hypotheses. The first hypothesis is that root activity by neighbouring clover causes localised changes in soil P availability that promote P uptake and growth of ryegrass. Second is the hypothesis that the roots of both species need to be in close proximity to each other in order to influence growth. Lastly the hypothesis that AMF associations facilitate growth and P uptake in the monocrop and intercropped ryegrass-clover systems is tested also. A split pot design using root barriers of varying porosity was used. This allowed the assessment of the impact of proximity of the two root systems on biomass production, soil P availability and P uptake through the elimination of four levels of resource exchange: physical interaction, exchange through mycorrhizal hyphae, nutrient mobilisation in the soil solution and a combination of the other three.

CHAPTER 2: THE AGRONOMIC EFFICIENCY OF CURRENT CBD AND CKD APPLICATION PRACTICE

2.1 Introduction

World demand for potassium (K) fertiliser (also referred to as K_2O or muriate of potash) for the year 2021 is estimated at 39.5 million tonnes (of K_2O) (FAO, 2019) and its use is projected to increase to 40.2 million tonnes by 2022 (Rawashdeh *et al.*, 2016). K fertiliser use isn't linked to the detrimental environmental effects associated with N and P use, but its supply relies on a finite resource of mined minerals such as sylvite, carnalite and langbeinite (Rawashdeh *et al.*, 2016; Santos *et al.*, 2017). The world supply of K fertiliser currently meets demand at 52.8 million tonnes per year. However, the increasing intensification of agriculture and the development of high-yielding crop varieties means that removal of K from soils in crop off-take may exceed input in some regions in the future (Kumar *et al.*, 2016; Rawashdeh *et al.*, 2016). Countries without their own K fertiliser reserves either import it or continue to strip K from their soil (van der Wiel *et al.*, 2020). Furthermore, increasing urbanisation is separating the centres of nutrient production (farms and rural communities) and areas of nutrient consumption (towns and cities), resulting in lost opportunities for recycling nutrients back into food systems through strategies such as manure use (Jones *et al.*, 2013). This had led to discrepancies in soil reserves between regions with surplus soil K (e.g.West Europe, Japan) and depletion of soil reserves in regions (eg. Africa) where imports are prohibitive (Sheldrick *et al.*, 2002).

Use of K fertilisers in regions such as Great Britain with ample K reserves (Jones *et al*., 2013) presents its own set of issues. Between 50% and 60% of nutrient inputs remain in agricultural soils after harvest (Highley *et al*., 2011; Smith *et a*l., 2016) and intensively managed dairy farms can produce high K surpluses through inputs such as K fertiliser and manure (Kayser and Isselstein, 2005), which may not be balanced by crop off-take. For example, Bengtsson *et al*. (2003) found that in a conventional dairy farm system, the K inputs from manure, urine and mineral fertiliser were not balanced by crop off-take, root-zone leaching and surface run-off, resulting in a K surplus of 39 kg ha^{-1}. Conversely, in an organic system, which did not rely on mineral fertiliser inputs had a K balance of −17 kg ha^{-1}. Excess application of K is not likely to remain in the soil for crop utilisation as it is highly mobile and prone to leaching, especially in sandy, acidic soils and when applied in large amounts (Kayser *et al.*, 2007; Römheld and Kirkby, 2010). Therefore, a system which has a surplus of K is more likely to leach it and any additional K added is wasted. As stated previously, the use of K fertiliser doesn't appear to have any direct environmental consequences, however the use of such fertilisers in areas where surpluses are likely to arise wastes a finite resource which could be deployed to areas where it is needed more. Additionally, excessive use of K fertiliser on land used for grazing is associated negative impact on the nutrient content of forage crops as well as contributing to various metabolic disorders such as hypomagnesaemia and hypocalcaemia which can affect up to 39% of livestock animals (Kayser and Isselstein, 2005; AHDB, 2023c; Finnan and Burke, 2013; Kumssa *et al*., 2019).

These nutrient imbalances could partly be addressed through adopting the principle of the circular economy. The circular economy has been defined as a gradual decoupling of economic activity from the consumption of finite resources and designing waste out of the system (Ellen Macarthur Foundation, 2018). This is seen as a departure from traditional linear "take, make and dispose" production models and aims to close the loop of material flow (such as nutrients/fertilisers) through a whole economic system and conserve natural resources (Ghisellini *et al.*, 2016; Geissdoerfer *et al.*, 2017; Troop *et al.*, 2017; Skene *et al.*, 2018). The four main principles of the circular economy are:

1. Design products with their entire life cycles in mind,
2. Maximise product life cycles,
3. Recycle materials from end-of-life products and,
4. Accomplish this across diverse industries and value chains (Baily *et al.*, 2013).

Ideas such as this have gained traction in recent years and organisations such as The European Commission have developed initiatives such as The Circular Economy Action Plan, which is part of the European Green Deal (European Commission, 2020). By developing ways to re-cycle nutrients back into food systems, the gap between areas of surplus and deficient K could be narrowed, therefore avoiding the waste of such an important resource. As seen in the previous chapter, wastes from various industries could be used for such a purpose.

The European cement industry largely supports the circular economy and as mentioned in the previous chapter, substitutes non-renewable materials (such as limestone) with waste material that is fed back into the cement kilns (The European Cement Association, 2016). Waste that can no longer be recycled into the kiln processes is either re-purposed as an agricultural amendment, stockpiled, or landfilled (Sreekrishnavilasam *et al.*, 2017). Currently Great Britain is a net exporter of K fertiliser, and Boulby Mine is the sole producer (Highley *et al.*, 2011). Considering that CBD has a high K content (see preceding chapter) and there are currently 10 kiln sites operating in Great Britain (MPA Cement, 2023a), they present an opportunity to recycle potassium back into the soil and therefore food system and replace K fertilisers. This approach would contribute to three of the four circular economy principles by:

- Allowing nutrients to be recycled through input into soil and off-take through crops and animal produce (principles 2 and 3).
- By-passing the need to landfill the CBD that is not recycled by the kiln through end-of-life use as an agricultural amendment (principle 3).
- Acting as a link between the cement industry (through waste management) and agriculture (through nutrient recycling) (principle 4).

However, this approach only addresses the re-direction of the K in waste products to a more productive end point. It does not address the surpluses which arise from over-application of K fertiliser. There is also potential for CBD to be used in ways where it may be contributing to K surpluses, which will be discussed below.

CBD is currently being deployed as a soil alkalising agent in Great Britain, however its use as a K fertiliser has not been addressed even though it may contain appreciable quantities of K (J Silverwood 2020, personal communication, 4 May). The literature reviewed previously indicates that when applied at the equivalent rate to K fertiliser, CBD can improve crop yields, increase soil available K and crop uptake of K and is therefore a suitable alternative to K fertiliser (Van Lierop, Tran and Morissette, 1982; Saralabai and Vivekanandan, 1992; Lalande, Gagnon and Royer, 2009). The reason that CBD is not applied at rates that could replace conventional K fertiliser is that its application is regulated by The Sludge (Use in Agriculture) Regulations 1989, Statutory Instrument No. 1263 (Anon, 1989) and the resulting permit fees mean that application of rates <5 t ha^{-1} are not cost effective and thus avoided (J Silverwood 2021, personal communication [email], 09 July). As the amount of CBD needed to meet crop K demand is less than that needed to correct soil pH, CBD is not currently used solely as a K fertiliser.

CBD therefore has potential as a K fertiliser independent of its value as an alkalising agent, yet the way its application is regulated prevents its use as such. This begs the question as to whether the current use for CBD makes agronomic sense, especially within the context of nutrient recycling and the circular economy principles outlined above. Re-cycling K into the food system by using CBD only makes sense if it is deployed in areas where there is a crop demand for K and does nothing to address the K surpluses which may arise from modern farming practices, especially in Great Britain (Jones *et al.*, 2013). As the K content of CBD is comparable to that of K fertiliser (see Chapter 1), the current practice of applying it at ~5 t ha^{-1} is likely to be adding K well above actual crop requirements. Whether this is true in practice has yet to be addressed. This leads to the question of what the best agronomic use of CBD is; as an alkalising agent, a K fertiliser or both? Therefore, this chapter aims to investigate whether there is a 'demand' for CBD as a K fertiliser and the central hypothesis is that it could replace a portion of the K fertiliser that is currently being used in England and Wales. Additionally, it will examine whether current application practices are agronomically optimal, with the hypothesis being that applying CBD at K fertiliser rates in areas where K is needed is the better use for the product. This will be achieved through:

- Gathering data from nation-wide soil K and pH testing.
- Obtaining CBD production and chemical analysis data from different cement kilns operating in England and Wales, and.
- Determining whether CBD production can meet a percentage the K fertiliser demand (based on actual fertiliser use by farmers) for each region.

This would identify where the CBD would be more efficient as a fertiliser or alkalising agent and identify areas where their use as an alkalising agent would result in excessive application of K.

2.2 Materials and Methods

2.2.1 Data Sources

National soil pH and available K analysis data was obtained from the Professional Agricultural Analysis Group (PAAG, 2019). The data comprises of soil analysis results reproduced as pH x K index matrices for percentage of samples collected. The samples were taken on UK agricultural soils submitted to PAAG laboratories during the period 1st June 2018 to 31st May 2019. The arable dataset consists of arable crops following a ley. Where no other cropping details were available, maze data was also included in the arable dataset. Data for current arable crops and forage maize following permanent grassland or grazed grass (i.e. pasture) was included alongside permanent grassland in the grassland dataset.

Figure 2.1 is adapted from the 'map of NUTS 1 regions of United Kingdom of Great Britain and Northern Ireland' (Nilfanion, 2012) and locations for cement plants taken from the 'cement manufacturers map 2019 '(MPA Cement, 2023b). CBD production data was taken from the four cement plants producing the CBD used by Silverwoods Waste Management Ltd. These are: Rugby (operated by CEMEX) and Ketton, Padeswood and Ribblesdale (operated by Hanson). Data for the other cement plants operating in the UK was not available at the time of writing and therefore this study is restricted to the four plants used by Silverwoods Waste Management Ltd. CBD production data and cement plant locations were supplied by Silverwoods Waste Management Ltd (J Silverwood 2020, personal communication [email], 12 June). Chemical analysis data of the CBD was provided by Silverwoods Waste Management Ltd, and the analysis of the CBD was done by NRM Laboratories, Berkshire. The neutralising value (%) and K concentration (mg kg^{-1}) were used for this study.

Recommended application rates for the CBD were determined using the older version of the The Rothamsted Lime Requirement Model (Rothlime) (McGrath and Goulding, 2002) as opposed to the current model (Sciphus Computing Ltd et al., 2021). The older model allows a ‘custom’ liming material to be entered and its neutralising value specified. This feature is missing from the newer model, which uses a fixed set of liming products as inputs. Because the neutralising value of CBD varies from more ‘standard’ products, the newer model cannot be used.

Land area data for England and Wales (excluding silage in Wales, which is missing from this dataset) was obtained from the ‘Structure of the agricultural industry in England and the UK at June (by regional and county/unitary authority (2018 to 2019))’ dataset (DEFRA, 2021a). Silage data for Wales was taken from the ‘Structure of the agricultural industry in England and the UK at June (annual time series (1984 to 2020))’ dataset (DEFRA, 2021a). The study was restricted to England and Wales because these regions are where CBD is mostly used (J Silverwood 2021, personal communication [email], 08 July). All English regions and Wales were used for the national summary (Table 2.7), and the following regions were used for the regional summaries: North West England, East England, East Midlands and Wales (Tables – 2.9-2.11). Only four regions were used for the regional summary because haulage of CBD is typically kept to a minimum, and the dust is spread in or near the region where it is produced (J Silverwood 2021, personal communication [email], 08 July). East England and East Midlands were combined due to East England having two cement plants and the East Midlands being the nearest region with the highest arable output (DEFRA, 2018a).

The land area dedicated to grass production was calculated from the ‘grazing livestock (LFA)’ and ‘Grazing livestock (lowland)’ columns in Table 2 (farm type – area (hectares)) (DEFRA, 2021a). The dairy column was used as a proxy for Silage production. The winter wheat and winter barley columns were used to calculate arable land area because these are the predominant arable crops grown in UK (DEFRA, 2018a).

The overall K used by farmers in England and Wales (summarised in Table 2.4) has been adapted from the British survey of fertiliser practice 2019 annual report Table b1.2a (‘Overall phosphate and potash use (kg/ha)'). The potash figures were converted to elemental K as outlined in in the 'calculations' section.

2.2.2 Calculations

The K supplied at different application rates (Table 2.6) was calculated using the chemical analysis data provided by Silverwoods Waste Management Ltd. and NRM laboratories. The K concentration of the CBD from each cement plants is measured as mg kg $^{-1}$ of elemental K. The value for the maximum recommended K fertiliser application rate was taken from the Nutrient Management Guide (RB209, AHDB, 2023b), Table 4.13('Phosphate and potash recommendations for all cereals – straw removed'). Oats required the highest single dose of K fertiliser at equivalent to 133kg ha^{-1} of elemental K and were therefore used to demonstrate the potassium requirements of a high K demand crop.

The total K applied (in tonnes) by agriculture in England and Wales (Tables 2.7- 2.11) was calculated by multiplying the land area for each cropping type by the relevant overall application rate (kg K ha^{-1}) and multiplied by 1000. The overall application rates were taken from the British survey of fertiliser practice 2019 annual report (DEFRA, 2020) tables EW1.1 and EW2.2.

The economic value of the K applied to the agricultural land in England and Wales as well as the economic value of the K present in CBD was calculated using the GB Fertiliser Price Series dataset (AHDB, 2023a). The average price of muriate of potash (MOP) from June 2022 to June 2023 was used. The price per tonne of MOP was converted to elemental K to compare it to CBD. One tonne of MOP contains 600kg of K_2O (IPNI Canada, 2019) or 468 kg of K, with an average value of £265.70. Therefore, the value of the K in MOP is £0.53 per kg and £530 per tonne. This £530 value per tonne of K was multiplied by the K production (t) from the cement plants and the total K applied by farmers to obtain the economic value of the CBD produced and economic value of the K used (Tables 2.7-2.11).

The fertiliser use data taken from the British survey of fertiliser practice 2019 and the fertiliser prices obtained from the GB Fertiliser Price Series were originally presented for muriate of potash (K_2O). To maintain consistency all K_2O data was converted to elemental K (by multiplying amount of K_2O by 0.83) before any calculations were made. Furthermore, the use of K_2O in the scientific literature is considered obsolete and the conversion was made to maintain accuracy (Lambers and Barrow, 2020).

To calculate the relationship of CBD/CKD application rate and soil pH, the Rothlime model (McGrath and Goulding, 2002) was used to construct dose-response curves for each dust. The relationship between application rate and soil pH was linear and therefore a linear equation was used to calculate the pH unit change per 1-3 t ha^{-1}. This equation is as follows:

$$pHIncrease = \left(Slope\ at\ StartingpH * Application\ Rate(kgha^{-1})\right) + Intercept\ at\ Starting\ pH$$

Table 2.1 summarises the resulting pH change per 1-3 t ha^{-1} at a range of starting pHs. This data was then used to ascertain whether application rates required to correct soil K rather than pH (< 3 t ha^{-1}, see Table 2.3) are likely to alter pH by more than 0.3 units.

Table 2.1: The pH unit change for different application rates of the CBD produced by four different cement plants operating in England and Wales on a clay soil. The rate of pH change differs depending on each CBD and starting pH, therefore the data presented is for the mean and standard deviation of four different starting pHs. Soil texture and cropping influence the leaching of Ca and therefore the ability of the liming material to influence soil pH (Goulding, McGrath and Johnston, 1989).

Application Rate	pH Unit Change							
	Padeswood		**Ribblesdale**		**Ketton**		**Rugby**	
	Arable	*Grass*	*Arable*	*Grass*	*Arable*	*Grass*	*Arable*	*Grass*
1 t ha^{-1}	$0.02^{\pm0.02}$	$0.03^{\pm0.01}$	$0.02^{\pm0.02}$	$0.02^{\pm0.02}$	$0.02^{\pm0.02}$	$0.03^{\pm0.02}$	$0.03^{\pm0.02}$	$0.06^{\pm0.01}$
2 t ha^{-1}	$0.07^{\pm0.01}$	$0.11^{\pm0.01}$	$0.07^{\pm0.03}$	$0.08^{\pm0.01}$	$0.07^{\pm0.01}$	$0.10^{\pm0.01}$	$0.10^{\pm0.01}$	$0.14^{\pm0.01}$
3 t ha^{-1}	$0.13^{\pm0.01}$	$0.18^{\pm0.02}$	$0.11^{\pm0.03}$	$0.13^{\pm0.02}$	$0.12^{\pm0.01}$	$0.17^{\pm0.01}$	$0.16^{\pm0.01}$	$0.23^{\pm0.02}$

2.2.3 Dose-response Pot Experiment

To observe how CBD changes soil pH compared to agricultural lime across a range of application rates, a dose-response experiment was conducted.

2.2.4 Soil Collection and Preparation

Soil was collected from a livestock farm in North Yorkshire (Pikeber Farm, Skipton, latitude: 54.002133, longitude: -2.306200). Soils from this area are described as being fairly fertile, free-draining and loamy (Cranfield Soil and Agrifood Institute, 2019), and when tested (in 1:25 water) the pH was ~5.6, making it suitable for the addition of a liming material. Further information on this soil is provided in Appendix A, Table 1, and Figure 2.

Soil was passed through a 5mm sieve to remove rocks and plant matter and then sterilised using a 68-litre soil steriliser (Thermoforce Ltd, Cumbria, Unkited Kingdom) for 90 minutes and stored in black polythene bags until needed. Lime- free grit sand (Moist Horticultural Sand - BLP205, Boughton Topsoil, Kettering, United Kingdom) was added to the soil at a 1:3 ratio. When the soil's moisture content was at field capacity, it was homogenised along with the sand and alkalising treatments in a cement mixer for four minutes in 10 L batches, then stored in sealed in black plastic bags and left for eight weeks at ambient temperature (~18.5°C) to allow the lime reaction to take place.

2.2.5 Treatments and Experiment Design

The treatments used for the experiment consisted of an un-amended control, and three different rates of agricultural lime and CBD. The CBD was collected by Silverwoods Waste Management Ltd (Clitheroe, United Kingdom) from the CEMEX Rugby facility in 2018. The lime and CBD treatments were applied at 1, 2.5 and 4 g l^{-1} (equivalent to 2, 5 and 8 t ha^{-1}). The CEMEX Rugby CBD had a neutralising value of 35.9% whereas the agricultural lime used had a neutralising value of 56.7%. The soil was placed in 1L pots and there were eight replicates per treatment, including the un-limed controls. *Pisum sativum* 'Alderman' (Mole's Seeds, United Kingom) were pre germinated in dishes containing paper towels wetted with de-ionised water. After five days the largest and smallest seeds were discarded, and the remaining ones planted one per pot. Watering took place every other day and the amount of water used was determined gravimetrically to replace evapo-transpiration. After five weeks the plants were harvested, and the soil from each pot was taken for pH analysis.

2.2.6 Soil PH Analysis

The soil was prepared for analysis by air-drying for seven days before being passed through a 2mm sieve and stored in sealable plastic bags. To measure pH, 10g of soil was mixed with 25ml of de-ionised water in a 50ml centrifuge tube, stirred and left to stand for an hour. The sample was then tested using a Orion™ Model 91-72 Sure-Flow pH Electrode (Thermo Fisher Scientific Inc., Waltham, USA) and pH meter (Denver Instruments, Bohemia, New York, USA). Soil samples were tested in triplicate, with the average being used for statistical analysis.

2.2.7 Statistical Analysis

Statistical analysis was performed using the R software package (R Core Team, 2021). A two-way ANOVA (Analysis of Variance) used to determine differences between treatments and rates of treatment application.

2.3 Results

2.3.1 CBD Production and Properties

Of the four cement plants used for this study, three are operated by Hanson Cement (Ketton, Padeswood and Ribblesdale) and one by CEMEX (Rugby). Ribblesdale operates in the North West of England, Rugby and Ketton operate in the East Midlands and Padeswood operates in Wales. Rugby is the biggest producer of CBD, with approximately 17,000 tonnes being produced a year by the plant. The CBD produced by the Rugby plant has the lowest K content at ~6%, which equates to an annual K production of 1,020 tonnes. However, the CBD produced by the Rugby plant has the highest neutralising value, at ~41.5%. Both the Ketton and Ribblesdale plants produce ~5000 tonnes of CBD a year. Ketton CBD has a K content of ~12.8% and produces ~640 tonnes of K annually. Ribblesdale CBD on the other hand, has a K content of ~16.8% and produces 840 tonnes of K annually. Both have a lower neutralising value than Rugby at ~33.7% and ~27.6% respectively. This means they will not be as effective as Rugby CBD at increasing soil pH; however their higher K content means they would be more effective as a K fertiliser. The Padeswood plant has the second lowest K content at ~8.3% but has the second highest neutralising value at ~36.9%. This indicates it may be better suited to use as a soil alkalising agent. It is also the lowest producer of CBD, with 3,500 tonnes produced annually, which equates to ~290.5 tonnes of K. The total CBD production of the four plants is 30,500 tonnes annually, which equates to ~2790.5 tonnes of K. These findings are summarised in Table 2.2.

The CBD produced varies within batches from the same plant, however multiple material analyses were not available for the Ketton and Padeswood plants and therefore the variability of the dusts could not be calculated. The variation in K content of the Ribblesdale and Rugby dusts is between 0.5 and 1.3% (Table 2.2). The neutralising value of Ribblesdale and Rugby CBD varies by 1.6 and 2.6%. Due to this variability, application rates to correct soil acidity (Table 2.5) and meet crop demand must be adjusted accordingly.

Table 2.2: The cement manufacturing plants used in this study, their CBD and K production, potassium content and neutralising value. The information was provided by Silverwoods Waste Management Ltd. As not enough data was provided to calculate standard errors for the Ketton and Padeswood CBD K content and neutralising value, they have been presented as 'NA'.

Company	Plant	Region	K Content (%)	Neutralising Value (%)	CBD Production ($t\ year^{-1}$)	K Production ($t\ year^{-1}$)
CEMEX	Rugby	UKF, East Midlands	6.02 ± 1.3	41.5 ± 2.6	17,000	1,020
Hanson Cement	Ketton	UKF, East Midlands	12.8 ± NA	33.7± NA	5,000	640
	Padeswood	UKL, Wales	8.3 ± NA	36.9 ± NA	3,500	290.5
	Ribblesdale	UKD, North West	16.8 ± 0.5	27.6 ± 1.6	5,000	840
				Total	30,500.0	2,790.5

Due to the PTE content of CBD (cadmium in particular), its application on agricultural land is regulated by The Sludge (Use in Agriculture) Regulations 1989 (Anon, 1989), the limits of which are described in Table 2.3 and 2.4. PTE analysis was provided for two of the four dusts studied; therefore, commentary is restricted to the Rugby and Ribblesdale dusts. As CBD is typically applied at 5-6 t ha^{-1}, its application is restricted to every 3 years to insure that the PTEs listed do not build up in the soil.

Table 2.3: PTE content of CBD produced by two of the cement plants studied (data was not available for the other two) compared to the limits imposed by The Sludge (Use in Agriculture) Regulations (Anon, 1989). The limits consist of: 1) the limit of detection in the dry matter of the substance (in this case CBD) being applied; and 2) the limit found in dried soil samples (25 soil cores amalgamated). Soil testing should occur when the sludge is first applied and every five years thereafter. The reported PTE concentrations in the two dusts studied is taken from an average of two different analyses performed in July and September 2019.

	PTE Content (mg kg^{-1}) of By-pass Dust Produced By:		Limits Imposed by The Sludge (Use in Agriculture) Regulations 1989				
Element	Rugby	Ribblesdale	[1] Limit of Detection (mg kg^{-1} of dry matter)	[2] Limit According to soil pH (mg kg^{-1} of dry matter)			
				5.0<5.5	*5.5<6.0*	*6.0-7.0*	*>7.0*
Cadmium (Cd)	36.3	55.5	1	3 for pH 5 and above			
Chromium (Cr)	32.65	29.8	25	25 across all pH			
Copper (Cu)	123.25	479	25	80	100	135	200
Lead (Pb)	449	1750	25	300 for pH 5 and above			
Mercury (Hg)	0.1	0.24	0.1	1 for pH 5 and above			
Nickel (Ni)	12.6	22.9	10	50	60	75	100
Zinc	291	309	50	200	250	300	450

Cadmium is of most concern, because at 6 t ha^{-1} it would exceed the limits outlined in Table 2.6 if applied annually. At an application rate of 2-4 t ha^{-1}, an annual application of CBD would not exceed the maximum application rate (Table 2.4). For all other elements an application rate of 2-6 t ha^{-1} would not reach the maximum rate whether applied annually or every 3 years.

Table 2.4: Amount of each PTE (kg ha $^{-1}$) applied at a range of CBD application rates. The text is highlighted red where PTE application would exceed the annual maximum rate for application to land if applied every year (see Table 2.5).

Element	Kg ha^{-1} of Each Element Supplied by Rugby CBD at:			Kg ha^{-1} of Each Element Supplied by Ribblesdale CBD at:			Maximum Application Rate (kg ha year^{-1})
	2 t ha^{-1}	*4 t ha^{-1}*	*6 t ha^{-1}*	*2 t ha^{-1}*	*4 t ha^{-1}*	*6 t ha^{-1}*	
Cadmium (Cd)	0.1	0.1	**0.2**	0.1	**0.2**	**0.3**	0.15
Chromium (Cr)	0.1	0.1	0.2	0.1	0.1	0.2	NA
Copper (Cu)	0.2	0.5	0.7	1.0	1.9	2.9	7.5
Lead (Pb)	0.9	1.8	2.7	3.5	7.0	10.5	15
Mercury (Hg)	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Nickel (Ni)	0.0	0.1	0.1	0.0	0.1	0.1	3
Zinc	0.6	1.2	1.7	0.6	1.2	1.9	15

2.3.2 Alternative Uses for CBD

CBD is currently used at rates designed to correct soil acidity and therefore the Rothlime model (McGrath and Goulding, 2002) was used to calculate recommended rates of CBD across a range of soil pHs, which are displayed in Table 2.5. The differing neutralising values for each of the dusts means that application rates can vary, with a 10 t ha^{-1} difference in application rates between the dusts with highest (Rugby) and lowest (Ribblesdale) neutralising value needed to reach a target pH 6.3 in a pH 5 soil. In practice the typical application rate is much lower than this at 5-6 t ha^{-1}(J Silverwood 2021, personal communication [email], 09 July). This is partly to avoid build-up of PTEs as mentioned previously, and to avoid the excess application of K. However, application rates lower than 5 t ha^{-1} are also avoided due to the permit application process required by The Sludge (Use in Agriculture) Regulations 1989 and resulting fees which render it cost ineffective (J Silverwood 2021, personal communication [email], 09 July). This means that CBD is not currently used at rates lower than 5 t ha^{-1} as a K fertiliser, a practice that may lead to inefficient application of K. Application rates of 1 t ha^{-1} and above of the Ribblesdale dust can result in K application which is above the maximum recommended amount of K in a single application for a cereal crop and grassland (Table 2.6). This varies between dusts with Ribblesdale having the highest potassium content and an application of 1t ha^{-1} (166 kg K ha^{-1}) exceeds the recommended maximum dose in one application (132.8 kg K ha^{-1} for oats, 99.6 kg for silage and 66.4 kg for grazing) (AHDB, 2023b). Rugby has the lowest K content, with an application of 4 t ha^{-1} (240 kg K ha^{-1} applied) exceeding the maximum dose.

Table 2.5: Recommended application rates of four by-pass dusts to correct soil acidity in a clay soil. The rates were calculated using the Rothlime calculator (McGrath and Goulding, 2002) with a target pH of 6 for grass and 6.5 for Arable (AHDB, 2023b). Note that for grassland, no more than 7.5 t ha^{-1} of lime should be applied in one application to account for slower increases in pH below the soil surface (AHDB, 2023b).

	Recommended Application Rate (t ha^{-1}) for a Clay Soil							
Soil pH	**Rugby**		**Ketton**		**Padeswood**		**Ribblesdale**	
	Grass	*Arable*	*Grass*	*Arable*	*Grass*	*Arable*	*Grass*	*Arable*
5	11	21	13	25	12	23	17	31
5.2	9	18	11	22	10	20	14	27
5.4	7	15	9	19	8	17	11	23
5.5	6	14	8	17	7	16	9	21
5.7	4	12	5	14	5	13	7	18
5.9	2	9	3	11	3	10	4	14
6	N/A	8	N/A	10	N/A	9	N/A	12

When compared to actual K fertiliser use (Table 2.7), the K supplied by CBD at a rate as low as 0.5 t ha^{-1} is between 2.1 and 2.8 times higher than the average rate used by farmers in England and Wales for tillage crops in 2019 (30 kg ha^{-1}). For grassland a rate of 0.5 t ha^{-1} would supply between 3.1 and 8.6 times the average rate used by farmers (10 kg ha^{-1}). Generally, CBD is not applied to soils with a K index of 3 and above and application is limited to once every three years to prevent build-up of PTEs in the soil and counteract the high K content of the dust (J Silverwood 2021, personal communication [email], 09 July).

Table 2.6: Average amount of potassium supplied at different application rates of CBD from the four cement plants used in this study. The red text indicates instances where K application would exceed the maximum recommended for a single application of potassium in a cereal crop (oats) (133 kg elemental K) as described in the RB209 (AHDB, 2023b). The maximum doses for silage and grazing are 99.6 and 66.4 kg ha^{-1} respectively.

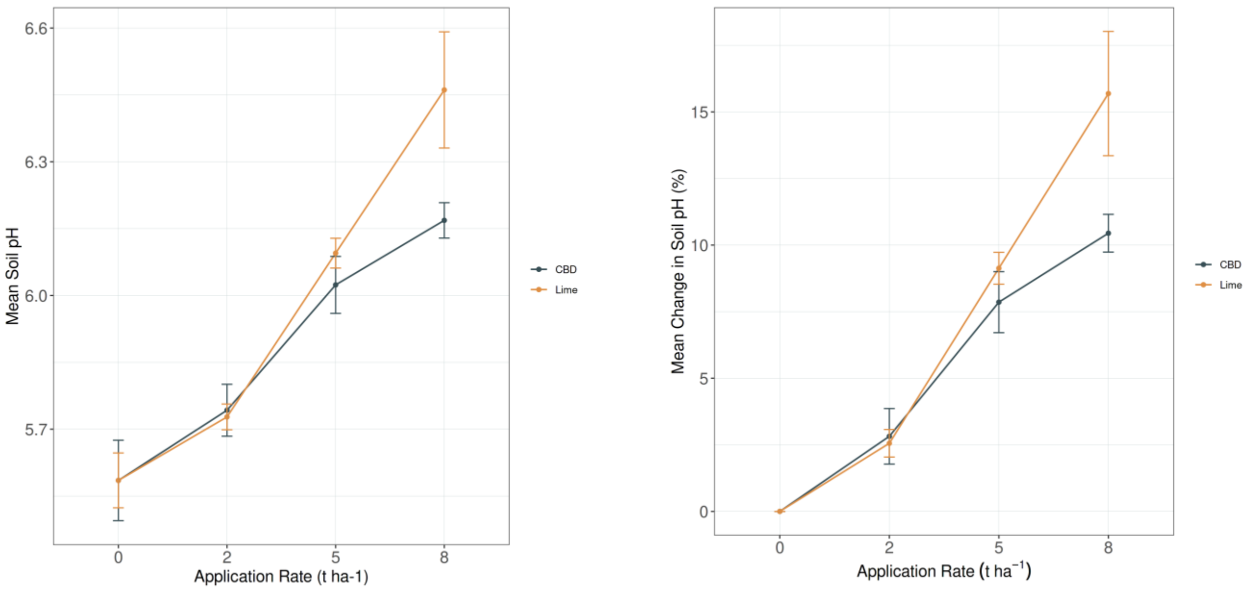
	K supplied (kg ha^{-1})			
Application Rate (t ha^{-1})	**Rugby**	**Ketton**	**Padeswood**	**Ribblesdale**
0.125	7.5	16	10.4	21
0.25	15	32	20.8	42
0.5	30	64	41.5	84
1	60	128	83.0	**168**
2	120	**256**	**166**	**336**
4	**240**	**512**	**332**	**672**
6	**360**	**768**	**498**	**1008**
8	**480**	**1024**	**664**	**1344**

Table 2.7: The total overall average K (converted from K_2O) rates used by farmers in England and Wales surveyed for the British survey of fertiliser practice 2022 (DEFRA, 2023). The overall application rate measures nutrient application rate over the sown area of all fields, irrespective of whether they received dressing of that nutrient or not. It is calculated as average filed rate multiplied by percent dressing cover.

	Overall Total K Use (kg K ha^{-1})		
Year	**Tillage Crops**	**Grass**	**All Crops and Grass**
2015	31.5	10.0	19.9
2016	32.4	10.0	19.9
2017	30.7	10.0	19.1
2018	29.1	10.0	18.3
2019	28.2	9.1	18.3
2020	24.1	9.1	15.8
2021	23.2	9.1	14.9
2022	19.9	5.0	11.6
Average	**27.4**	**9.0**	**17.23**

As CBD is currently only used to correct soil acidity in England and Wales, Tables 2.8a and 2.8b were constructed to identify soils for which CBD would be the 'ideal' solution for correcting both soil acidity and meeting crop K demand at the same time. A soil where CBD could be used at a rate designed to correct soil acidity, but which would also supply enough K to meet demand without over-supplying would be considered 'ideal' in this case. It would have to be at a pH which needed minor correction (to keep the application rate lower than 2 t ha^{-1} depending on the CBD used) and of a low K index (0) to account for the amount of K being added. For the Rugby CBD, this represents 3% of grassland samples or, ~118,444 ha. For the Ketton, Padeswood and Ribblesdale dusts, no soils fall into this category, meaning that their use at liming rates over-supplies K every time. This equates to 53% of grassland samples and 32% of arable samples or ~2,092,506 and ~ 674,480 ha of farmland respectively. The majority of samples where both pH and K correction are needed (50% of grassland and 32% of arable land) would also be over supplied with K if the Rugby CBD was applied at liming rates.

A small percentage of samples (1% of grass and 7% of arable) would benefit from lime application but existing soil K supplies are adequate thus CBD would not be applied. However, if it were feasible to apply at lower rates as a K fertiliser then ~ 1,697,693 ha of grassland (43%) and ~ 906,333 ha of arable land (43%) would be eligible for receiving any of the four dusts studied. If this were the case, application of CBD would not need to be limited to every three years to account for PTE build-up in the soil. Additionally, analysis of soil pH from the dose-response pot trial indicates that application of the Rugby CBD at 2 t ha^{-1} produces a pH change of less than 5% (Figure 2.2). Out of the four dusts studied, the Rugby CBD has the highest neutralising value (41.5%, see Figure 2.1) and it is therefore assumed that the other three dusts would have a smaller effect on pH. This suggests that CBD could be used as a K fertiliser in soils where pH was not needed as well as lower pH soils.



a **b**

Figure 2.1: Changes in soil pH at different application rates of lime and CEMEX Rugby by-pass dust on a pH 5.6 soil in a pot trial. There was a significant effect of application rate on soil pH for both agricultural lime and CBD ($p < 0.001$). However, a CBD application rate of 2 t ha^{-1} produce less than a 5% change in soil pH, indicating that it could be used as a K fertiliser at rates less than 2 t ha^{-1} in soils where pH correction is not needed.

Table 2.8a: Matrices of the percentage of soil samples in different pH classes and K indices taken from different agricultural soils across the United Kingdom from 01/06/18 to 31/5/19 (PAAG, 2019). The samples are categorised according to whether the CBD produced by each cement plant could be used to correct soil pH or as a K fertiliser. Whether the CBD can be used to correct pH or K is dependent on the application rate, with lower rates being more suitable for K correction alone. CBD rates lower than 3 t ha^{-1} do not alter soil pH by more than 0.3 units (see Table 2.1). The Ketton, Padeswood and Ribblesdale plants have been analysed together because their K content results in over application when applied to correct pH.

Ketton, Ribblesdale and Padeswood

	Can be Used at Liming rates to Correct pH and K	Can be Used at Liming Rates to Correct pH but K Over Supplied	Can be Used to Correct for pH but K Not Needed	Can be used at low rate to Supply K.	Correction for pH and K Not Needed	No Sample Collected
Arable	0%	32%	7%	43%	17%	N/A
Grass	0%	53%	1%	43%	3%	N/A

Percentage of arable samples

	K Index						
pH	**0**	**1**	**2-**	**2+**	**3**	**4**	**5**
<5.0	0.1	0.2	0.2	0.1	0.1	0.01	0
5.0-5.4	0.3	1.3	0.9	0.5	0.4	0.1	0.01
5.5-5.9	0.7	3.9	3.8	2.1	1.7	0.3	0.04
6.0-6.4	0.7	6.1	7.0	4.4	3.8	0.6	0.1
6.5-6.9	0.4	5.5	7.3	4.8	4.5	0.9	0.1
7.0-7.4	0.2	3.2	4.6	3.2	3.4	0.8	0.2
7.5-7.9	0.1	2.0	3.6	3.1	3.9	1.1	0.3
8.0-8.4	0.1	1.2	1.9	1.5	1.6	0.3	0.1
8.5-9.0	0.01	0.1	0.2	0.1	0.1	0.02	0

Percentage of grassland samples

	K Index						
pH	**0**	**1**	**2-**	**2+**	**3**	**4**	**5**
<5.0	0.3	0.9	0.4	0.1	0.1	0.01	0
5.0-5.4	1.6	6.5	4.1	1.7	1.0	0.1	0.03
5.5-5.9	3.0	13.0	10.1	5.3	4.5	0.8	0.2
6.0-6.4	1.9	8.7	7.3	4.4	4.6	1.2	0.3
6.5-6.9	0.7	3.1	2.8	1.9	2.2	0.7	0.2
7.0-7.4	0.2	0.7	0.8	0.6	0.8	0.3	0.1
7.5-7.9	0.1	0.3	0.4	0.3	0.5	0.2	0.1
8.0-8.4	0.04	0.2	0.1	0.1	0.1	0.05	0.02
8.5-8.9	0.01	0.01	0	0.01	0.01	0	0

Table 2.8b: Matrices of the percentage of soil samples in different pH classes and K indices taken from different agricultural soils across the United Kingdom from 01/06/18 to 31/5/19 (PAAG, 2019). The samples are categorised according to whether the CBD produced by the Rugby cement plant could be used to correct soil pH or as a K fertiliser. Whether the CBD can be used to correct pH or K is dependent on the application rate, with lower rates being more suitable for K correction alone. CBD rates lower than 3 t ha^{-1} do not alter soil pH by more than 0.3 units (see Table 2.1).

Rugby

	Can be Used at Liming rates to Correct pH and K	Can be Used at Liming Rates to Correct pH but K Over Supplied	Can be Used to Correct for pH but K Not Needed	Can be used at low rate to Supply K.	Correction for pH and K Not Needed	No Sample Collected
Arable	0%	32%	7%	43%	17%	N/A
Grass	3%	50%	1%	43%	3%	N/A

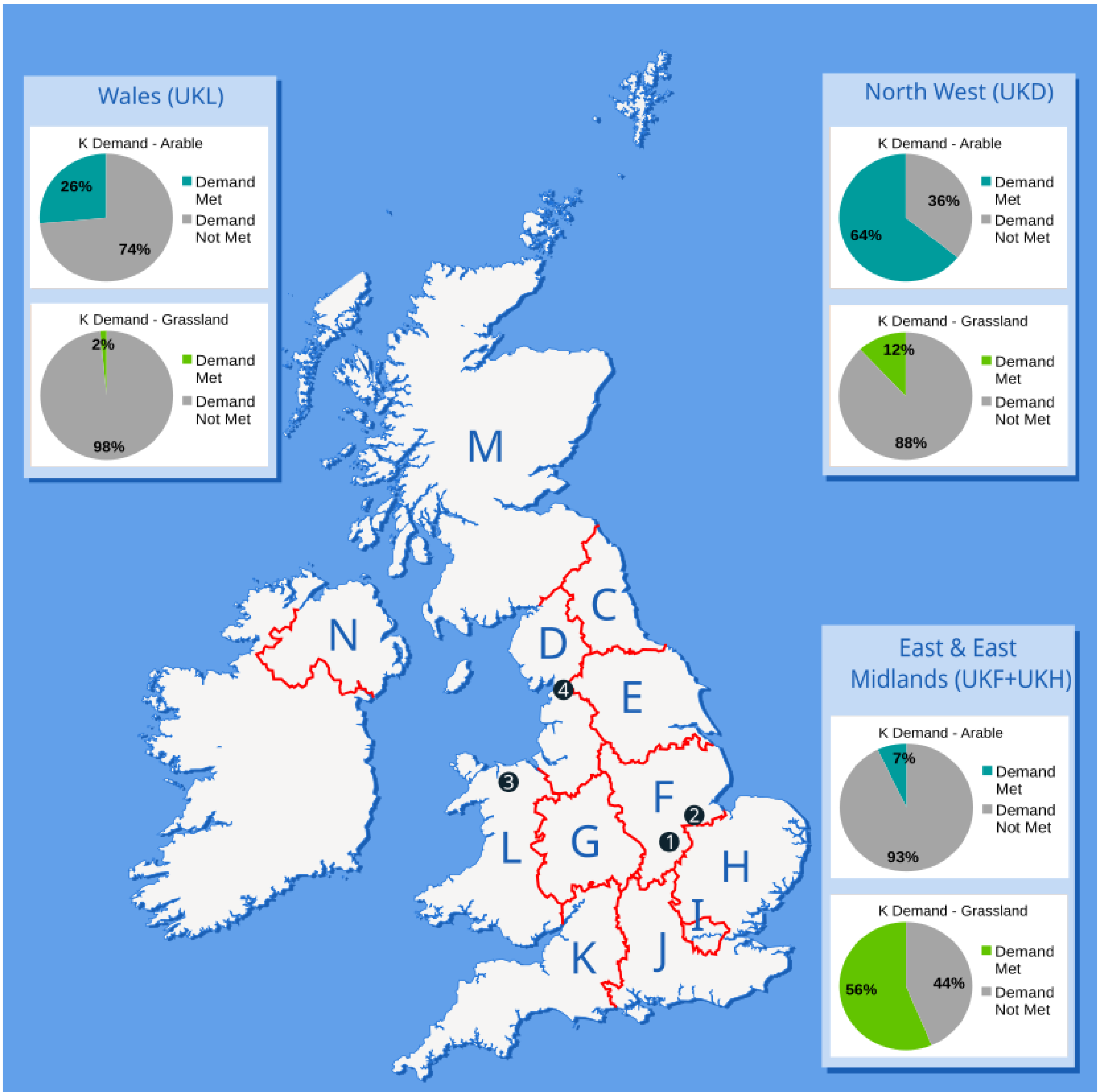
Percentage of arable samples

	K Index						
pH	**0**	**1**	**2-**	**2+**	**3**	**4**	**5**
<5.0	0.1	0.2	0.2	0.1	0.1	0.01	0
5.0-5.4	0.3	1.3	0.9	0.5	0.4	0.1	0.01
5.5-5.9	0.7	3.9	3.8	2.1	1.7	0.3	0.04
6.0-6.4	0.7	6.1	7.0	4.4	3.8	0.6	0.1
6.5-6.9	0.4	5.5	7.3	4.8	4.5	0.9	0.1
7.0-7.4	0.2	3.2	4.6	3.2	3.4	0.8	0.2
7.5-7.9	0.1	2.0	3.6	3.1	3.9	1.1	0.3
8.0-8.4	0.1	1.2	1.9	1.5	1.6	0.3	0.1
8.5-9.0	0.01	0.1	0.2	0.1	0.1	0.02	0

Percentage of grassland samples

	K Index						
pH	**0**	**1**	**2-**	**2+**	**3**	**4**	**5**
<5.0	0.3	0.9	0.4	0.1	0.1	0.01	0
5.0-5.4	1.6	6.5	4.1	1.7	1.0	0.1	0.03
5.5-5.9	3.0	13.0	10.1	5.3	4.5	0.8	0.2
6.0-6.4	1.9	8.7	7.3	4.4	4.6	1.2	0.3
6.5-6.9	0.7	3.1	2.8	1.9	2.2	0.7	0.2
7.0-7.4	0.2	0.7	0.8	0.6	0.8	0.3	0.1
7.5-7.9	0.1	0.3	0.4	0.3	0.5	0.2	0.1
8.0-8.4	0.04	0.2	0.1	0.1	0.1	0.05	0.02
8.5-8.9	0.01	0.01	0	0.01	0.01	0	0

2.3.3 National Picture of K Demand, K Supply and Economic Value of CBD Production



Number	Company	Plant	Region	Potassium Content (%)	Neutralising Value (%)	Production (t year⁻¹)	K Production (t year⁻¹)
1	CEMEX	Rugby	UKF	6.02 ± 1.3	41.48 ± 2.6	17,000	1020
2	Hanson Cement	Ketton	UKF	12.8 ± NA	33.7± NA	5,000	640
3		Padeswood	UKL	8.29± NA	36.9 ± NA	3,500	290.5
4		Ribblesdale	UKD	16.8 ± 0.5	27.63 ± 1.6	5,000	840

Figure 2.2: A map of the NUTS1 C-N regions of the United Kingdom of Great Britain and Northern Ireland, adapted from Nilfanion, (2012) and MPA Cement (2023b). The circled numbers represent the four cement production facilities used by Silverwoods Waste Management Ltd as sources of cement by-pass dust. The ability of the cement plants to meet the K requirements for the four selected regions (plants 1 and 2 are combined) is displayed in the pie charts. Further information on annual production numbers and nutrient content are provided in the Table at the bottom of the image. K production is expressed as elemental K, not K_2O. There was only one chemical analysis report for the Ketton and Ribblesdale plants, so variation in K content and neutralising value could not be calculated.

All regions in England and Wales (regions C-L see Figure 2.3) were used to produce a national picture of K demand. As no CBD production data for Scotland and Northern Ireland was available at the time of writing, they were excluded from analysis. Silage and grazing figures were used to calculate the land area required for grassland in England and Wales, whereas winter wheat and winter barley were used as proxies for arable farming.

The total farmland used for grassland and arable farming in England and Wales is 6,055,875 ha. Of this, 3,948,124 ha is grassland farming, and 2,107,751 ha is arable land (Table 2.9). 38,909 tonnes of K were used on grassland and 51,016 tonnes of K are used on arable land in 2019. At current UK prices, this equates to £ 44,900,986 and £ 58,872,464 respectively, giving a combined value of £ 103,773,450 (Table 2.9).

Waste CBD from all four cement plants studied, when combined produce 30,500 tonnes of CBD annually, which contained 2,730.5 tonnes of elemental K. At current fertiliser prices, the potential economic value of this K is £ ~3,150,997 if the CBD was considered as a K fertiliser rather than a liming agent (Table 2.9). Altogether, the four cement plants produce enough K to meet 7% of the nation's annual K demand for grassland or 5% of the nation's arable demand for K (Figure 2.4 and Table 2.9). Alternatively, it can meet 3% of the combined grassland and arable demand combined.

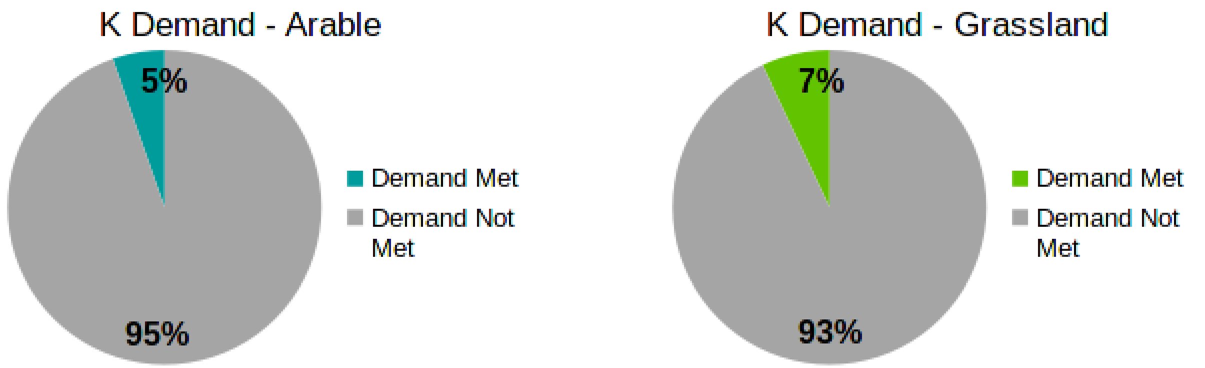


Figure 2.3: The percentage of K demand from grassland or arable farming in England and Wales (regions C-L) which can be met by the combined K production from the four cement plants used in this study.

Table 2.9: A summary of CBD and K production for the cement plants used in this study, K use in England and Wales and the economic value of the K present in the CBD produced and K used in England and Wales. Overall Application Rate is taken from the British Survey of Fertiliser Practice (DEFRA, 2020) and defined as quantity of K used (kg) divided by total crop area (ha) including areas without nutrient application. Winter wheat and barley are used as proxies for arable farming as a whole. Land area is adapted from DEFRA (2021b). The values for the application rate are converted from K_2O.

Dust	Ketton, Padeswood, Ribblesdale & Rugby
Annual Production (t)	30,500
Annual K Production (t)	2,730.5
Total Value of K Present in Cement Dust (£)	3,150,997

	Silage	**Grazing**	**Total Grass**	**Winter Wheat**	**Winter Barley**	**Total Arable [*]**
Overall rate applied (kg K ha-1) [1]	15	7	--	23	28	--
Land Area (ha) [2]	1,260,540	2,687,584	**3,948,124**	1,699,833	407,918	**2,107,751**
Total Applied K (t) [3((1x2)/1000)]	18,832	20,076	**38,909**	39,504	11,511	**51,016**
Total Economic Value of K (£) [3] x 1,154]	21,732,128	23,167,704	**44,900,986**	45,587,616	13,283,694	**58,872,464**

2.3.4 Regional Picture of K Demand and K Supply from CBD Production

2.3.4.1 North West England (UKD)

Farming in the North West is predominately pasture based (DEFRA, 2021b), with 7,031 tonnes of K applied to the 756,084 ha used for grazing and silage in 2019 (Table 2.9). The value of the K applied to land used for grazing and silage is worth approximately £ 8,113,774. The land area reserved for growing winter wheat and barley is 52,614 ha, and 1,305 tonnes of K were applied to this land in 2019. The economic value of the K applied to winter wheat and barley is £ 1,505,970 and the total amount of K used by the farmers in this region is valued at £ 9,619,744.

This region is supplied by one cement plant: the Hanson Cement Ribblesdale facility. The Ribblesdale plant produces 5,000 tonnes of CBD annually, which equates to approximately 840 tonnes of K. This K enough to meet 12% of grassland demand, or 64% of arable demand and is valued at £ 969,360 (Figure 2.3).

Table 2.10: CBD and K production from the Hanson Ribblesdale cement plant. K use in the North West of England (UKD). And the economic value of the K present in the CBD produced and K used in UKD. Overall Application Rate is taken from the British Survey of Fertiliser Practice (DEFRA, 2020) and defined as quantity of K used (kg) divided by total crop area (ha) including areas without nutrient application. Winter wheat and barley are used as proxies for arable farming as a whole. Land area is adapted from DEFRA (2021b). The values for the application rate are converted from K_2O.

Dust	Ribblesdale
Neutralising Value (%)	27.6
K content (%)	16.80
Annual Production (t)	5000
Annual K Production (t)	840
Total Value of K Present in Cement Dust (£)	969,360

	Silage	**Grazing**	**Total Grass**	**Winter Wheat**	**Winter Barley**	**Total Arable [*]**
Overall rate applied (kg K ha-1) [1]	15	7	--	23	28	--
Land Area (ha)[2]	185,107	570,976	**756,084**	36,049	16,565	**52,614**
Total Applied K (t)[3((1x2)/1000)]	2,766	4,265	**7,031**	838	467	**1,305**
Total Economic Value of K (£) [3] x 1,154]	3,191,964	4,921,810	**8,113,774**	967,052	538,918	**1,505,970**

2.3.4.2 East England and East Midlands (UKF & UKH)

To determine how much of the demands of East England (UKF) and the neighbouring East Midlands (UKH) can be met (Table 2.11) the production of two plants (Hanson: Ketton and CEMEX: Rugby) located in the East of England (UKF) has been combined.

Arable farming is dominant in the region (DEFRA, 2021b), with 935,739 ha being reserved for winter wheat and barley compared to the 317,999 ha reserved for grassland. 22,485 tonnes of K are applied to winter wheat and barley a year, and this K is valued at £ 25,947,690. Considerably less K is used for the grassland in the region, with 2,840 tonnes applied annually at a value of £ 3,277,360. The total annual K use for the region is 24,965 tonnes, which is valued at £ 28,809,610. Both cement plants combined produce 1,600 tons of K (22,000 tonnes of CBD) annually, with an economic value of £ 1,846,400. Production could meet 7% of arable demand for the region or 56% of grassland demand.

Table 2.11: CBD and K production from the CEMEX Rugby and Hanson Ketton cement plants. K use in East England and the East Midlands (UKF & H). And the economic value of the K present in the CBD produced and K used in UKF & H. Overall Application Rate is taken from the British Survey of Fertiliser Practice (DEFRA, 2020) and defined as quantity of K used (kg) divided by total crop area (ha) including areas without nutrient application. Winter wheat and barley are used as proxies for arable farming as a whole. Land area is adapted from DEFRA (2021b). The values for the application rate are converted from K_2O.

Dust	Rugby	Ketton
Neutralising Value (%)	41.5	33.8
K content (%)	6.0	12.8
Annual Production (t)	17,000	5,000
Annual K Production (t)	1600	
Total Value of K Present in Cement Dust (£)	1,846,400	

	Silage	**Grazing**	**Total Grass**	**Winter Wheat**	**Winter Barley**	**Total Arable [*]**
Overall rate applied (kg K ha^{-1}) [1]	15	7	--	23	28	--
Land Area (ha) [2]	62,083	255,915	**317,999**	787,318	148,421	**935,739**
Total Applied K (t) [3((1x2)/1000)]	928	1,912	**2,840**	18,297	4,188	**22,485**
Total Economic Value of K (£) [3] x 1,154]	1,070,912	2,206,448	**3,277,360**	21,114,738	4,832,952	**25,947,690**

2.3.4.3 Wales (UKL)

Grassland makes up the majority of farming in Wales, with 2,000,529 ha being used for silage and grazing (Table 2.11). K demand for silage and grazing is 18,371 tonnes a year, which is valued at £ 21,200,134. Arable farming is less prevalent in Wales, with only 43,000 ha being reserved for growing winter wheat and barley, which receive 1,099 tonnes of K annually. Total K demand for the region is 19,470 tonnes a year and it is valued at £ 22,468,380. The K applied to grassland is worth £ 21,200,134 and the K applied to arable land is worth £ 1,268,246.

The Padeswood plant, operated by Hanson Cement produces 3,500 tonnes of CBD a year. As Padeswood has the second lowest K content (8.3%), K production is only 290.5 tonnes annually (Table 2.2). This means that it could supply 2% of the grassland demand in Wales or 26% of the demand for arable farming (Figure 2.3). The economic value of this K is £ 335,237.

Table 2.12: CBD and K production from the Hanson Padeswood cement plant. K use in Wales (UKL). And the economic value of the K present in the CBD produced and K used in UKL. Overall Application Rate is taken from the British Survey of Fertiliser Practice (DEFRA, 2020) and defined as quantity of K used (kg) divided by total crop area (ha) including areas without nutrient application. Winter wheat and barley are used as proxies for arable farming as a whole. Land area is adapted from DEFRA (2021b). The values for the application rate are converted from K_2O.

Dust	Padeswood
Neutralising Value (%)	36.9
K content (%)	8.30
Annual Production (t)	3500
Annual K Production (t)	290.5
Total Value of K Present in Cement Dust (£)	335,237

	Silage	**Grazing**	**Total Grass**	**Winter Wheat**	**Winter Barley**	**Total Arable [*]**
Overall rate applied (kg K ha-1) [1]	15	7	--	23	28	--
Land Area (ha) [2]	458,837	1,541,692	**2,000,529**	23,000	20,000	**43,000**
Total Applied K (t)[3((1x2)/1000)]	6,855	11,516	**18,371**	535	564	**1,099**
Total Economic Value of K (£) [3] x1,154]	7,910,670	13,289,464	**21,200,134**	617,390	650,856	**1,268,246**

2.4 Discussion

Farmers in Great Britain primarily use CBD as a soil alkalising agent, yet its K content means it can also be seen as a ‘two-for-one’ product, as an alternative to both lime and K fertiliser. The current approach of only using it as a liming agent sees this K as an added ‘bonus’ to the product’s pH altering properties, suggesting its potential as a sole K fertiliser is being overlooked. Applying CBD at liming rates may not be its best agronomic use, as this likely results in over application of K and loss of applied K through leaching. Theoretically, applying CBD to agricultural land makes sense as a circular nutrient economy strategy as it recycles K that would otherwise be wasted when sent to land fill, but this circular approach only works if the K being applied is not leached from agricultural soils. If used as a K fertiliser, CBD could replace 36,000 tonnes of K which would otherwise come from a non-renewable resource. Therefore, this study aimed to assess whether using CBD as a source of K is feasible in England and Wales.

The K present in CBD is also a valuable economic resource if it were to be treated as a fertiliser. The K in the CBD produced by the four cement plants has an economic value of £3,878,143 (Table 2.9). Currently, the cost of spreading the CBD to land is mostly met by the waste producer (the cement company) which means that farmers using the dust save money by using it as a liming agent (J Silverwood 2021, personal communication [email], 09 July). Again, this approach appears to ignore CBD’s potential as a K fertiliser, leading to the waste of a valuable commodity that could decrease fertiliser costs. However, applying CBD as a K fertiliser is only feasible if there is product demand and a different application practice can be adopted as discussed below.

This study indicates that CBD production from four cement plants operating in England and Wales could theoretically meet 7% of grassland or 5% of arable K demand in 2019 based on crop type and soil K status (equating to 147,543 ha and 197,406 ha of farmland respectively)

(Figure 2.4 and Table 2.9). This varies by region as CBD is usually applied within the county of the dust's origin (J Silverwood 2021, personal communication [email], 09 July). CBD production in the North West can meet 64% of arable K demand or 12% of grassland demand; production in East England and the East Midlands can meet 7% of arable demand or 56% of grassland demand and production in Wales can meet 26% of arable demand and 2% of grassland demand. These findings demonstrate that use of CBD as a K fertiliser can meet a sizeable portion of agricultural K demand in England and Wales.

CBD clearly has a potential as a K fertiliser, however current practice and typical application rates (5-6 t ha^{-1}) treat it as an alkalising agent first and foremost (J Silverwood 2021, personal communication [email], 09 July). This may be problematic when considering the amount of K applied at these rates (Table 2.6). For example, depending on the CBD used, 6 t ha^{-1} supplies 360^{-1} kg K ha^{-1}. The recommended maximum application of K in one dose for a crop with a high K requirement such as oats grown on an index 0 soil is 132.8 kg K ha^{-1}, meaning that using CBD as a liming agent at 6 t ha^{-1} would over-supply K by at least 277 kg ha^{-1}.

As CBD is commonly applied to grassland, the over application of K is even higher. Silage requires 99.6 kg K ha^{-1} at most in a single application and land used for grazing requires only 66.4 kg K ha^{-1} (AHDB, 2021b), thus applying 5-6 t ha^{-1} CBD (recommended by Silverwoods Waste Management Ltd.) over applies K by up to 942 kg ha^{-1} (see Table 2.6). This is partly mitigated by restricting application of CBD to once every 3 years (J Silverwood 2021, personal communication [email], 09 July). However, even a cropping system with relatively high K demands still over applies K. For instance, a four cut grass system used for silage in an index 0 soil requires 871.5 kg K ha^{-1} compared to the 1008 kg ha^{-1} supplied by a single 6 t ha^{-1} application of Ribblesdale CBD (Table 2.6). The gap between application and removal is even higher for a lower demand system such as an index 2+ soil with two cuts, as this system requires only 99.6 kg K of the 1008 kg K ha^{-1} supplied by 6 t ha^{-1} of the Ribblesdale dust. For this reason, CBD is rarely applied to soils at 2+ and above (J Silverwood 2021, personal communication [email], 09 July). However, it is still questionable whether this is an efficient practice since K is susceptible to leaching when applied in large and in sandy soils prone to K leaching (Kayser *et al.*, 2007; Römheld and Kirkby, 2010). It is unlikely that the K applied by a single application of CBD at a rate of ~6 t ha^{-1} would remain in the soil for the three years until the next application.

In principle, it appears that using CBD aligns with the circular economy concept of recycling materials from end-of-life products (i.e., waste materials) by recycling waste (and nutrients) from the cement manufacturing process back into the food system. It therefore seems paradoxical that it is being used in such a way that the K it contains is essentially being thrown away.

Although excessive K application does not have any direct negative environmental impact, it is not without consequences. Certain crops, especially grasses, will take up more K than required for their functioning in a phenomenon known as luxury uptake (Finnan and Burke, 2013) in which K is simply stored by the plant and does not translate to increased growth (Winkler and Zotz, 2010). Additionally, high K inputs disrupt Ca and Mg uptake by plants thereby decreasing forage quality and affecting the diet of grazing livestock (Kayser and Isselstein, 2005). Furthermore, high amounts of dietary K can contribute to several animal metabolic disorders (EBLEX, 2008; Finnan and Burke, 2013). With much of the CBD being applied in England and Wales going to pasture it is worth questioning whether applying CBD at liming rates has detrimental effects on livestock. As far as the author is aware, there are no investigations to this effect in the literature and there have been no negative effects reported to the CBD supplier by the farmers using it (J Silverwood 2019, personal communication, 08 May).

It also makes little economic sense to apply CBD as an alkalising agent since, as stated before, the potential value of the K in CBD is ~£ 3,150,997 when compared to the equivalent K in conventional K fertiliser (K_2O). However, the issue of over application is partly due to the restrictions imposed by The Sludge (Use in Agriculture) Regulations 1989 (Anon, 1989) and the resulting fees required to obtain a permit to spread CBD to agricultural land. The same application fee applies regardless of the amount of CBD used, which in turn encourages the use of higher application rates, which in turn leads to over application of K (J Silverwood 2021, personal communication [email], 09 July). This highlights an aspect of current policy which needs to be reviewed to consider the agronomic inefficiency of treating CBD as a waste product. It also raises the question as to whether CBD should be seen as a waste product at all considering its usefulness as a K fertiliser. The main barrier to CBD being viewed as such is its PTE content (J Silverwood 2019, personal communication, 08 May). Yet paradoxically it is the regulation itself which is keeping application rates high. Applying lower rates of CBD as a K fertiliser would partially negate the issue of soil PTE build-up.

When applying CBD at rates lower than 6 t ha^{-1}, depending on the dust used, the annual amount of PTEs being applied to the soil would not reach the limits outlined by The Sludge (Use in Agriculture) Regulations 1989 (Anon, 1989) (Table 2.4). One application of 2 t ha^{-1} of either the Rugby or Ribblesdale CBD would apply 0.1 kg ha^{-1} of cadmium, which is below the 0.15 kg ha year^{-1} limit. The Rugby CBD could also be applied at 4 t ha^{-1} and still only add 0.1 kg ha^{-1} of cadmium to the soil. This would mean CBD could be applied yearly as a K fertiliser instead of every 3 years as a liming agent, yet due to a permit being required, the application fees make it financially prohibitive to do so. Again, whilst it makes economic sense for the supplier of the CBD to treat it as a liming agent, it ignores the value of the K which is being wasted by these practices.

Current practice may also limit the use of CBD to soils which require pH adjustment. Table 2.8 determined if there were any soils in the UK where CBD could be applied at a liming rate without over-applying K. Of all the grassland soil samples taken by The Professional Agricultural Analysis Group (PAAG, 2019), just 3% fitted these criteria when applying the Rugby dust. No samples fitted these criteria for the other dusts. Therefore, when used as a liming agent, K is being over applied in almost every case. However, dust use at a lower rate

(<2 t ha^{-1}) would allow it to be used across a wider range of soils, including soils above pH 6-6.5 as a K fertiliser whilst eliciting a <5% change in pH (Figure 2.2). In this context, CBD is suitable for use on 75% of arable soils and 96% of grassland soils. This again raises the question of whether CBD should be used as a liming agent when its use as a K fertiliser could be expanded to a greater number of soils.

Currently, CBD application is regulated in such a way that encourages application rates designed to amend soil acidity, resulting in excessive application K that may not increase crop growth and encourages leaching of K from the soil. This practice overlooks the potential for CBD to be used as a K fertiliser in England and Wales, which could replace 5-7% of K demand, depending on how it is used.

However, the limitations of this study raise more questions which need to be answered to fully understand the potential of CBD as an agricultural amendment. Firstly, this study makes assumptions based on the best available data at the time, which may not give a complete picture of the production of CBD and the use of K in the Great Britain. Although ten cement plants operate in Great Britain (MPA Cement, 2021), only data from the four studied was available at the time of writing. It is therefore conceivable that CBD production could meet much more of the K demand than anticipated in this investigation. However, CBD production by these other 6 plants, and their K and PTE content is unknown. As the analysis was only conducted for a single year (2019), it does not consider any changes to farming practice or CBD production rates which may have taken place since.

The dataset provided by The Professional Agricultural Analysis Group (PAAG, 2019) is suitably robust, comprising 21,666 samples in total and includes a process for detecting errors. Whilst this informs which soils may benefit from CBD application, it doesn't indicate the intensity of cropping (and therefore crop demand for K) on the land they were taken from, or whether the soil was likely to leach K. Whether farmers would fertilise this land (and therefore use

CBD) is not known, especially when considering that actual application rates of K are lower than those recommended (RB209, AHDB, 2023b) Therefore Table 2.7 only indicates which soils would be suitable for CBD application.

Analysis of the CBD used for this study was also limited, with the Ketton and Padeswood only having one set of analyses available, whereas the Ribblesdale and Rugby plants had three and five sets of analyses done respectively and therefore an average value for these plants was used. The author could not obtain more analyses at the time of writing. Furthermore, PTE analysis was only available for the Ribblesdale and Rugby plants, meaning it was not possible to fully understand how applying all four dusts would influence the build-up of PTEs in agricultural soil. Further analysis would provide a more accurate picture of the variability of the CBD produced by the cement plants.

As this investigation principally utilised available datasets, the performance of CBD compared to more traditional sources of lime and K fertiliser was not assessed. This gap between the theory and actual practice of using CBD was addressed in the next chapter of this thesis by undertaking a field trial comparing two sources of CBD to conventional K fertiliser and agricultural lime. It aims to investigate whether the extra K added by CBD application enhances plant growth over the standard application of K fertilisers, how CBD application affects the availability of soil K and whether PTE uptake of plants would reach concerning levels after a 6 t ha^{-1} application.

CHAPTER 3: COMPARING PASTURE RESPONSES TO CEMENT BY-PASS DUST, CEMENT KILN DUST, AGRICULTURAL LIME AND POTASSIUM FERTILISER IN NORTHERN ENGLAND

3.1 Introduction

As indicated in Chapter 1, cement by-pass dust and cement kiln dust (CBD and CKD) application can promote crop growth and yield, increase soil pH at depths up to 20 cm following surface application and increase plant available soil Ca, K and Mg (Van Lierop, Tran and Morissette, 1982; Lafond and Simard 1999; Rodd *et al*., 2004; Rodd *et al*., Lalande, Gagnon and Royer , 2010; Shaheen *et al*., 2017), making it useful as both an alkalising agent and a fertiliser. Extrapolating the effects of CBD/CKD application on British soils requires data from Australian (Dann, Dear and Cunningham, 1989), Canadian (Van Lierop *et al*., 1982; Rodd *et al*., 2004; Rodd *et al*., 2010), Egyptian (Shaheen *et al*., 2017) and Korean (Moon *et al*.,2013) studies. However, CBD/CKD are currently being applied commercially to fields in Great Britain (GB) as soil alkalising agents providing that the soil does not have a pH lower than 5, the soil is tested three weeks before application, after first application and every six months to five years thereafter and the product provider keeps a register of application (Anon, 1989; GOV.UK, 2018). These procedures are to ensure that Potentially Toxic Elements (PTEs) are not building up in the soil and that soil pH remains at a level where PTE availability and therefore plant uptake is low (Table 2.3) (Anon, 1989). While this indicates demand in GB for products such as CBD/CKD, whether these products are effective as an alkalising agent, or a potassium (K) fertiliser is unknown. How these products affect growth and yield of British crops, and K availability and pH of British soils is unknown. The effects of CBD/CKD and conventional lime/fertiliser products has not yet been directly compared in Britain.

Management of K nutrition is important for both crop and livestock production, being required for turgor maintenance, cell growth and stomatal regulation in plants (Mengel *et al*., 1982; Pettigrew, 2008) and weight gain, pregnancy, and lactation in livestock (ward, 1966;

Dove *et al*., 2016). However, excess K application can diminish intake and absorption of other minerals in both crops and livestock. K can antagonise plant uptake of Ca_{2+} and Mg^{2+} causing nutrient deficiencies (Fageria, 2001). High dietary K (dry matter content above 2.5%) reduces absorption of Mg and Ca in ruminant livestock resulting in Hypomagnesaemia, a fatal neurological disease (EBLEX, 2008).

Both CBD and CKD are currently used solely as liming agents in GB. Applying 5 t ha $^{-1}$ of the CKD used for this project supplies 373 kg K ha^{-1} (Table 3.2), well above the 12 - 35 kg K ha $^{-1}$ average rate recorded by the British Survey of Fertiliser Practice for grassland and tillage crops (DEFRA, 2018). Since the average application rate for CBD/CKD in GB is 5 t ha^{-1} (J Silverwood 2020, personal communication, 4 May) and luxury uptake of K has been observed in numerous crop species (Øgaard *et al*., 2001; Karam *et al*., 2009; Jiang *et al*., 2018; Soratto *et al*., 2020), this could increase the risk of nutrient deficiencies in plants and livestock. Conversely, applying CBD at 500 kg ha $^{-1}$ supplies only 37 kg of K, meaning that it can be used at lower rates below purely as a K fertiliser for grassland if pH correction is not needed. This brings current application rates of CBD/CKD in GB into question as it could lead to plant and animal nutrition deficiencies through excess application of K.

The Sewage Sludge in Agriculture: Code of Practice for England, Wales, and Northern Ireland (GOV.UK, 2018) outlines the limits for soil PTE content when applying waste products such as CBD/CKD, however, monitoring of plant uptake of PTEs is not required. Pot trials have revealed that application of CBD (1% w/w) increases Cu bioavailability and tissue concentrations of sorghum (*Sorghum bicolor*) by 38% and 4.6% respectively compared to control (Shaheen *et al*., 2017). CBD application (10 g kg $^{-1}$) increased tissue Cu concentrations by 91% compared to control in field grown Rapeseed (*Brassica napus*) (Rodd *et al*., 2010). However, as regulation in England, Wales and Northern Ireland does not require testing of plant tissues and does not provide any PTE limits for plant tissue concentration (Anon, 1989; GOV.UK, 2018), it is difficult to determine if PTE uptake resulting from CBD or CKD application is problematic.

This chapter aims to characterise and compare CBD and CKD to agricultural lime applied at rates recommended for a soil currently used for pasture in terms of neutralising value and chemical composition as potential liming agents/fertiliser. The products will be compared in a field experiment conducted on established pasture to replicate UK industry practice. The experiment will test the hypothesis that CBD, CKD, application will be comparable to lime + K fertiliser in terms of improving plant growth, increasing soil pH, soil nutrient availability (K and P) and nutrient uptake (Ca, Mg, K and P) compared to a control. Additionally, plant tissue PTE content will be assessed to address whether plant uptake is significantly increased when compared to an untreated control.

3.2 Materials and Methods

3.2.1 Site Description

Figure 3.1: Image of the trial site. The total trial area is marked in red and measures 500m^2. This area is divided into 24 plots arranged in blocks of 12.

The experiment was conducted on a livestock farm located in Clitheroe, Lancashire, UK (Morton House Farm, latitude: 53.856893, longitude: -2.475272). The field is primarily used for grazing. Soils in this region are described as acid, loamy upland soils with a wet peaty surface and low fertility (Cranfield University, 2018). Average annual rainfall is 1294mm with average temperatures ranging from 1 - 19 °C throughout the year. The field where the plot is located has not been limed for over 10 years and consequently the soil pH was measured (in water at 1:2.5) as 5.7 (Sciphus Computing Ltd, McGrath, S. and Goulding, K., 2021). The recommended application rate of lime is 5 t ha $^{-1}$ for this soil. An analysis of soil nutrient content is provided in Table 3.1, and supplementary data provided in Appendix A, Table 1 and Figure 1.

Table 3.1: The available nutrients and recommended fertiliser application rates for the field site. Fertiliser rates were taken from the Nutrient Management Guide (RB209) (AHDB, 2023b).

Nutrient	Available (mg l^{-1})	Index	Recommended Fertiliser Rate (kg ha $^{-1}$)
Phosphorus (P)	52.8	4	0
Potassium (K)	27	0	150
Magnesium (Mg)	76	2	0

3.2.2 Treatments

The treatments were surface applied to an established pasture consisting of perennial ryegrass (*Lolium perenne* L.). Six treatments consisted of an untreated control, lime, CBD, CKD, K fertiliser and lime plus K fertiliser. Application rates for each treatment are provided in Table 3.2. Potassium sulphate was chosen as the K fertiliser for this experiment as the K supplied by CBD and CKD is also in this form. The application rate was chosen because that is the average application rate for CBD and CKD in GB (J Silverwood 2020, personal communication, 4 May). The two dusts used were supplied by Silverwoods Waste Management (Clitheroe, United Kingdom), who obtained them from two GB CEMEX plants. The by-pass dust (CBD) originated from the Rubgy plant (Warwickshire, United Kingdom) and the cement kiln dust (CKD) from South Ferriby (Lincolnshire, United Kingdom). The lime used was J Arthur Bowers Garden Lime (Westland Horticulture Ltd., United Kingdom). N was not supplied to the plots in either year due to a miscommunication with the landowner. The soil was sampled and analysed before treatment application on 03/01/19. The treatments were then applied on 14/01/19 across 24 10 m^2 (5 x 2 m) plots arranged in a randomised block design with a 1m border between each plot to provide ease of access. A schematic of the experimental plot is provided in Figure 3.2. The top row of plots was removed from analysis due to large variations in biomass production and soil pH, K and P from the rest of the plots. Therefore, each plot was replicated three times.

Table 3.2: The neutralising value and application rates of each of the treatments applied. Analysis of the CBD and CKD was performed by NRM Laboratories (Bracknell, United Kingdom).

Treatment	Neutralising Value (%)	K content (%)	Rate (t ha^{-1})	Rate per plot (kg)
Lime	56.7	NA	5	5
By-pass Dust (CBD)	35.9	7.5	5	5
Kiln Dust (CKD)	31	7.9	5	5
Potassium Sulphate	NA	48	150 (kg ha^{-1})	0.31

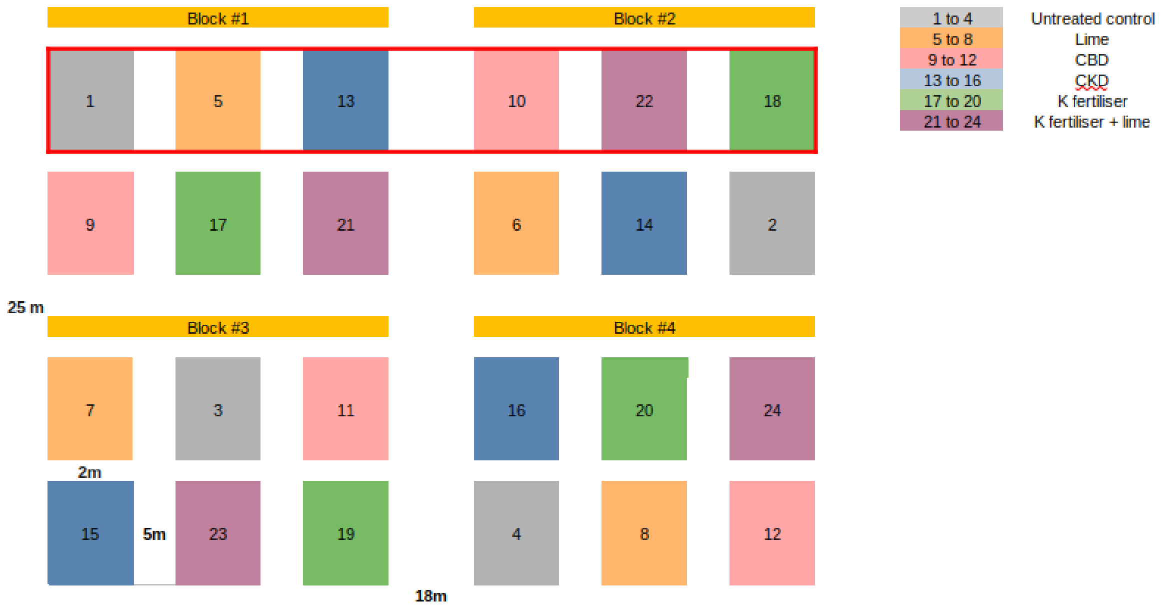


Figure 3.2: The layout of the field experiment. Each plot measures 10m^2 and is arranged in a randomised block. The plots outlined in red were removed from analysis as their yield varied substantially from the rest.

3.2.3 Soil Sampling

Seven soil cores were taken from each plot in a "W" pattern across the whole plot (schematic outlined in Appendix B, Figure 1). Sampling depth was 15cm and samples were taken with a steel soil corer with a 59mm inside diameter. The first set of samples were taken in January 2019 (before treatment was applied), at each harvest (June and August of each year) and again in May and October of each year.

The soil cores were amalgamated with others from the same plot. The soil was prepared for analysis by air-drying at 27°C, until constant weight was achieved before grinding and being passed through a 2mm sieve and stored in sealable plastic bags.

3.2.4 Determination of Soil PH

To measure pH, 10g of the soil sample was mixed with 25 ml of de-ionised water in a 50 ml centrifuge tube, stirred and left to stand for an hour. The sample was then tested using an Orion™ Model 91-72 Sure-Flow pH Electrode (Thermo Fisher Scientific Inc., Waltham, USA) and pH meter (Denver Instruments, Bohemia, New York, USA).

3.2.5 Determination of Extractable K

Two grams of the air-dried soil was placed in 50 ml centrifuge tubes and 30 ml of 1M ammonium acetate was added before being shaken end-over-end for 15 minutes at 30 rpm and then centrifuged at 3000 rpm (RCF:2012) for a further 15 minutes. The supernatant was passed through Whatman No.1 filter paper into a 100 ml volumetric flask. This process was repeated two more times to produce 90 ml of extract. Extractable K was determined from the extract samples using a flame photometer (model 410, Sherwood Scientific Ltd, Cambridge, UK). Standards for K emission were set at: 0, 1, 2, 3, 4 and 5 ppm.

3.2.6 Determination of Extractable P

Plant available phosphorus was determined by sodium-bicarbonate extract (Olsen *et al*., 1954). One gram of airdried and 2mm sieved soil was added to a 50 ml centrifuge tube along with 20 ml 0.5 M $NaHCO_3$ (adjusted to pH 8.5 using 1 M NaOH). The tubes were shaken end-over-end for 30 minutes at 30 rpm, then centrifuged at 3000 rpm (RCF: 2012) for 5 minutes before being filtered through Whatman no.2 filter paper. Concentration of extractable P was determined using the molybdenum blue batch method (DGT Research Ltd, 2024) and analysed using a microplate reader (BMG Labtech, Ortenberg, Germany). Four stock reagents were made prior to analysis, with reagent D being made on the day of analysis. These reagents were:

A. 2.5M H_2SO_4,

B. 1g of ammonium molybdate diluted in 25 ml of de-ionised water,

C. 0.07g of potassium antimonytartrate diluted in 25 ml of de-ionised water,

D. 0.44g of ascorbic acid diluted in 25 ml de-ionised water

A mixed reagent was made up on the day of analysis which consisted of 10 ml of reagent A, 3 ml of reagent B, 1 ml of reagent C and 6 ml of reagent D. For analysis, 200 µl of the sample extract or standard were added to a microplate well (Corning™ Costar™ 96-Well, Cell Culture-Treated, Flat-Bottom Microplate Corning Incorporated, United States) followed by 40 µl of the mixed reagent and left to stand at room temperature for 15 minutes. Once the colour had fully developed, the samples were read at an absorbance of 880 nm. Calibration standards for each microplate were set at: 0, 0.2, 0.4 and 0.6 ppm.

3.2.7 Harvest Procedure

Three samples from each plot were taken at the time of harvest to assess biomass production from each treatment. To ensure sampling was random, a meter square quadrat was thrown onto each plot three separate times and the plant material from inside of each quadrat was collected and sealed in airtight plastic bags before being dried and weighed. The samples were oven dried at 105 °C for 24 hours before being ground in a ball mill in preparation for nutrient analysis. An average dry weight of the three quadtrats from each plot was then recorded for each sampling date.

3.2.8 Tissue Sampling and Analysis

One tissue sample was taken in June and August of each year (comprising of four samples in total). In the first year, analysis was performed at the Lancaster University laboratories using the nitric acid extraction method. Approximately 0.25 g of tissue was digested for 15 minutes with 5 ml 70% anistar HNO_3 using a MARS 5 Microwave Digestion System with MARSXpress vessels (CEM UK, United Kingdom). The samples were diluted to 20% HNO_3 using purified water (Milli-Q® Integral Water Purification System, Merck, Darmstadt, Germany) for storage. Samples were diluted again to 2% HNO_3 for analysis. This was achieved by adding 1 ml of the sample to 9 ml purified water, passing it through 0.45 micron a syringe filter into an acid washed 15 ml centrifuge tube.

Samples were analysed for nutrient and PTE content using Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES). The samples for the second year's harvest were sent away to NRM Laboratories (Bracknell, United Kingdom) for analysis as the Lancaster University laboratories were closed during the COVID-19 lock-down. A standard reference material sample (Trace Elements in Spinach Leaves 1570a, National Institute of Standards and Technology, Maryland, USA) was included with the samples sent away for analysis to ensure consistency between analysis methods.

3.2.9 Partial Nutrient Balance

For this experiment potassium use efficiency was calculated using the Partial Nutrient Balance (PNB) method, which calculates the amount of K that is taken out of the system compared to how much is applied. A PNB of 1 indicates that K input is balanced by the off take from the system, whereas a PNB of less than one suggests that K input exceeds removal and thus soil build-up of K will occur (not accounting for losses through leaching) (Fixen *et al.*, 2015).

The formula for PNB is as follows:

$PNB = U_h/F$

Where U_h is the K content of the harvested portion of the crop, calculated as:

*Biomass(g) * Tissue K Concentration (mg g^{-1});*

and where *F* is the amount of K applied (g).

3.2.10 Statistical Analysis

Statistical analysis was performed using the R software package (R Core Team, 2021). Differences between treatments and sampling dates were determined using multi-way analysis of variance (ANOVA) and post hoc analysis was performed using Tukey's HSD (honestly significant difference) test. Relationships between variables were assessed using the linear regression analysis. The data for biomass, tissue Ca concentration and tissue Mg concentration was log transformed prior to analysis to account for the data being non-parametric.

3.3 Results

3.3.1 Summary

Table 3.3 provides a summary of the effect of harvest and/or sampling date and treatment application on the different parameters measured in this experiment. K fertiliser, CBD, and CKD application all significantly increased biomass production compared to control. CBD application significantly increased soil K availability compared to control and lime treated plots. Lime application significantly increased leaf tissue Ca concentration compared to K fertiliser and lime + K. CBD and CKD application significantly increased leaf tissue K concentration compared to all the other treatments. Lime application significantly increased leaf tissue Mg concentration compared to K fertiliser, lime, lime + K, CBD, and CKD. K fertiliser and lime + K application both reduced tissue Mg content compared to the control. Lime + K application reduced leaf tissue P concentration compared to control and the other treatments had no effect. All responses measured declined over time, but the extent depended on the treatment applied.

Table 3.3: The effect of treatment application, sampling date and the interaction between treatment application and sampling date on the different parameters measured in this experiment. Differences in the means of the different treatments and sampling dates were assessed using ANOVA.

	Biomass	**Soil pH**	**Soil K**	**Soil P**	**Tissue Ca**	**Tissue K**	**Tissue Mg**	**Tissue P**
Treatment Effect	p< 0.01	NS	p<0.05	NS	p<0.001	p<0.001	p<0.001	p<0.01
Temporal Effect	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001	p<0.001
Treatment time Interaction	NS	NS	NS	NS	NS	p<0.001	P<0.001	p<0.001

3.3.2 Biomass Production

Dry weight declined significantly ($p<0.001$) over time across all treatments. As there was no interaction effect between treatment application and harvest date, the post hoc tests were performed on each harvest date separately (Figure 3.3). The first harvest took place 5 months after initial treatment application and produced the highest biomass out of all the harvests (Figure 3.3). Treatment had a significant effect for the first two harvests, but any differences dissipated by the latter two. K fertiliser, CBD and CKD all increased dry weight significantly compared to control at the first harvest (35%, 61% and 57% respectively). The control plots produced a dry weight of 409.67 g m^2, the K fertiliser plots 552.62 g m^2, CBD treated plots 661.48 g m^2 and CKD treated plots 645.86 g m^2. Lime and lime + K fertiliser also increased dry weight, but this was to a lesser degree than the other treatments (487.06 g m^2 and 647.52 respectively). At the second harvest only, CKD treated plots produced biomass that was significantly greater than the control (27%). K fertiliser produced the second highest biomass (173.27 g m^2), but this was not significantly different from the control. A summary of the dry weight produced by each treatment at each harvest date is provided in Appendix B, Table 1.

As CBD and CKD act as an alkalising agent and a K fertiliser, the possibility of there being an additive effect of these two factors was investigated. The CBD and CKD plots were removed from the data set and the remaining factors were analysed (Table 3.4). Biomass was increased with the addition of lime and more so with the addition of K fertiliser, however the greatest increase was seen by adding K fertiliser and lime together, which indicates that there is a significant additive effect on biomass production of adding both lime and K fertiliser. This can explain why CBD and CKD outperformed lime in this experiment.

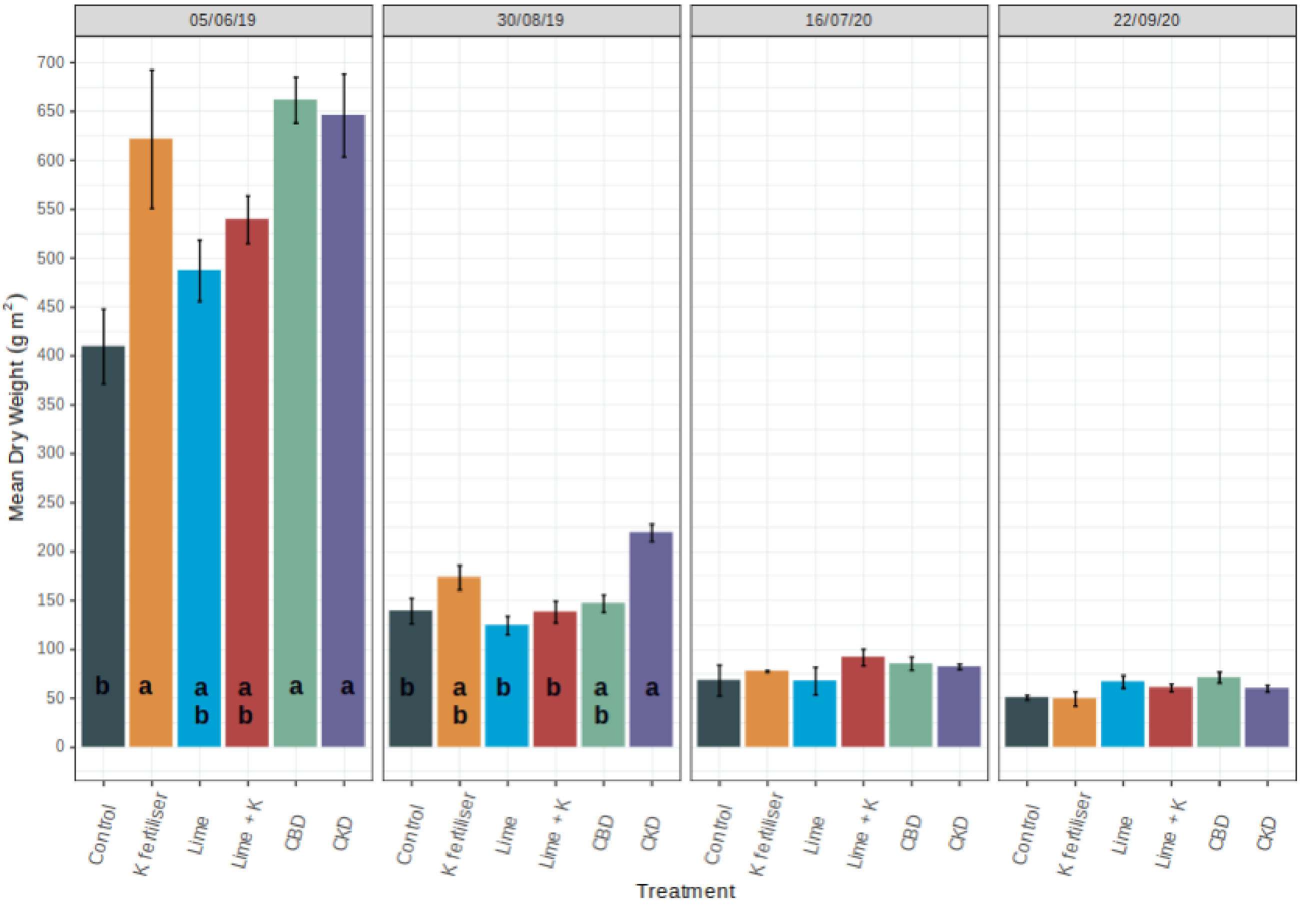


Figure 3.3: The effect of the different soil amendments on the biomass production (measured as dry weight in g m^2) of perennial ryegrass (*L. perenne* L.) grown in the field. Data are means ± SE of 3 plots. The letters inside the bars indicate significant differences in the means as determined by Tukey's pair-wise comparison. As there was no interaction effect between treatment application and harvest date, the letters of mean discrimination refer only to the corresponding harvest date and are note related to the other harvest dates. Where there are no letters presented, there was no significant difference between means.

Table 3.4: Two-way ANOVA results of a subsection of the dataset where CBD and CKD were removed. The data are means ± SE of 3 replicates of 4 treatments. The letters next to the means indicate significant differences in the means as determined by Tukey's pair-wise comparison.

Treatment	Mean Biomass (g m^2)	Treatment Significance
Control	167 ± 44 b	$p<0.05$
K Fertiliser	213 ± 63 ab	
Lime	169 ± 53 b	
Lime + K Fertiliser	235 ± 76 a	

To further explore the relationships between biomass production and the different factors analysed, a series of linear regression analyses were performed (Figure 3.4). Soil pH had a positive relationship with biomass production (R^2 36%, Figure 3.4a) which was significant ($p<0.001$). Soil K availability was more strongly correlated with biomass production (R^2 50%, $p<0.001$, Figure 3.4b). Soil P availability followed a similar pattern (R^2 52%, $p<0.001$, Figure 3.4c).

The leaf tissue concentration of the nutrients studied had a positive association with biomass production and this varied between the nutrients studied (Figure 3.5). Biomass production was most strongly correlated with tissue K concentration ($p<0.001$, R^2 57%), followed by tissue Ca concentration ($p<0.001$, R^2 56%), tissue Mg concentration ($p<0.001$, R^2 41%) and P concentration ($p<0.001$, R^2 36%).

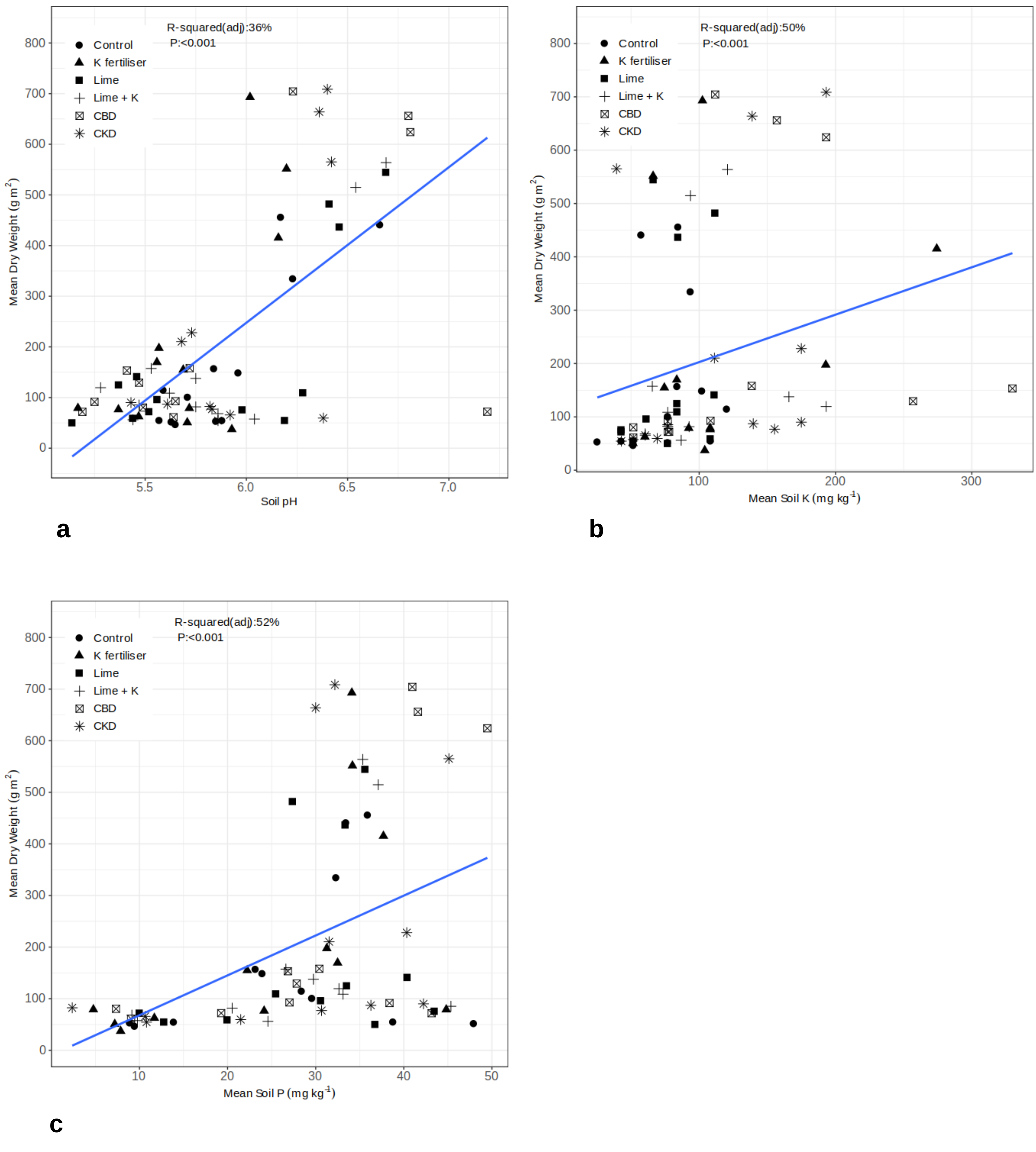


Figure 3.4: The relationship between soil pH (a), soil K availability, or (b) soil P availability (c) on biomass production. The differing symbols represent the different treatment applied. Each symbol represents one of 12 replicates (3 replicates across 4 sampling dates). The text along the top of the plot represents the adjusted R^2 and P value obtained using linear regression analysis.

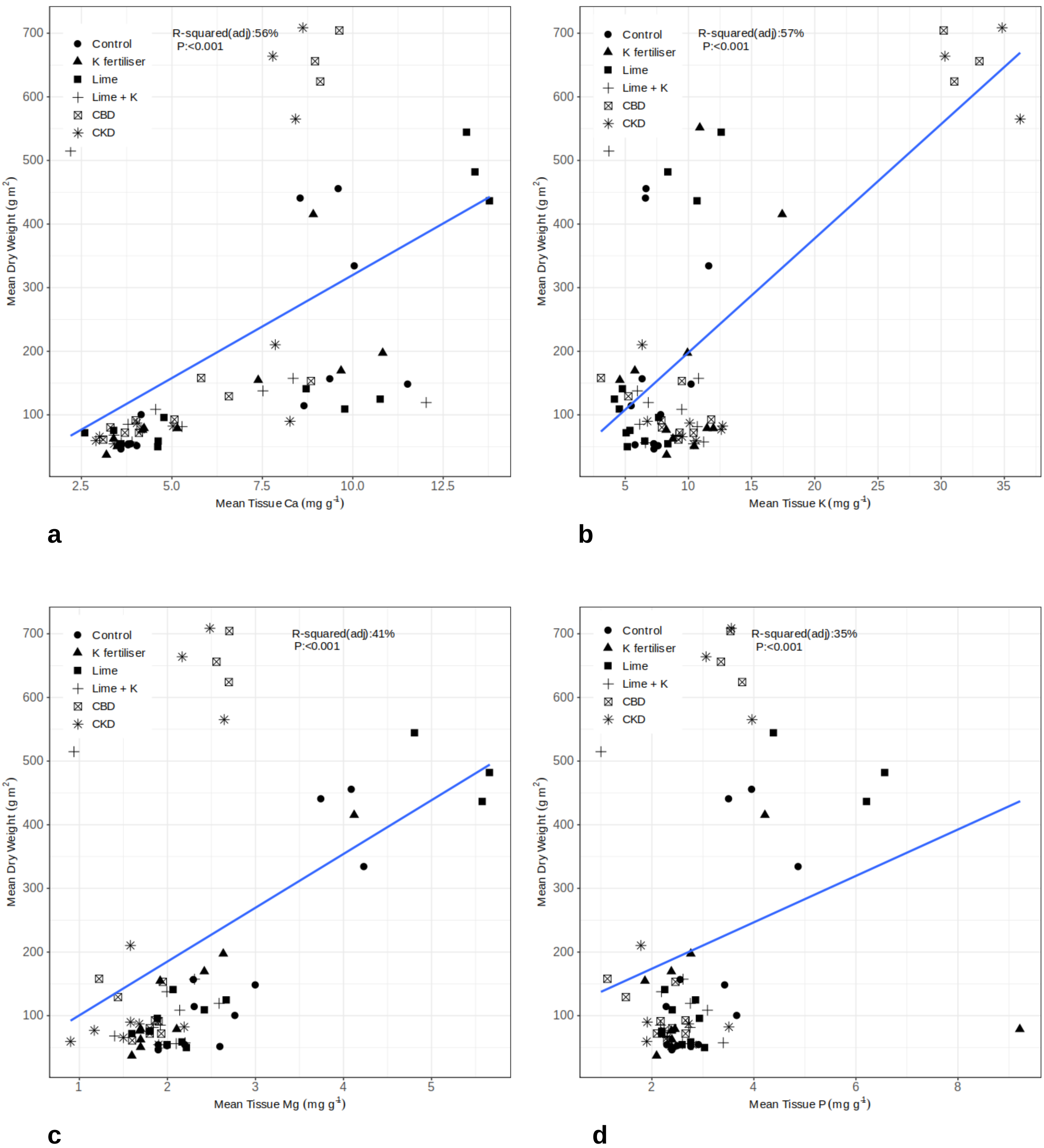


Figure 3.5: The relationship between leaf tissue Ca (a), K (b), Mg (c), or P (d) concentration on biomass production. The differing symbols represent the different treatment applied. Each symbol represents one of 12 replicates (3 replicates across 4 sampling dates). The text along the top of the plot represents the adjusted R^2 and P values obtained using linear regression analysis.

3.3.3 Soil PH

Soil pH initially increased from 5.7 (averaged across all treatments) before product application (03/01/19) to 6.4 after product application (05/06/19) before decreasing to 5.3 towards the beginning of 2020. Sampling date was the only factor that significantly impacted soil pH ($p<0.001$). By the end of the experiment, the lime, lime + K fertiliser and the CKD treated plots had the highest pH but again, were not deemed significantly different from control.

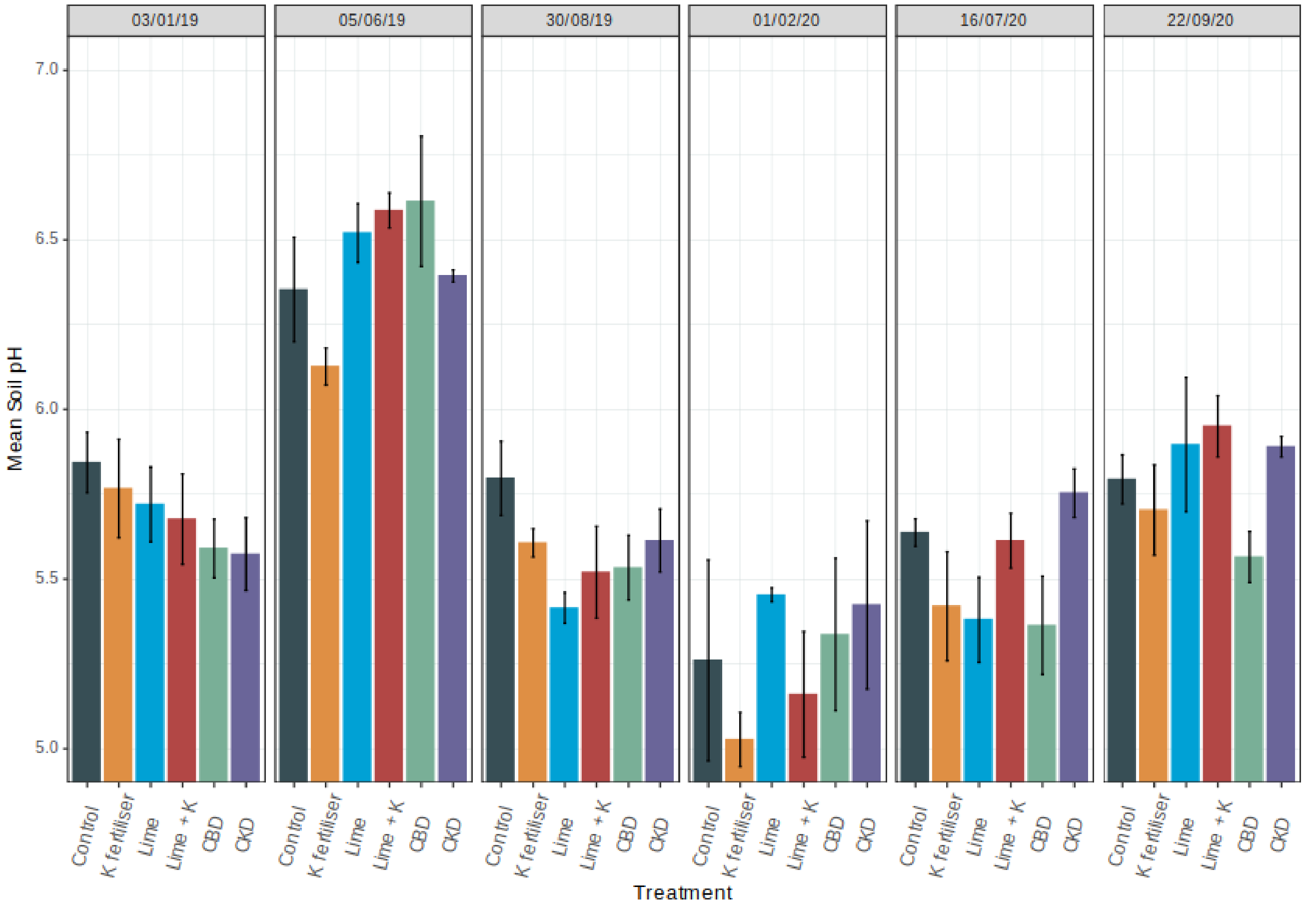


Figure 3.6: The effect of the different soil amendments on soil pH over 6 sampling dates. The bars represent means ± SE of 3 plots.

3.3.4 Soil K Availability

Both harvest date and treatment application significantly affected soil K availability ($p<0.001$ and $p<0.05$ respectively. See Figure 3.6). CBD increased soil K availability the most compared to control (1.4-fold), however this effect dissipated after the first year. The control plots had a K availability of 102.06 mg kg^{-1} compared to the 241.72 mg kg^{-1} of the CBD plots. The K availability of the control plots decreased over time and by the end of the experiment had the lowest K availability at 39.95 mg kg^{-1}. The lime treated plots followed a similar pattern decreasing to 45.81 mg kg^{-1} from 87.60 mg kg^{-1}. K fertiliser application produced the second highest K availability (147.90 mg kg^{-1}) at the initial sampling date, which gradually declined to 72.16 mg kg^{-1} by the end of the experiment. CKD treated plots followed a similar pattern to those treated with CBD, with the highest K availability (140% increase from control) being recorded at the second sampling date (241.72 mg kg^{-1}), 7 months after application. CBD was much more effective at increasing K availability than CKD initially but the drop in the second year was sharper. The decline in K availability in CKD treated plots was more gradual, although initial values were lower than those seen with CBD. By the end of the experiment plots treated with K fertiliser, lime + K, CBD and CKD all had similar K availability. Control plots and those treated with lime alone were lower but not significantly different. A summary of the soil K availability produced by each treatment at each harvest date is provided in Appendix B, Table 3.

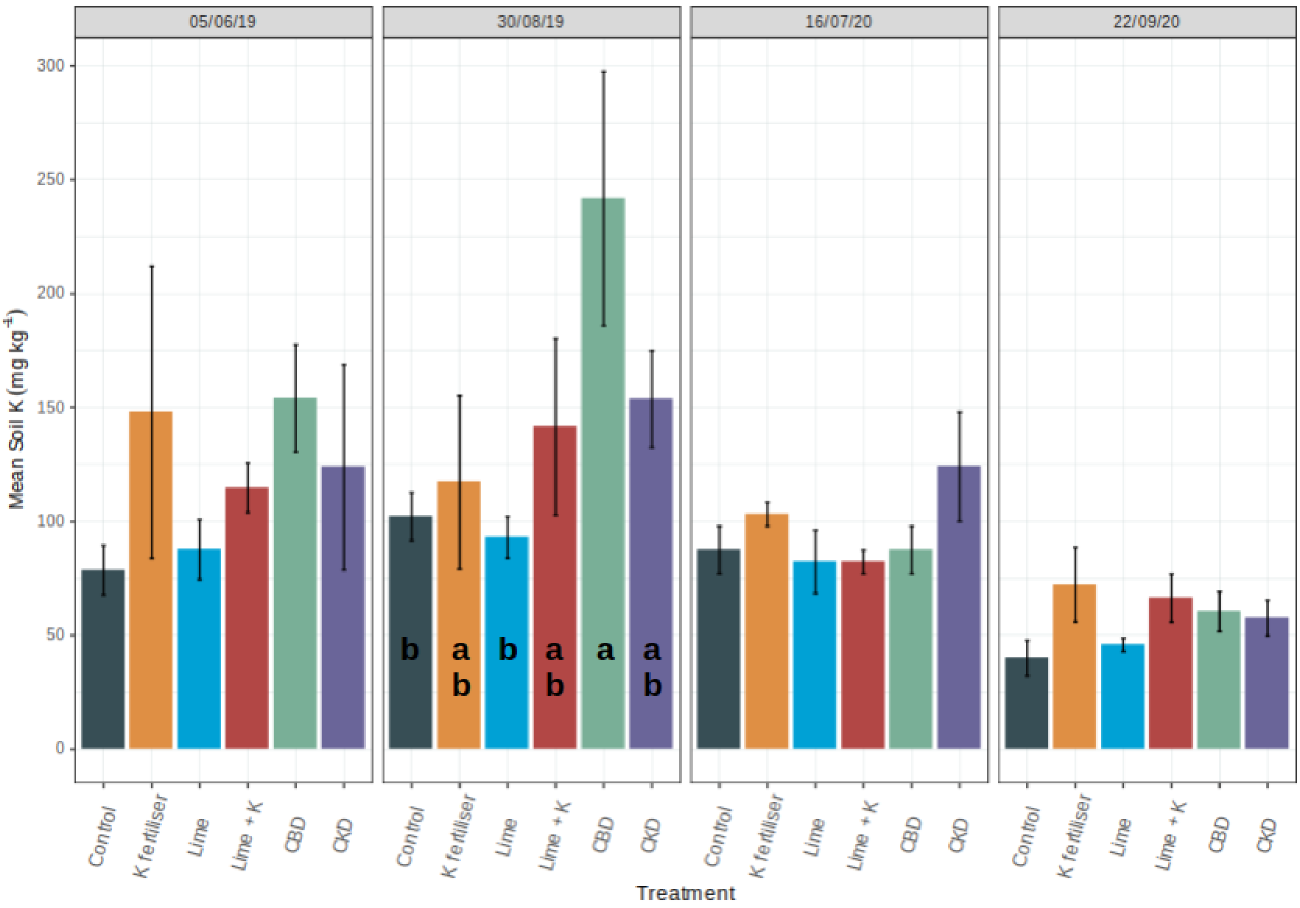


Figure 3.7: The effect of the different soil amendments on soil K availability over 4 sampling dates. Data are means ± SE of 3 plots. The letters inside the bars indicate significant differences in the means as determined by Tukey's pair-wise comparison. As there was no interaction effect between treatment application and harvest date, the letters of mean discrimination refer only to the corresponding harvest date and are not related to the other harvest dates. Where there are no letters presented, there was no significant difference between means.

3.3.5 Soil P Availability

Soil Olsen P declined over time regardless of the products applied ($p<0.001$), which had no significant effect. Olsen P was lowest at the final harvest, declining from 36.42 to 13.75 mg kg^{-1} across all treatments. There were no statistical differences between the different treatments. There was also no correlation between soil pH and soil P availability.

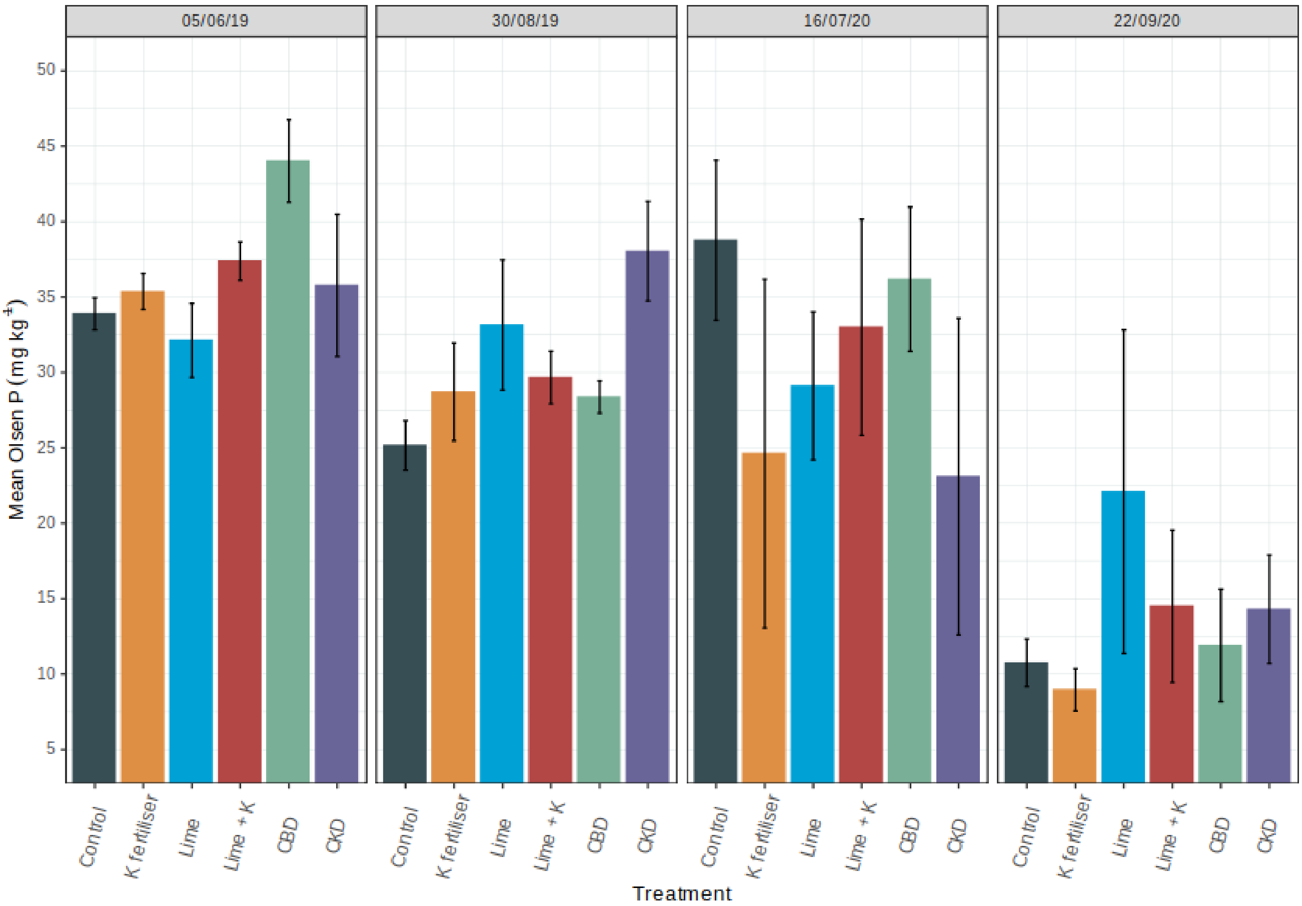


Figure 3.8: The effect of the different soil amendments on soil P availability over 4 sampling dates. Data are means ± SE of 3 plots.

3.3.6 Tissue Ca

At the initial harvest, lime application increased leaf tissue Ca concentration by 43% compared to the untreated control plots ($p<0.01$). The control lots had a mean Ca concentration of 9.40 mg g^{-1} and the limed ones 13.44 mg g^{-1}. CBD and CKD application produced similar Ca concentrations to the control initially (9.23 and 8.28 mg g^{-1} respectively). After the initial harvest, tissue Ca concentrations decreased significantly across all treatments ($p<0.001$) and did not differ between treatments. Thus, lime application only transiently increased tissue Ca concentrations (see also Appendix B, Table 5).

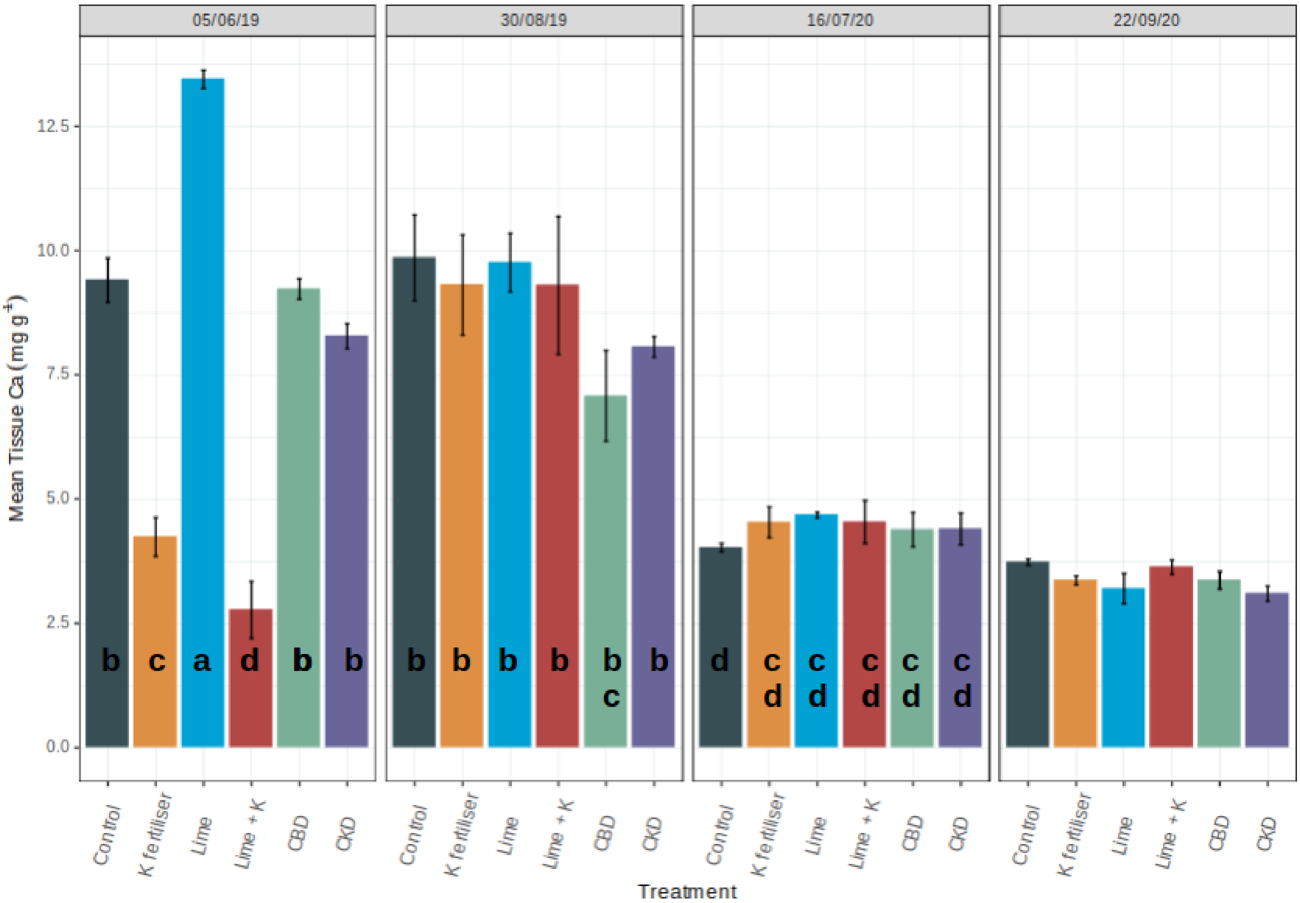


Figure 3.9: The effect of the different soil amendments on leaf tissue Ca concentration over 4 sampling dates. Data are means ± SE of 3 plots. The letters inside the bars indicate significant differences in the means as determined by Tukey's pair-wise comparison. As there was no interaction effect between treatment application and harvest date, the letters of mean discrimination refer only to the corresponding harvest date and are not related to the other harvest dates. Where there are no letters presented, there was no significant difference between means.

3.3.7 Tissue K

CBD and CKD application significantly increased tissue K concentration by 280% and 310% respectively, compared to all other treatments, including the control ($p<0.001$). The control plots had a K concentration of 8.31 mg g^{-1} compared to the 31.42 mg g^{-1} of the CBD plots and the 33.79 mg g^{-1} of the CKD plots. The other treatments did not produce K concentrations that were significantly different from the control (Figure 3.10 and Appendix B, Table 6). Tissue K concentration declined significantly over time and this effect differed depending on the treatment applied ($p<0.001$ for both harvest date and the interaction between treatment application and harvest date). CBD and CKD treated plots had the sharpest decline such that K concentrations were similar between treatments by the second harvest.

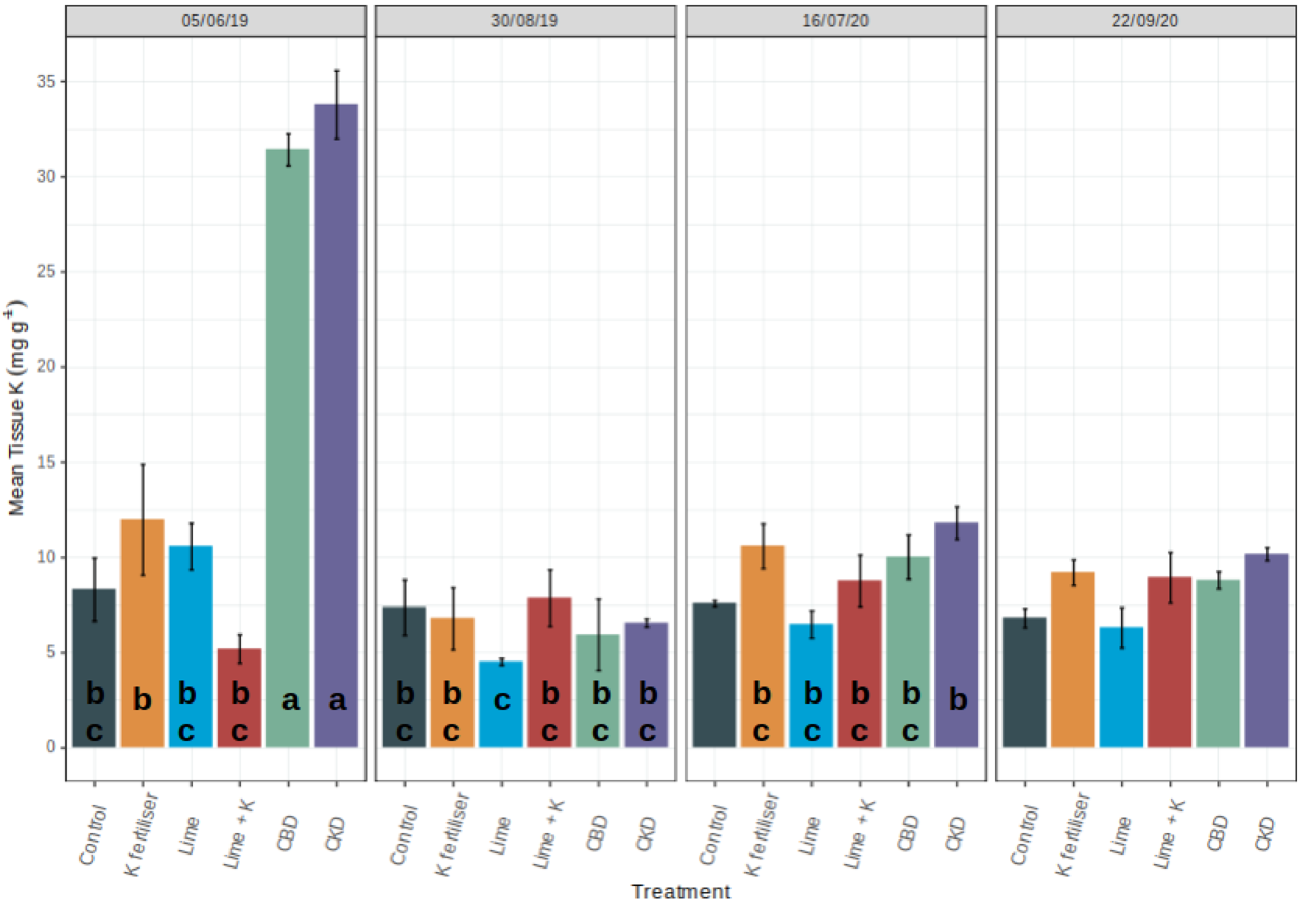


Figure 3.10: The effect of the different soil amendments on leaf tissue K concentration over 4 sampling dates. Data are means ± SE of 3 plots. The letters inside the bars indicate significant differences in the means as determined by Tukey's pair-wise comparison. Where there are no letters presented, there was no significant difference between means.

The PNB of K potassium containing products was calculated to compare the agronomic efficiency of the K supplied by CBD, CKD, K fertiliser and lime + K (Figure 3.9). These four products were chosen because they either alter pH, supply K or both, and are therefore comparable. The PNB for the CBD, CKD, K fertiliser and lime + K remained lower than 1, indicating that the K inputs for this experiment exceeded the K taken off by harvesting, however the extent of this varied by treatment and harvest. At the first harvest, CKD and CBD had a PNBs that were almost twice as high as K and lime + K fertiliser. The PNB of all products increased with every harvest date, however CBD and CKD remained higher throughout.

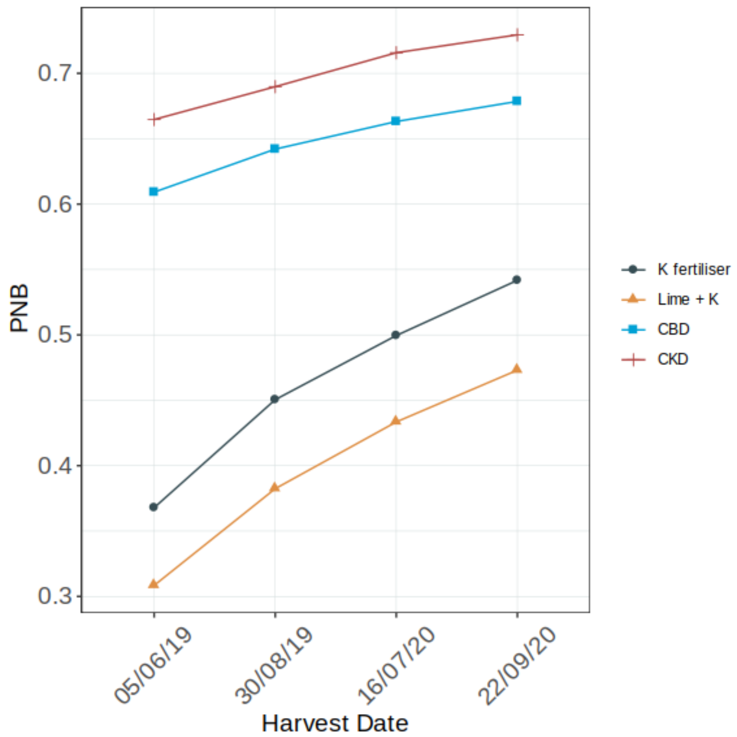


Figure 3.11: Partial Nutrient Balance (PNB) of perennial ryegrass treated with lime + K fertiliser, CBD and CKD. Data are means of 3 plots.

3.3.8 Tissue Mg

Treatment application, harvest date and the interaction between treatment application and harvest date all significantly ($p<0.001$) influenced leaf tissue Mg concentration. Initially, lime application increased Mg concentration compared to the CBD and CKD treatments but did not differ from the control. Control plots had a tissue Mg of 4.02 mg g^{-1} compared to limed plots which had 5.53 mg g^{-1}, CBD which had 2.65 mg g^{-1} and CKD which had 2.42 mg g^{-1}. K fertiliser and lime + K decreased Mg concentration compared to control (2.27 mg g^{-1} and 1.02 mg g^{-1} respectively). However, from the second harvest onwards Mg concentration remained higher in the control plots and at the final harvest (2.54 mg g^{-1}) and, CKD treated plots had significantly lower tissue Mg concentration than the control (1.58 mg g^{-1}). Tissue Mg increased as soil pH increased ($p<0.001$), however this relationship only accounted for 15% of the variation in tissue Mg in this experiment.

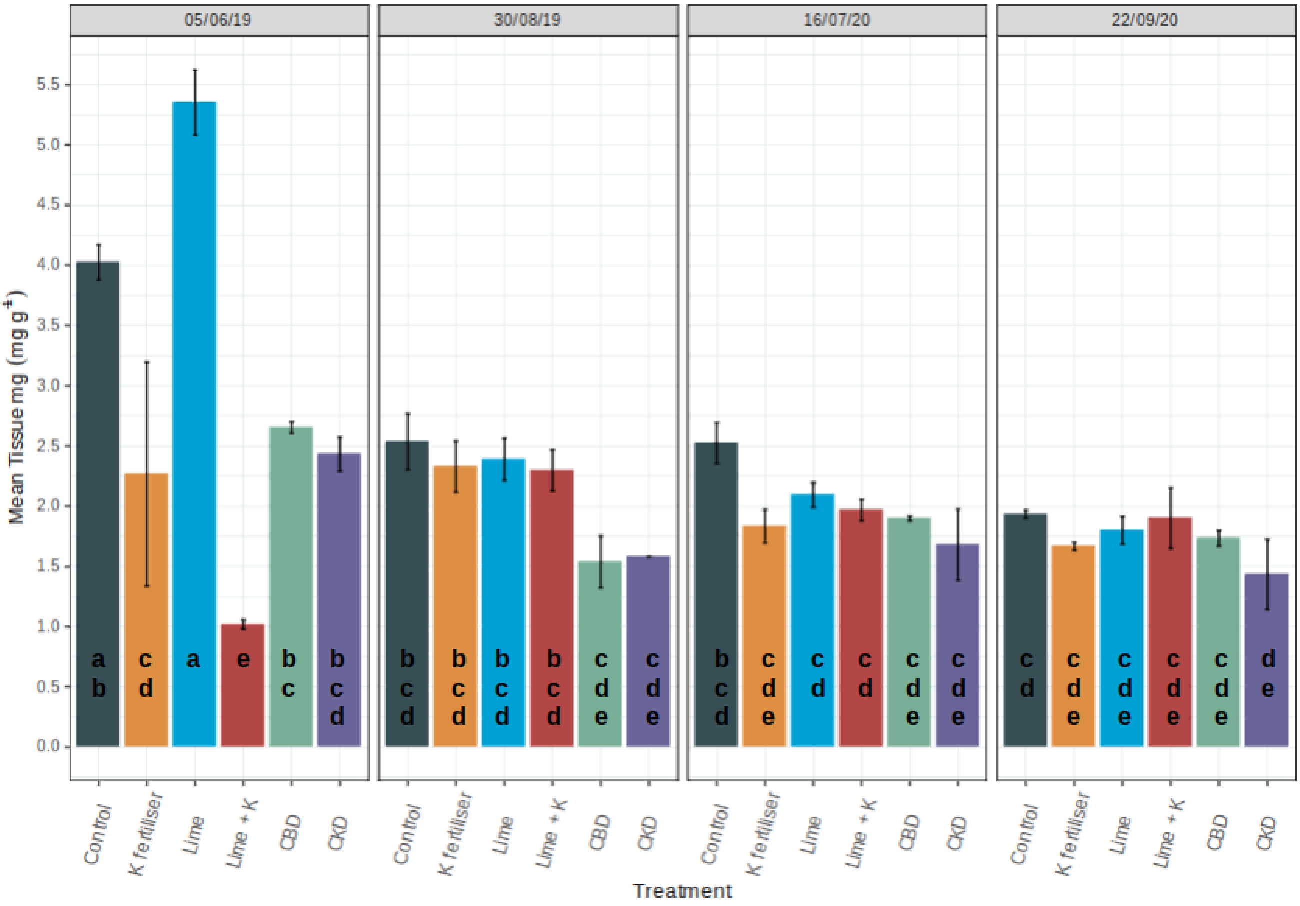


Figure 3.12: The effect of the different soil amendments on leaf tissue Mg concentration over 4 sampling dates. Data are means ± SE of 3 plots. The letters inside the bars indicate significant differences in the means as determined by Tukey's pair-wise comparison.

3.3.9 Tissue P

Leaf tissue P concentration was influenced by treatment application at the first harvest ($p<0.001$) (Figure 3.13, Appendix B, Table 8). The interaction between treatment application and harvest date was also significant ($p<0.001$), meaning that tissue P concentration declined over time, but the extent of the decline differed between treatments. Lime application increased leaf tissue P by 40% compared to control at the first harvest date (5.72 mg g^{-1} and 4.12 mg g^{-1} respectively). CBD and CKD application did not differ from control and lime + K fertiliser reduced P concentration by 73% compared to the control (1.11 mg g^{-1}).

The P concentration of the lime and control treatments decreased over time. K fertiliser treated plots remained mostly the same except for the 16/07/19 harvest, which was slightly elevated, however there was no significant difference in the P concentration from the beginning to the end of the experiment. The P concentration of lime + K plots also remained mostly the same throughout the experiment, with no significant differences seen between the first and last harvests. The P concentration of CBD and CKD treated plots decreased also. The leaf tissue P concentration of CBD treated plots was 3.56 mg g^{-1} at the first harvest and decreased to 2.27 mg g^{-1} by the final harvest. The leaf tissue P concentration of CKD treated plots decreased from 3.53 to 2.33 mg g^{-1}. By the end of the experiment, there were no differences between the treatments. Soil pH only had a small positive influence on leaf tissue P concentration ($p<0.05$, R^2 6%, Figure 3.4d).

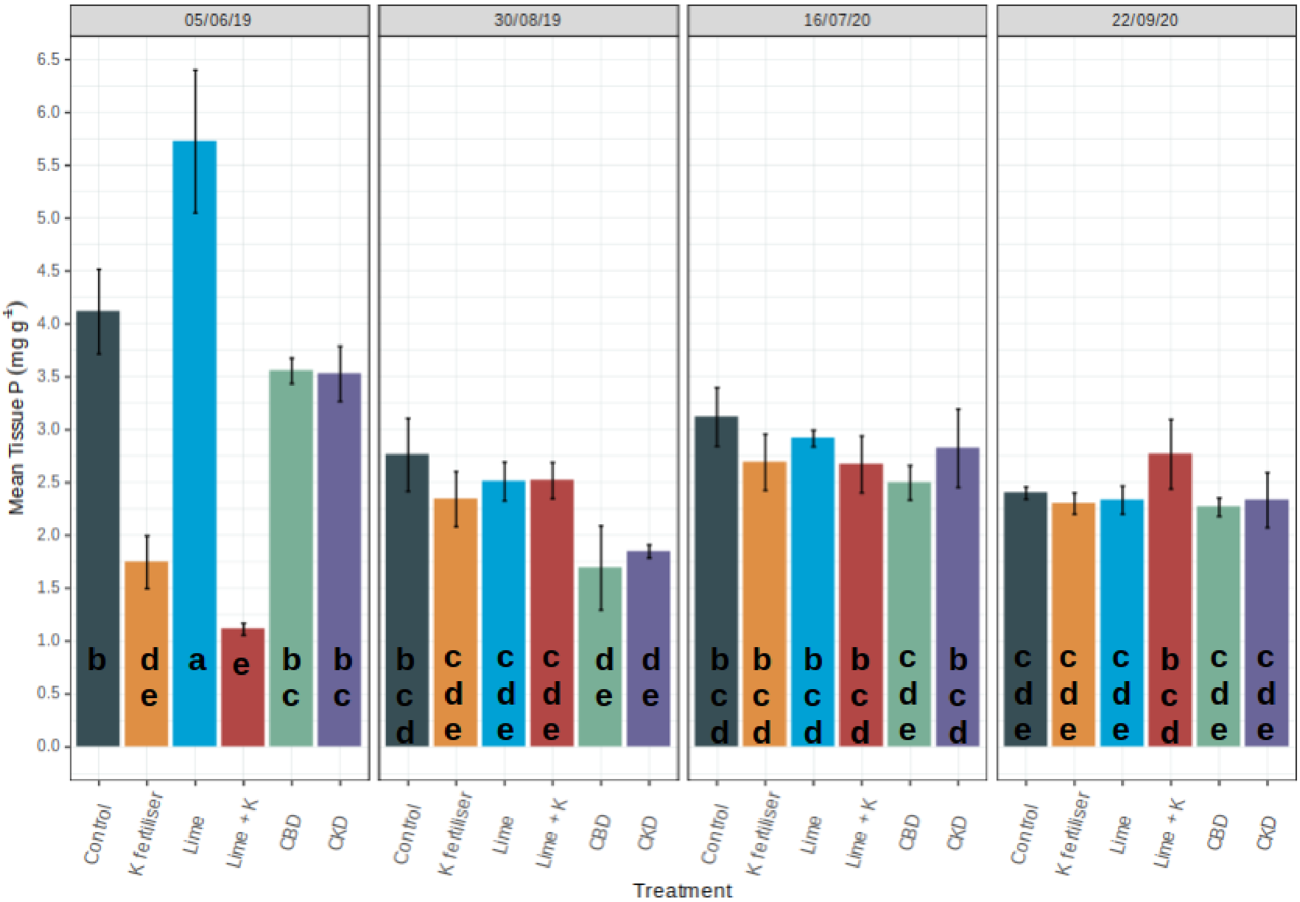


Figure 3.13: The effect of the different soil amendments on leaf tissue P concentration over 4 sampling dates. Data are means ± SE of 3 plots. The letters inside the bars indicate significant differences in the means as determined by Tukey's pair-wise comparison.

3.3.10 Tissue PTE Content

PTE concentration of leaf tissue did not differ significantly between the untreated control plots and those treated with CBD or CKD. Although CBD and CKD increased soil pH which can in turn decrease the availability of PTEs, there was no correlation between leaf tissue concentration of any of the elements assessed and soil pH (Table 3.5).

Table 3.5: The leaf tissue PTE concentration (mg g $^{-1}$) of perennial ryegrass treated with CBD, CKD, and lime + K fertiliser. Data are means ± SE of 3 plots.

	PTE concentration of plant tissue (mg g $^{-1}$)				
	As	*Cd*	*Cr*	*Pb*	*Se*
Significance	NS	NS	NS	NS	NS
Control	3.5 ± 0.9	10.6 ± 3.8	4.9 ± 0.5	5.7 ± 2.3	2.7 ± 0.8
CBD	1.9 ± 0.5	9.6 ± 2.5	9.1 ± 2.7	4.4 ± 1.2	1.6 ± 0.8
CKD	0.64 ± 0.3	5.9 ± 0.8	5.7 ± 0.8	3.8 ± 1.3	1.0 ± 0.6
Correlation With pH	NS	NS	NS	NS	NS

3.4 Discussion

This experiment set out to determine if CBD and CKD were as effective as agricultural lime and/or K fertiliser at promoting the growth of a ryegrass pasture growing on a soil with low K availability that required pH correction. Both CBD and CKD increased biomass significantly compared to the untreated control plots (Figure 3.3). The biomass produced by the CBD and CKD plots was comparable to that of the plots treated with K fertiliser supplied at the recommended rate and higher than the plots treated with lime and a combination of lime and K fertiliser. The combination of alkalising agent and K application appeared to have an additive effect on biomass production as when CBD and CKD were taken out of the analysis, lime + K produced the highest biomass. This is reflected in the findings of Lalande *et al.*, (2009), who observed that lime and K fertiliser on their own did not promote maize (*Zea mays* L.) yield compared to the CKD treated plots. However, biomass decreased sharply by the second harvest, where only plots treated with CKD had higher biomass than the control. In contrast to this experiment, the growth promoting effects observed by Rodd *et al*. (2010) carried over into the succeeding year with CKD increasing yield compared to the control and limed plots by 38% and 25% respectively. These contrasting results could be explained by the fact that the field in this experiment did not receive any N inputs and consequently N deficiency is likely the reason for the drop-off in biomass after the first year. Due to the limitations of the analysis methods used in this experiment, it was not possible to assess N uptake to verify this.

CKD application each year increased the yield of potato by 15-99% when applied at 0.5-2 t ha^{-1} (averaged across two fields over two years (Lafond and Simard, 1999)). In contrast, lime application reduced yield by 5-21% when applied at the same rate, which was attributed to decreased extractable K and Mg content. Furthermore, commercial fertiliser application (as K_2O at 50-200 kg ha^{-1}) only increased yield by up to 33%. Again, this highlights the additive effect of the alkalising properties and K content of the CKD as the lime and K fertiliser on their own were not enough to meet the yield promotion observed in the CKD treated plots. Experiments by Van Lierop, Tran and Morissette (1982) found that CKD increased yield as well as K_2SO_4 when applied at equivalent rates, increasing the yield of potato, barley and alfalfa yield by 8%, 17% and 14% when compared to control when applied at 200 kg ha^{-1}. These findings support those observed in this experiment and imply that the growth promoting effects of the CBD and CKD result from an additive effect of their alkalising properties and K content.

In addition to plant growth, the soil alkalising effect of CBD and CKD was compared to that of lime (figure 3.5). CBD application increased soil pH to a similar degree as lime and lime + K fertiliser at the second sampling date, four months after initial application. CKD on the other hand, did not change pH to a degree which was different from control at this point. However, by the end of the experiment the soil pH in CKD treated plots was similar to that of lime and lime + K. On the final sampling date, the CBD treated plots were lower than the other treatments, including the control. The difference in soil pH response between the two cement dusts may have been due to differences in particle size as the CBD had a fine, powdery consistency and the CKD was comprised of larger aggregates. As the efficacy of a liming agent depends on its reactivity, which in turn relies on particle size (Goulding, 2016), the CBD would be quicker to react and therefore change soil pH to a greater degree in a shorter amount of time than the CKD, which would have taken longer to react and increase soil to a lesser degree but over a longer period. Therefore, over the span of two years, CKD was as effective as lime and lime + K at increasing soil pH and CBD less so as it appears more reactive. Interestingly, the soil pH of all the plots fluctuated over the course of the experiment and appeared to follow a seasonal pattern. All plots saw an increase in pH by June of the first year (2019), before decreasing again by August with a smaller increase seen again in July of 2020. Seasonal trends in several soil parameters including pH have been observed in the literature (Wuest, 2015). This is thought to be a result of seasonal temperature changes affecting microbial activity and thus nutrient cycling and the rate of reactions such as the lime reaction in soil (Campbell *et al*., 1999). As the soil pH in this experiment increased in the warmer months and decreased in winter, this is likely the explanation for the variation observed.

At the first sampling date after treatment application, CBD, CKD, and K fertiliser increased soil K availability by up to 140% compared to the control plots and those treated with lime. Almost 3 months later, the soil K availability of the CBD plots was nearly double that of the CKD, K fertiliser and lime + K plots. This effect lasted until 18 months after treatment application. Soil K availability declined over time and by the end of the experiment there were no treatment differences, as expected due to off-take by the four harvests. These findings indicate that CBD and CKD were as effective as conventional fertiliser at increasing soil K availability in addition to their soil alkalising properties and would require annual re-application to maintain soil K status. Likewise, Lafond and Simard (1999) and Lalande *et al.* (2009) observed similar increases in soil K availability resulting from CKD application. Although CBD treatment increased the K availability considerably more than the K fertiliser and lime + K, it does not mean that the increase is being utilised by the ryegrass, especially as the effect is not maintained in the second year. Given the propensity of K to be leached from soils (Kayser *et al*., 2007; Römheld and Kirkby, 2010), it is possible that the extra K added by CBD application is being lost. Because of this, plant K uptake and K use efficiency were also examined.

When compared to K fertiliser, lime + K fertiliser, and the control, the application of CBD and CKD enhanced tissue K content. This is to be expected as the amount of K supplied by CBD and CKD (373 and 379 kg ha^{-1}) at the 5 t ha^{-1} required to correct soil acidity is considerably greater than the 150 kg ha^{-1} supplied by the fertiliser used. However, there was a considerable drop off in tissue K content after the first harvest, after which, K fertiliser, lime + K, CBD and CKD treated plants all had similar tissue K content. The PNB for the K and lime + K treatments was significantly lower than the CBD and CKD and therefore more K was being put into these plots than taken out. The PNB for all treatments increased over time, which is to be expected as there was only one input of K at the beginning of the experiment. However, the PNB remained below 1 across all treatments, meaning that further application of any of the treatments is likely to result in K build up in the soil and/or risk leaching. Even though CBD and CKD application is more efficient in terms of PNB, this does not mean that the K being added is not being wasted because the increased K uptake from CBD and CKD application did not translate to a growth advantage over the K or lime + K treatments. This indicates that luxury uptake is occurring, which can occur in grasses during periods of rapid growth and risks reducing Mg uptake (Øgaard *et al*., 2001; Karam *et al*., 2009; Jiang *et al*., 2018; Soratto *et al*., 2020), although this was not the case in this experiment (Figure 3.10). Because the excess K supplied from CBD and CKD application is not required for plant growth and a lower application rate could be sufficient to meet crop demand. However, as mentioned previously, current regulation in GB means CBD/CKD cannot be applied every year at liming rates and applying at lower rates is not profitable to the businesses supplying the CBD/CKD (J Silverwood 2021, personal communication [email], 09 July). Therefore, although lower, more frequent application rates of CBD and CKD could be used as K fertiliser substitutes, this is unlikely to happen in GB under current regulation (Sludge (Use in Agriculture) Regulations 1989. Statutory Instrument No. 1263 (Anon, 1989)). Guidance for these regulations claims they are in place to promote sustainable agricultural practice (Anon, 2018), yet when applied to use of CBD/CKD it is promoting unsustainable practice through wasting a valuable source of K that could otherwise be used in place of conventional fertiliser. It therefore raises the question as to whether this guidance is fit for its intended purpose, especially as interest the use of diverted industrial waste as agricultural amendments is increasing (Singh *et al*., 2021; Mabrouk *et al*., 2023).

While the P index of the soil in the field site was sufficient to meet the crop demand (see Table 3.1 and RB209 (AHDB (2023b)), the effect of the alkalising treatments on soil P availability (measured as Olsen P) was analysed as soil pH affects P availability (Brady and Weil, 2017). Both lime and CKD decreased P availability in some cases (Lalande *et al.*, 2009; Rodd *et al.*, 2010), and the soil pH prior to treatment application was below the optimal range for P availability (pH 5.2). However, Olsen P did not vary between the treatments during the experiment (Figure 3.10). Soil P availability declined by the end of the experiment, likely due to off take rather than altered soil pH as the soil pH remained in the optimal range throughout. Furthermore, soil pH and soil P availability were not correlated. In contrast, lime application increased P uptake even though soil P availability was high initially (Figure 3.11). CBD and CKD had no effect on P uptake compared to control plots. However, P concentration explained little of the variation in biomass production (R^2 35%), probably because P availability was not limiting to growth as there were already sufficient reserves in the soil. Therefore, in this is experiment it was not possible to assess whether CBD or CKD could improve P uptake through remediation of soil pH. This also meant that it was not possible to determine any potential interactions between CBD and CKD and P fertiliser application. Although a positive relationship between liming and soil P availability has been demonstrated (Kisinyo *et al*. 2013; Osundwa *et al*., 2013; Börjesson and Kirchmann, 2022), liming to a pH of above 6 can result decreased P solubility through precipitation with Ca (Haynes, 1984; Hinsinger, 2001; Curtin and Syeres, 2001; Bolan *et al*., 2003) which in turn can decrease dry weight production in some species (Bartlett and Picarelli 1973; He *et al*., 2010; Rothwell, Elphinstone and Dodd, 2015). Therefore, more experimentation is required to address potential changes in P availability resulting from pH increases and Ca supply from CBD and CKD application. Additionally, this experiment was restricted to one species (perennial ryegrass), which is one of several species used for grazing livestock (McCarthy *et al*., 2020).

The uptake of the other nutrients studied was not changed meaningfully by CBD or CKD application either. Leaf tissue Ca concentrations were not impacted by CBD or CKD application, whereas lime application resulted in an increase when compared to the control and other treatments. Leaf tissue Mg concentration responded in a similar manner, with lime application increasing concentration compared to control and CBD/CKD application producing no difference from control. This may have been due to the greater increase in soil pH resulting from lime application (Figure 3.10 and 3.5). Therefore, the biomass increases seen with CBD and CKD application appear to be a result of improved K availability and uptake for several reasons. Firstly, the field site soil was determined to be K index 0 (AHDB, 2023b) and was therefore limiting to growth if left unamended and as a result, the untreated control plots had the lowest biomass production of all the treatments. Soil K availability and K uptake were both correlated with biomass production (R^2: 50% and 57% respectively). Furthermore, all plots where K was applied (through either fertiliser, CBD or CKD) produced higher biomass the than the control and lime treated plots, which did not receive a form of K. Finally, there is an additive effect of both the application of K fertiliser and liming agent as when CBD and CKD are removed from the analysis of biomass production, lime + K application produces the highest biomass compared to the other treatments (Table 3.4).

CKD and CBD application didn't alter uptake of As, Cd, Cr, Pb and Se compared to control (Table 3.5). It therefore it appears that any PTEs that are being added are not being taken up by the plants. These findings are supported by Lalande *et al.*, (2009) who found that CKD application of up to 10 t ha^{-1} have been found to have no effect on availability of Cd, Cr, and Pb. Soil pH did not influence uptake of these elements but it also but unclear if further acidification over time would change this dynamic as their availability will increase in soils with a pH lower than 5 (Xian and Shokohifard, 1989; Eich-Greatorex *et al*., 2007; Kumar *et al*., 2022). As the experiment was conducted over two years, the results cannot tell us whether this has any long-term implications as presumably regular application of CBD or CKD will add to the stores of these elements in the soils.

In summary, CBD and CKD are as effective as lime combined with K fertiliser at improving biomass, K availability and K uptake in a low K soil requiring pH correction. However, as these effects are only seen in the harvests for the first year, re-application of CBD/CKD at liming rates might be necessary to make it comparable to conventional fertiliser and lime application practice in terms of growth promotion. But the amount of K applied by applying CBD/CKD at rates required to correct soil pH is above that required by the plants for growth, meaning that the rest of the K is being lost as soil K availability declines after the first year also. Therefore, re-application at lime rates would also waste more K, meaning it is more agronomically efficient to apply CKD/CBD at rates designed to improve soil K status than to correct for pH, especially for CKD which was less effective than lime in increasing soil pH when applied at the same rate. Although the addition of PTEs to the soil resulting from CBD/CKD application is potentially problematic, it does not influence uptake of these elements. While this study utilised a field planted with a single species (ryegrass), numerous studies have demonstrated the potential of mixed swards to improve soil fertility without additional fertiliser inputs and clover is often used to improve livestock nutrition and soil fertility (Bryant *et al*., 2017; Dineen *et al*., 2018). Therefore CBD/CKD could be combined with nutrient management methods such as intercropping to improve soil fertility and nutrient uptake whilst minimising inputs such as traditional sources of fertiliser. However, it is unclear how different pasture species such as clover would respond to CBD/CKD application. Clover prefers slightly acidic soil pH and an increase in pH resulting from CBD/CKD application could impact the growth and/or nutrient uptake of clover. Therefore, further experimentation is required to determine if this is an effective strategy.

CHAPTER 4: THE EFFECT OF INTER-PLANT COMPETITION ON RESPONSE TO LIME, CBD, AND P FERTILISER APPLICATION

4.1 Introduction

Legume based agriculture is becoming increasingly important as a source of crop available N due to the increasing costs of artificial fertilisers (Pulina *et al.*, 2023) and environmental concerns regarding application rates in excess of crop demands (Xu *et al.*, 2020). Mixed pasture with white clover (*Trifolium repens* L.) as the predominant forage legume has a long history in parts of Western Europe (Peyraud, Le Gall & Lüscher, 2009). Clover is recommended by the AHDB as an addition to British livestock systems as a source of protein for ruminant livestock (EBLEX, 2017) that will preferentially consume it over ryegrass (Sharp, Edwards & Jeger, 2012).

There are numerous benefits of adding legumes such as white clover to different cropping systems, including pasture. They add biodiversity, break pest and disease cycles and improve soil structure by adding organic matter (Stagnari *et al.*, 2017). Furthermore, their most valuable contribution is improving soil fertility through symbiotic nitrogen fixation (Houngnandan *et al.*, 2000) and enhancing phosphorus mobility in the rhizosphere (Bekele *et al.*, 1983; Hinsinger and Gilkes, 1997). Herbaceous and grain legumes can leave substantial amounts of N in the soil after harvest (Kihara *et al.*, 2010), producing yield benefits equivalent to 150-350 kg ha^{-1} fertiliser N input (Peyraud, *et al.*, 2009). This potential reduction in N fertiliser input mitigates greenhouse gas emissions associated with its production and makes adding legumes a suitable alternative to synthetic N in low input cropping systems (Stagnari *et al.*, 2017). Phosphorus mobilisation can be facilitated by adding legumes via several mechanisms, such as rhizosphere acidification (which releases phosphate bound in applied rock phosphate) by and root exudation of citrate (which releases phosphate bound to calcium-phosphate (Ca-P) complexes) (Pypers *et al.*, 2007). Furthermore, legume exudation of organic acids can form stable complexes with Fe and Al thus decreasing P precipitation in the soil solution (Teles *et al.*, 2017). Other strategies include symbiosis with mycorrhizal fungi and the formation of proteoid roots (as seen in lupin species) that alter soil pH through carboxylate exudation, thereby mobilising P through chelation of soil minerals (Péret *et al.*, 2011; Preece and Peñuelas, 2020).

The mobilisation of P by legumes can benefit neighbouring plants, for example, maize (*Zea mays* L.) produced 43% more grain yield when grown with faba bean (*Vicia faba* L.) compared to a maize monocrop when grown in a phosphorus deficient soil (Li *et al.*, 2007). Exudation of citrate and acid phosphatase from faba bean increases P availability in the rhizosphere that promotes root proliferation, P uptake and shoot growth in neighbouring maize (Zhang *et al.*, 2016). Similar interactions have been observed in field pea (*Pisum sativum*)/maize mixes, where field pea lowered rhizosphere pH by secreting acid and alkaline phosphatase that increased Olsen-P by ~11% and P uptake in maize by three-fold when the roots of the two species were allowed to occupy the same rhizosphere (Zhu *et al.,* 2022). Alfalfa (*Medicago sativa* L.) facilitates P uptake in neighbouring maize, through Alkaline phosphatase (APase) activity and carboxylate secretion (Wang *et al.*, 2020). Though it is possible that clover can mobilise applied P for a neighbouring ryegrass crop through root exudation of carboxylates or organic acids (Wollmann *et al.*, 2018), it remains unclear whether white clover would also improve P uptake for both species as seen other legume/grass systems.

Although adding clover to mixed pastures is beneficial for both livestock and cohabiting plants, its responses to nutrient inputs can vary from other species in a mixed system. Clover responses to added N and P can vary in mixed swards, which may result from increased competition from co-occurring ryegrass (Gillingham *et al.*, 2008). Complementary interactions between the two species may not be present when clover is sown at a lower density than ryegrass (Brooker *et al.*, 2015), therefore nutrient management may also depend on clover and ryegrass ratios. Interactions between supplied nutrients and species in mixed systems is further compounded by differing responses to lime application. Clover has a higher tolerance of acid soils than ryegrass (Junquan *et al.*, 2007), and liming on mildly acidic (~pH 5.4) soils can significantly inhibit clover productivity, with the effect lasting up to 6 years (Smith *et al.*, 1998). However, liming and complete fertilisation (macro and micronutrients) can increase dry-matter production of clover and ryegrass grown together by 17 and 50% respectively (Campillo *et al.*, 2005). Therefore, it is feasible that liming agents such as CBD/CKD application could form part of a complete lime/fertilisation strategy in a mixed ryegrass/clover system to meet the lime requirements of ryegrass and clover. To date, the effect of applying a liming agent to different pasture species grown together or as a monocrop has not been studied in Great Britain, though work in New Zealand suggests liming to pH 6.5 could reduce P availability and uptake in ryegrass/clover pastures (Smith and Sinclair, 1998). This raises two questions:

- Could the productivity of a ryegrass-based system be improved by adding white clover in combination with a liming agent application?
- Could adding white clover improve the P uptake of ryegrass depending on the P status of the system?

This experiment aims to answer these questions in a mesocosm system with perennial ryegrass and white clover grown as a monocrop and intercrop, supplied with lime or CBD and with and without P fertiliser to test the following hypotheses:

1. Lime and CBD application will increase soil P availability and P uptake in both crops.
2. Intercropping ryegrass with clover will increase biomass production and P uptake in ryegrass.
3. P application + intercropping will improve P uptake in ryegrass more than if no P was added.

Plant productivity and nutrient uptake will be monitored as well as soil nutrient availability post application to determine if nutrient uptake affects plant growth.

4.2 Materials and Methods

4.2.1 Location

A mesocosm experiment was set up at the Lancaster Environment Centre (Lancaster University, United Kingdom) where the mesocosm pots were left to establish outside without cover (Figure 4.1b). The site receives an average of 1048.8 mm rainfall per year, 1507.3 sunshine hours and average annual minimum and maximum temperatures of 7.2 and 12.9 °C respectively. The experiment ran from February 2019 to October 2020.

4.2.2 Soil Collection

Topsoil was collected from a livestock farm in North Yorkshire (Pikeber Farm, Skipton, latitude: 54.002133, longitude: -2.306200) using an excavator. Soils from this area are described as being fairly fertile, free-draining, lime-rich and loamy (Cranfield University, 2018), however when tested (in 1:25 water) the pH was 5.5, making it suitable for the experiment. An analysis of available nutrients is described in Table 4.1 and supplementary information in Appendix A, Table 1, and Figure 2.

Table 4.1: The available nutrients and recommended fertiliser application rates for the pot trial. Fertiliser rates were taken from the Nutrient Management Guide (RB209) (AHDB, 2023b).

Nutrient	Available (mg l^{-1})	Index	Recommended Fertiliser Rate (kg ha^{-1})
Nitrogen (N)	N/A	N/A	75
Phosphorus (P)	10	1	100
Potassium (K)	68.5	1	150
Magnesium (Mg)	67.7	2	50

Soil was passed through a 5mm sieve to remove rocks and plant matter. Lime- free grit sand (Moist Horticultural Sand - BLP205, Boughton Topsoil, Kettering, United Kingdom) was added to the soil at a 1:4 by volume, and soil mixtures were homogenised with a cement mixer in 15 L batches for 5 minutes.

4.2.3 Plant Selection and Cultivation

Clover (*Trifolium repens* L. var 'Winter White', Farm Seeds, Lincolnshire, United Kingdom) and perennial ryegrass (*Lolium perenne* L. var 'Esquire', Emmorsgate Seeds, Norfolk, United Kingdom) were established in plug trays (84 cells with dimensions of 3.4 x 3.4 x 4.5 cm) in the greenhouses at Lancaster Environment Centre for 5 weeks, then hardened off in an unheated greenhouse for a week and planted out in 18.5 L pots (height: 30 cm x width: 15 cm) in April 2019. The plug trays were filled with the same soil as the mesocosms to maintain consistency and were watered to field capacity daily. Twenty-five plants were arranged in a 5 x 5 grid in every mesocosm (Figure 4.1a), and they contained either ryegrass as a monocrop, clover as a monocrop or a mixture of clover and ryegrass (13 ryegrass and 12 clover per mesocosm). In the spring, autumn, and winter months the mesocosms were rain fed and from May to August the plants were watered to run off every other day.

a **b**

Figure 4.1: (a) The planting schematic of intercropped mesocosms where 'R' represents a ryegrass plug and 'C' a clover plug. Monocropped mesocosms were laid out in the same grid but with one species: (b) the mesocosms *in situ* outside Lancaster Environment Centre.

4.2.4 Experimental Treatments

Treatments consisted of an untreated control and lime and CBD applied at 6 t ha^{-1}. The CBD used was the same one as used in the previous chapter. This rate was determined using the Rothlime web application (Rothlime, 2017) to target a soil pH of 6.3, using the neutralising value of the lime. CBD was omitted from this experiment to simplify the analysis. This was because the aim was to assess the interaction of the liming effect, P fertiliser and cropping method. N and Mg fertiliser were also added to each mesocosm at the equivalent of 50 kg ha^{-1}, as recommended by the Nutrient Management Guide (RB209, AHDB 2023b). An additional N application was applied at the beginning of the second year to account for any losses from the previous year. Two phosphorus treatments were applied, no added phosphorus (P-) or phosphorus added at the recommended rate for this soil (P+). This resulted in 12 different treatment types (Table 4.2) applied to 3 mesocosms arranged in randomised blocks of six mesocosms. Treatments were applied as a surface application after the plants had established for 8 weeks.

Table 4.2: The different treatments added to the mesocosm experiment. Different rates of lime and P fertiliser were added to different mixtures of clover and ryegrass.

Treatment Number	Lime Rate	P Treatment	Plants
1	0 t ha^{-1}	P-	ryegrass
2	0 t ha^{-1}	P-	clover + ryegrass
3	0 t ha^{-1}	P-	clover
4	0 t ha^{-1}	P+	ryegrass
5	0 t ha^{-1}	P+	clover + ryegrass
6	0 t ha^{-1}	P+	clover
7	6 t ha^{-1}	P-	ryegrass
8	6 t ha^{-1}	P-	clover + ryegrass
9	6 t ha^{-1}	P-	clover
10	6 t ha^{-1}	P+	ryegrass
11	6 t ha^{-1}	P+	clover + ryegrass
12	6 t ha^{-1}	P+	clover

4.2.5 Soil Sampling and Analysis

Four sub samples were taken from each mesocosm before planting and at every harvest thereafter. Samples were taken from a depth of 15cm at random locations across the pot that had not been previously sampled using a hand-held steel soil corer with a 20mm inside diameter. Soil sample preparation and analysis for pH, K and P was carried out in the same manner as outlined in Chapter 3.2.3.

4.2.6 Harvest, Tissue Sampling and Analysis

The mesocosms were harvested in July and October of 2019 and October of 2020. The harvest in August 2020 was not conducted due to delays caused by the COVID-19 lockdown. Each mesocosm was harvested in its entirety with plants cut at 5mm above the soil level. For the mesocosms containing clover and ryegrass mixtures, samples were separated for each species. The samples were then oven dried for 24 hours at 105 °C and then to measure dry weight. A sub sample of the dry biomass was taken from each mesocosm after weighing to assess tissue nutrient concentration. For the 2019 harvests, the dried leaf tissue was ground using a ball mill and prepared for analysis by ICP-OES using microwave digestion in nitric acid. In 2020 the samples were analysed by Hillcourt Farm Research Ltd (Gloucestershire, United Kingdom), to account for the time lost when the Lancaster University laboratories closed during the COVID-19 lockdown. A standard reference material sample (Trace Elements in Spinach Leaves 1570a, National Institute of Standards and Technology, Maryland, USA) was included with the samples sent away for analysis to ensure consistency between analysis methods.

4.2.7 Statistical Analysis

Statistical analysis was performed using the R software package (R Core Team, 2023). Differences between treatment responses were analysed with multi-way ANOVA and relationships between biomass production, treatment application and shoot nutrient concentration were analysed with ANCOVA.

The efficiency of the two cropping systems was assessed by calculating the Land Equivalent Ratio (LER). This is a concept that outlines the relative land area required for a monoculture to produce the same yield as a polyculture (Mead and Willey, 1980) and is calculated using the following formula:

$$\frac{IY1}{MY1} + \frac{IY2}{MY2}$$

Where *IY1* is the intercropped yield of the first species, *MY1* is the monocropped yield of the first species, *IY2* is the intercropped yield of the second species and *MY2* is the monocropped yield of the second species.

An LER greater than one indicates that intercropping has a positive impact on the plants growing in the system and is therefore more beneficial to growing each crop as a monoculture. An LER lower than one suggests that intercropping is detrimental to the growth of both species (Mead and Willey, 1980).

4.3 Results

4.3.1 Biomass Production

The biomass data for both species was log transformed prior to analysis to account for non-parametric data distribution. Lime and CBD application had no significant effect on the dry weight of the white clover (Figure 4.2a and Appendix C, Table 1). P fertiliser application also had no effect regardless of alkalising product application or cropping method. Monocropped clover produced significantly higher dry weight than their intercropped counterparts regardless of cropping date or P fertiliser addition ($p<0.001$). Monocropped plants produced a mean of 50.59 g per pot, which was 39% greater than the 30.76 g per pot produced by the intercropped plants. Dry weight production declined by each harvest date regardless of other treatments ($p<0.001$). Dry weight at the first harvest (22/07/19) was 71.22 g per pot and declined by 80% to 14.18 g per pot by the final harvest (12/10/20).

Alkalising product application had a significant effect on biomass production in perennial ryegrass ($p<0.05$)(Figure 4.2b and Appendix C, Table 2). Lime increased dry weight per pot by 23% compared to the control and CBD increased 14% compared to the control. The difference in dry weight between the mesocosms where lime and CBD were applied was not significant. Control mesocosms produced 23.08 g per pot across other treatment combinations and limed and CBD treated mesocosms produced 29.22 g and 26.49 g per pot respectively. This was independent of other treatments and did not change across harvest dates. P fertiliser application had no significant effect. Intercropping significantly increased ryegrass dry weight ($p<0.05$) compared to monocropping independent of lime, CBD or P fertiliser application. There was a significant interaction effect between cropping method and harvest date ($p<0.001$). Dry weight increased after the first harvest date and the effect was more pronounced in the intercropped plants. In the monocropped mesocosms, dry weight at the first harvest (22/07/19) was 22.40 g per pot and it increased by 19% to 26.54 g per pot by the second harvest date (14/10/19), after which it did not change significantly. The dry weight of the intercropped mesocosms increased from 16.21 to 36.79 g per pot (127%) from the first to second harvest, and again did not change significantly by the final harvest date (12/10/20).

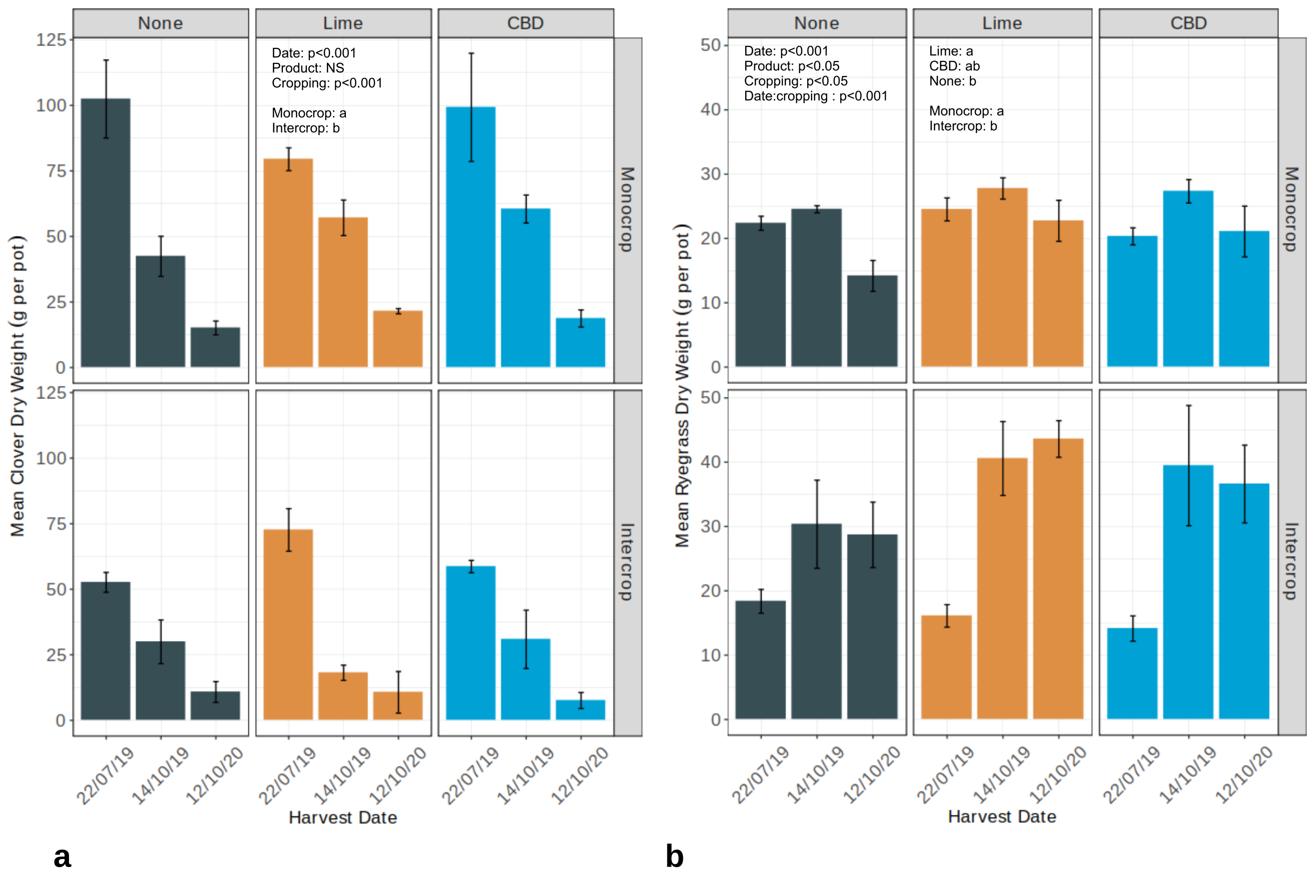


Figure 4.2: Biomass production of white clover (a) and perennial ryegrass (b) grown as either a monocrop or intercrop where either lime, CBD or nothing was applied to the soil surface. Bars are means ±SE of three mesocosms. As there was no interaction effect observed between cropping methods, product application and harvest date, no method of mean discrimination is provided for all treatment combinations.

4.3.2 Land Equivalent Ratio

The efficiency of the two cropping systems was determined by calculating the land equivalent ratio (LER). The LER for all the P fertiliser and alkalising agent combinations was greater than 1, meaning that intercropping was more effective than monocropping regardless of P status and lime application. When P fertiliser was withheld, mesocosms that received no alkalising product had an LER of 2.05, those that received lime had an LER of 1.87 and those that received CBD 1.62. When P fertiliser was supplied mesocosms that received no alkalising treatment had an LER of 1.98, those that received lime had an LER of 1.76 and those that received CBD 1.47.

Table 4.3 – *The land equivalent ratio (LER) of the different P fertiliser treatments and product application. An LER of greater than one indicates that intercropping positively affects growth and yield of the intercropped species. An LER of less than one indicates that intercropping is detrimental to the growth of both species (Mead and Willey, 1980). The results of this experiment indicate that intercropping was beneficial across all the fertiliser and product treatments.*

P Fertiliser Application	Product	LER
No Added P	None	2.05
No Added P	Lime	1.87
No Added P	CBD	1.62
Added P	None	1.98
Added P	Lime	1.76
Added P	CBD	1.47

4.3.3 Soil PH

Cropping method and P fertiliser application had no significant influence on the soil pH in this experiment (Figure 4.3 and Appendix C, Table 3). Both harvest date and alkalising product application had a significant ($p<0.001$ for both) effect and there was a significant interaction effect between the two factors ($p<0.001$). Lime and CBD application both increased pH significantly by the first harvest date compared to the mesocosms that received no treatment. Mesocosms treated with lime and CBD did not differ from each other. At the first harvest date (22/07/19) limed mesocosms had a 0.8% higher pH compared to the control and CBD treated mesocosms increased pH by 8% compared to control. At 14/10/19 limed mesocosms increased pH by 8% compared to control and CBD application increased pH by 10%. By the final harvest date (12/10/20) both alkalising agents increased pH by 10% compared to the control.

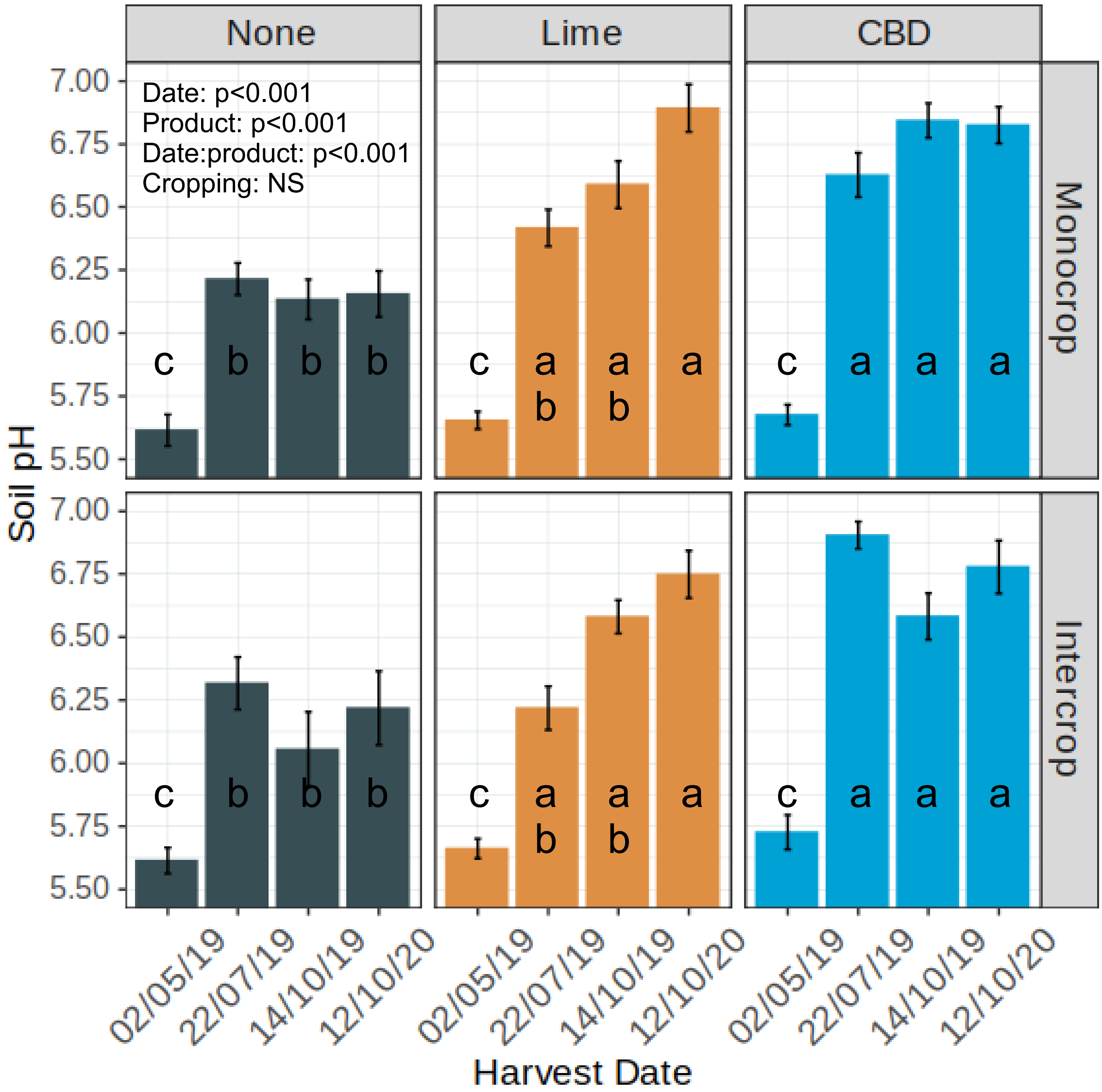


Figure 4.3: Soil pH of limed and un-limed mesocosms across 4 sampling dates. Bars are mean ± SE of 3 mesocosms, with letters of mean discrimination indicating treatment differences.

4.3.4 Soil P Availability

Alkalising product application had no significant effect on soil P availability (Figure 4.4 and Appendix C, Table 4). Soil P availability declined significantly from the first to last sampling date ($p<0.001$) and this varied depending on P fertiliser application ($p<0.05$). At the 22/07/19 sampling date, there was no difference between the mesocosms where P fertiliser was applied or withheld. By 14/10/19, mesocosms treated with P fertiliser had 37% higher mean P availability than those where P was withheld. By the final sampling date (12/10/20), the mesocosms treated with P fertiliser had 24% higher mean P availability than those without. Across all sampling dates, mesocosms that had P withheld had a mean P availability of 16.5 mg kg^{-1} and P application increased availability to 20.0 mg $kg-^{1}$, which represents an increase of 21%.

The cropping method used for each mesocosm had a significant effect on soil P availability that was independent from the effects of the other factors measured ($p<0.05$). Mesocosms containing a monocrop of either species had a mean soil P availability of 19.8 mg kg^{-1}, whereas intercropped mesocosms had a mean P availability of 16.8 mg $kg-^{1}$, which represents a decline of 15%. Plant species had no significant effect on the soil P availability of the monocropped mesocosms. The monocropped mesocosms containing ryegrass had a mean P availability of 20.0 mg kg^{-1} and clover mesocosms had a mean P availability of 19.7 mg kg^{-1}.

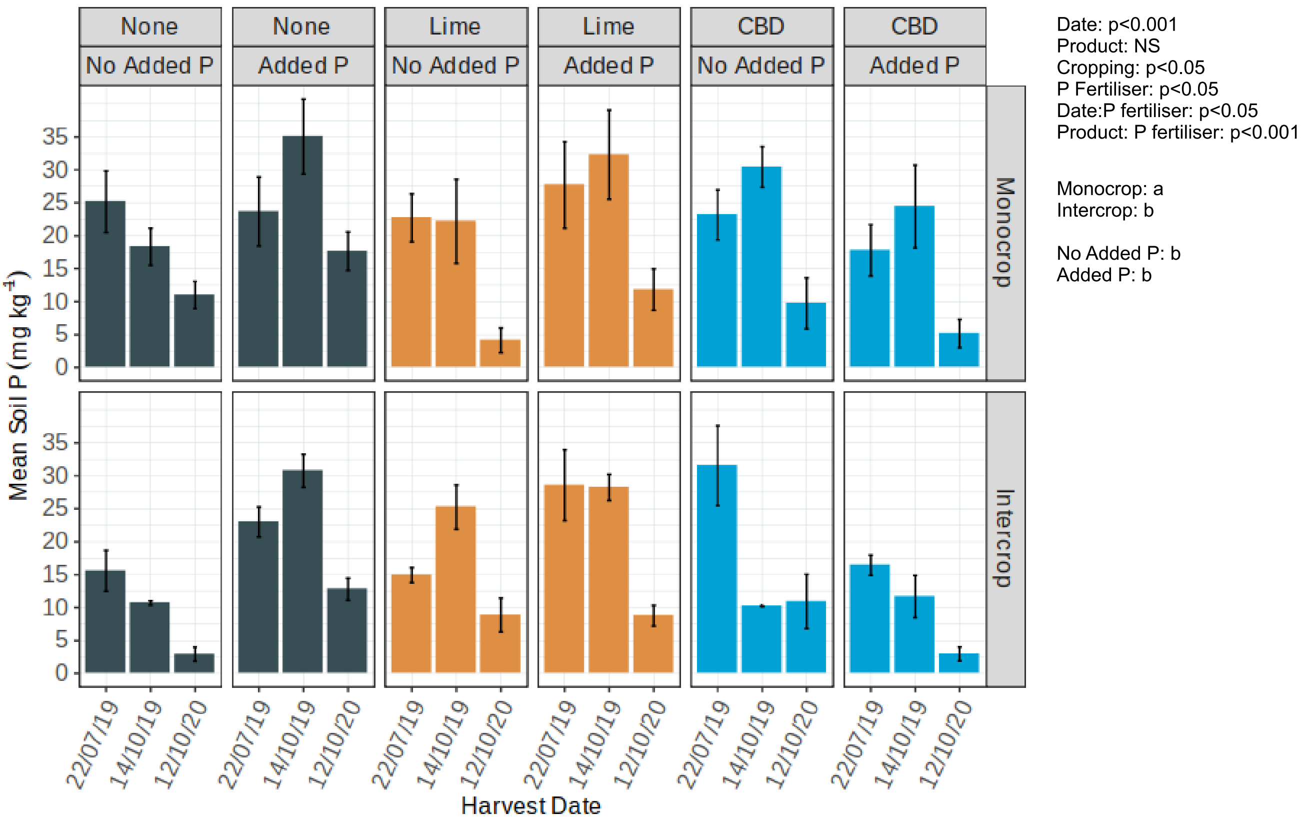


Figure 4.4: Soil P availability across three harvest dates. Bars are means ± SE of 3 plots. As there was no interaction effect between any of the treatments, mean discrimination was not indicated for all treatment combinations.

4.3.5 Relative Leaf Tissue P Concentration

Monocropped plants that received no P fertiliser or alkalising product were used as the baseline (which was set as 1) for each sampling date (Figure 4.5). The other treatment combinations where then compared to this baseline to calculate the relative tissue P at each harvest date.

P fertiliser application, cropping method and alkalising agent application all had a significant effect on the relative concentration of leaf tissue P in white clover ($p<0.01$, $p<0.01$ and $p<0.05$ respectively)(Figure 4.5, Appendix C, Table 5. There was also a significant interaction effect of cropping method and P fertiliser application ($p<0.01$).

Overall, monocropping white clover increased relative P by 12% compared to intercropping (0.91 compared to 0.81). The combination of added P fertiliser and intercropping produced a relative tissue P of 0.93 and added P plus monocropping 0.91. These two combinations did not differ from the no added P monocropped plants. The combination of intercropping and no added P fertiliser reduced relative tissue P by 31% to 0.69. This was significantly lower than the other treatment combinations.

The effect of alkalising product application was independent of cropping method and P fertiliser application. The mesocosms that received no product application, and the limed ones did not significantly differ from each other (1 and 0.92 respectively), whereas CBD application significantly decreased tissue P by 21% (0.79).

Alkalising product and P fertiliser application had no significant effect on relative tissue P of perennial ryegrass (Figure 4.6 and Appendix C, Table 6). Cropping had a significant effect ($p<0.01$) as did the interaction of cropping and P fertiliser ($p<0.05$). Intercropping combined with P fertiliser application increased tissue P by 12% compared to the control, with a relative tissue P value of 1.12. Intercropping without added P produced a relative tissue P value close to that of the control at 0.97, as did monocropping combined with P fertiliser at 0.99.

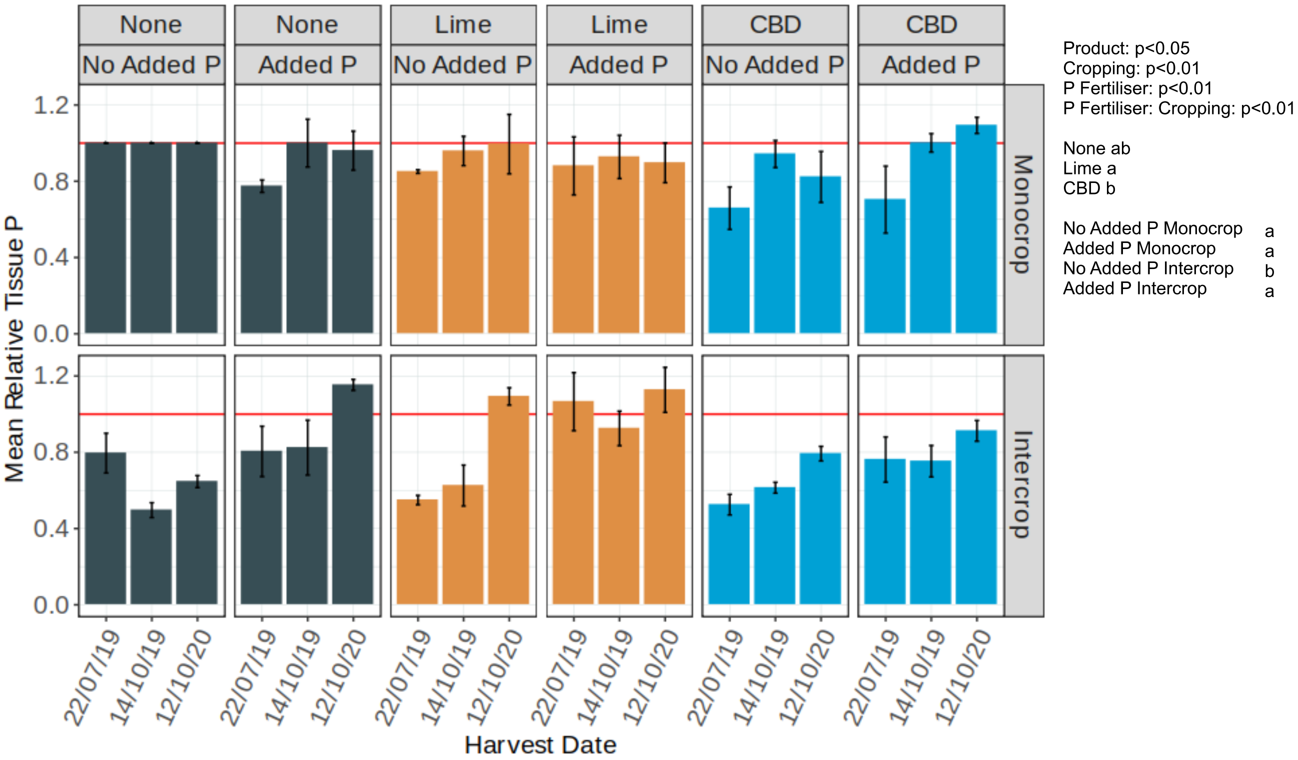


Figure 4.5: Incremental changes in leaf tissue P concentration of white clover across different cropping dates, cropping systems, P fertiliser and lime treatments. The results presented are normalised to the untreated, monocropped plants (1.0) which acted as a control. As the data is relative to the control, pot-hoc mean discrimination for individual harvest dates was not performed. Data are means ± SE of 3 plots.

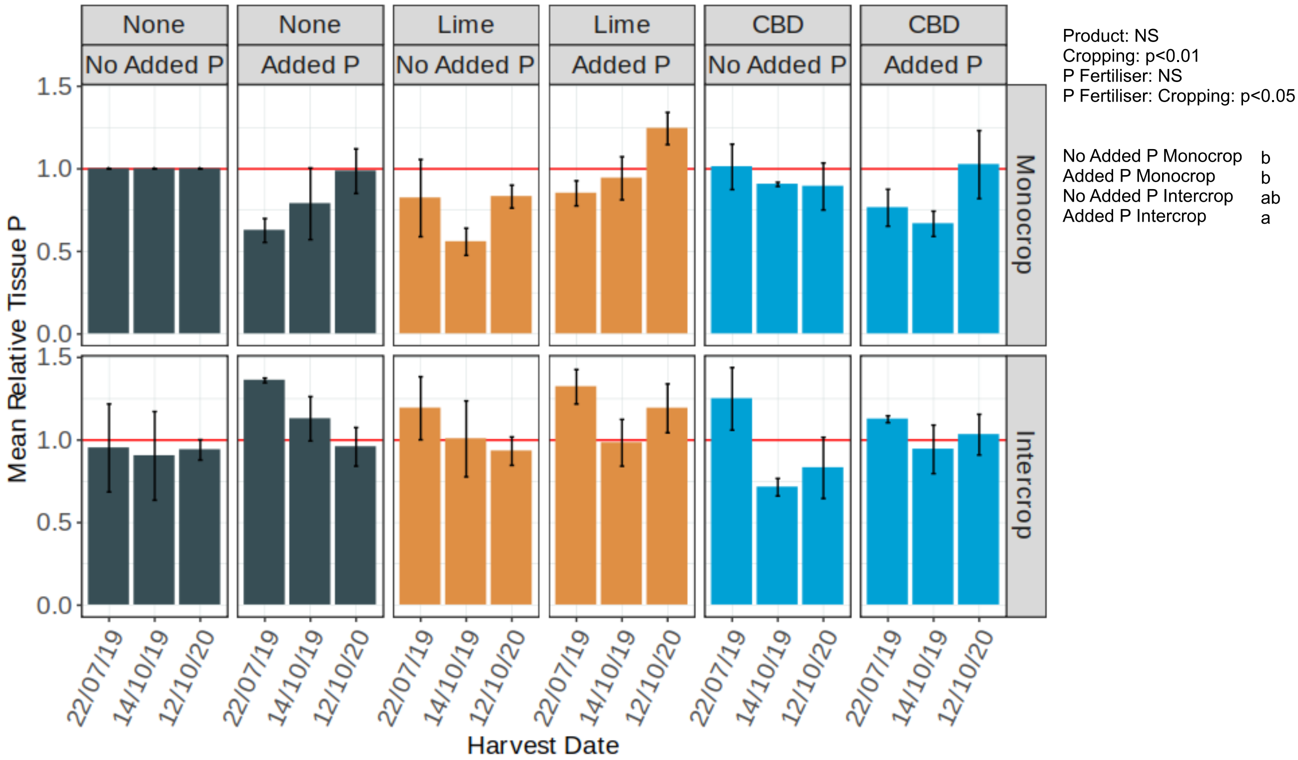


Figure 4.6: Incremental changes in leaf tissue P concentration of perennial ryegrass across different cropping dates, cropping systems, P fertiliser and lime treatments. The results presented are normalised to the untreated, monocropped plants (1.0) which acted as a control. As the data is relative to the control, pot-hoc mean discrimination for individual harvest dates was not performed. Data are means ± SE of 3 plots.

4.3.6 Soil K Availability, Tissue Ca and Mg Concentration

Other soil and plant tissue responses were also measured during the experiment to assess whether other underlying differences between treatments may have influenced growth (Tables 3.4, 3.5). In most cases, sampling date was the most significant factor impacting these responses.

P fertiliser application significantly increased tissue K concentration. Tissue K concentration was also positively correlated with growth (R^2 22%), however as cropping method had no impact on K concentration, it is unlikely that this explains the differences in biomass production between cropping methods.

In addition to harvest date, cropping method affected leaf tissue Mg concentration of clover, with intercropped plants having the greater Mg concentration. However, this was not correlated with biomass production. Lime application increased the tissue Ca concentration of the ryegrass plants (R^2 4%, $p<0.05$).

Table 4.4: Soil K availability was predominantly affected by harvest date ($p<0.001$). No other factors had a significant influence.

Factor	Effect on Soil K
Harvest/Sample Date	P: <0.001
Alkalising Product Application	NS
P Application	NS
Cropping Method	NS
Correlation with Growth (both species)	NS

Table 4.5: In the white clover, tissue K, Ca and Mg concentration were all influenced by the harvest date ($p<0.001$). Tissue Ca, K and Mg declined over time regardless of treatment. Lime application significantly increased tissue Ca in ryegrass. Intercropped clover had significantly higher Mg concentration than the monocropped plants.

	Tissue K	**Tissue Ca**	**Tissue Mg**
	Clover		
Harvest/Sample Date	p <0.001	p <0.001	p <0.001
Lime Application	NS	NS	p<0.01
P Application	p <0.05	NS	NS
Cropping Method	NS	NS	p <0.05
Correlation with Growth	p <0.05, R^2: 22%	p <0.05, R^2: 17%	p <0.05, R^2 3%
	Ryegrass		
Harvest/Sample Date	P: <0.001	NS	P: <0.001
Lime Application	NS	P:<0.05	NS
P Application	NS	NS	NS
Cropping Method	NS	NS	NS
Correlation with Growth	NS	NS	NS

4.4 Discussion

Intercropping increased ryegrass biomass production in the mesocosms where lime and CBD was applied, although lime application magnified this effect more than CBD. Moreover, lime and CBD addition mitigated a decline in ryegrass biomass over time in the monocropped mesocosms. Therefore, it appears that adding white clover to a perennial ryegrass-based pasture enhanced the growth promoting effects of lime application. As soil pH was not correlated with ryegrass growth in the intercropped mesocosms, this increase in growth likely wasn't directly influenced by changes to soil pH. Alternatively, ryegrass growth was better correlated with lime/CBD-induced increases in nutrient availability (such as P, Ca, Mg and K) than with soil pH *per se* (Hillard *et al.*, 1993). Thus, changes in nutrient availability resulting from lime/CBD application and clover addition may explain the differences in ryegrass growth between the intercropped and monocropped mesocosms. However, lime or CBD application on its own did not increase soil P availability and uptake in either crop or cropping system, meaning this experiment's first hypothesis (lime and CBD application will increase soil P availability and P uptake in both crops) can be rejected.

Rhizosphere activities of the clover in the intercropped mesocosms may explain both intercropping-induced increases in ryegrass growth and its apparent lack of response to lime/CBD application in terms of P availability and uptake. Although legume rhizobial associations increase the availability of N through symbiotic nitrogen fixation (SNF) (Zhong *et al.*, 2022), applying 50 kg N ha^{-1} at the start of the experiment and after the first harvest may have suppressed SNF (Li *et al.*, 2018), potentially ruling out growth promotion through this mechanism. However, the sampling and analysis methods used to determine soil and plant tissue nutrient content did not include N analysis.

Legumes can acidify the rhizosphere as a nutrient uptake strategy (Teles *et al.*, 2017; Zhu *et al.,* 2022), which could explain the differences in ryegrass growth observed and why soil pH had no correlation with growth in the intercropped ryegrass mesocosms. Localised pH decreases in the rhizosphere of the intercropped mesocosms could have buffered against increases in the wider soil volume when lime or CBD was applied. Lime application can also reduce P uptake by forming poorly mobile Ca-P complexes (Curtin and Syeres, 2001; Hinsinger, 2001; Bolan *et al.*, 2003), but root exudation of malate and citrate by legumes can release P from these complexes (Pypers *et al.*, 2007). It is therefore possible that clover could release P from Ca-P complexes created by lime or CBD application. This could explain why lime or CBD application did not directly affect ryegrass P uptake, because P may have been mobilised by the clover regardless of lime application in the intercropped mesocosms.

This experiment sampled soil by using a soil corer at random points across the mesocosm, with samples amalgamated before analysis to produce an average reading for the whole mesocosm. It did not differentiate between samples taken close to the plants and ones taken near the mesocosm edges where the planting was less dense. Although meaningful changes to soil chemistry and nutrient uptake could occur close to the roots as a result of interactions between the species, analysis of soil pH and P availability close to the root system of either species was not possible in this experiment. The high root density at the end of the first growing season made it difficult to sample from around the rhizosphere or rhizosheath without damaging the roots. As the experiment was run over two years, destructive sampling methods would have altered the cropping density and potentially skewed the results. Therefore, the sampling method used would have missed any subtle changes to the soil chemistry nearer the roots.

To account for these limitations in soil sampling, foliar P concentration of both species was also analysed. Adding white clover improved P uptake of the ryegrass grown alongside it (evidenced by the increased leaf tissue P concentration - Figures 4.5a and b) at both levels of P regardless of whether lime or CBD was applied. Intercropping plus P application produced the highest P concentration in ryegrass leaf tissue when compared to the control. This supports the second and the final hypothesis; that intercropping ryegrass with clover will increase biomass production and P uptake in ryegrass and that P application plus intercropping will improve P uptake in ryegrass more than if no P was added. Interestingly, the intercropped plants where P was withheld had a similar P concentration to the monocropped plants where P was supplied. Therefore, clover can be added to a ryegrass pasture where lime is supplied to improve P availability without additional P inputs. This can be supported by the fact that soil P availability also decreased over time across all treatment and cropping combinations, indicating P uptake by the plants. However, biomass was independent of tissue P concentration in both species. This is most likely because tissue P concentrations in both species did not fall below the critical value (2 mg g^{-1}) associated with a 10% decrease in yield (Rangeley and Newbould, 1985 a and b; Smith, *et al.*, 1985). The leaf tissue P concentrations for the plants in this experiment ranged between 2.9 – 4.1 mg g^{-1} and for clover 2.1 – 4.8 mg g^{-1} (averaged between 3 replicates per treatment). Although the additional P uptake in ryegrass intercropped with clover did not confer increases in biomass production, the Ca, P, Mg content of pasture species is essential for growth, physiological functions, and productivity in livestock (Mokolopi, 2019). Therefore, the addition of white clover to a pasture can have an additive effect on livestock nutrition when combined with lime and P fertiliser.

Intercropping was detrimental to the growth of the clover grown alongside the ryegrass (Figure 4.1a), which was not remediated by adding lime or P fertiliser. This may present a problem when considering the effectiveness of using such a cropping system depending on the intended use. One of the main reasons that farmers add clover to pastures is to increase overall pasture yield, replacing N fertiliser input with N_2 fixation and increasing the nutritional value for livestock consumption (Dineen *et al.*, 2018). If overall pasture yield is the target, then the overall biomass production of both species would have to offset losses in clover yield. For this experiment, this would mean the land area required by clover and ryegrass grown together as an intercrop would need to be less that of each crop grown as a separate monocrop to obtain the same biomass. The LER (Table 4.3) for all the lime, CBD and P treatment combinations exceeded 1.0, signifying that intercropping is the more productive system regardless of whether lime, CBD or P is applied. Therefore, the reduction in clover biomass production resulting from intercropping is not detrimental to the productivity of the system, even in systems with low P inputs. Reported LERs for cropping various species of ryegrass and clover vary greatly, with LERs as low as 0.91 (Dunea *et al.*, 2014) and as high as 8.44 (Simić *et al.*, 2011) reported, which vary depending on the grass and clover ratio (Giambalvo *et al.*, 2011; Pappa *et al.*, 2012; Rady, 2016). As this experiment used only one ratio, further experimentation is required to determine which combination of intercropping, lime/CBD and P addition maximises productivity.

In summary, the growth promoting effects of lime and CBD application on a perennial ryegrass pasture can be further increased by adding white clover, irrespective of P fertiliser application. However, application of either lime or CBD did not increase soil P availability or uptake in either species. Instead, P uptake in ryegrass was promoted by intercropping with clover and P fertiliser application. Interestingly, P uptake in the ryegrass was promoted by the presence of clover when P fertiliser was withheld and the intercropped mesocsoms where P was withheld produced similar ryegrass tissue P concentrations to the monocropped ones where P was supplied. Therefore, adding clover can increase the efficiency of P fertiliser. The addition of clover could also counteract P immobilisation (formation of Ca-P compounds) resulting from lime and CBD application, as P uptake was similar between the limed and un-limed mesocosms. The findings of the research raise multiple questions regarding the interaction between the two species, as it is unclear whether clover rhizosphere activity (e.g., root exudates) changes P availability only close to the root (thus requiring neighbouring ryegrass roots to occupy the same soil) or can benefit plants growing in a wider soil volume.

It was also difficult to determine how clover facilitated P uptake, as legume species can deploy several mechanisms including rhizosphere acidification, exuding P mobilising compounds and forming symbiotic associations with soil microorganisms such as arbuscular mycorrhizal fungi (AMF). Grass pea facilitated maize P uptake in P deficient conditions through direct rhizospheric interaction between the two species, as a 30 µm mesh root barrier prevented root interactions and additional maize P uptake (Zhu *et al.* 2022). Similar methods could be adopted to investigate rhizospheric interactions between perennial ryegrass and white clover and how they influence P uptake and growth. By utilising mesh barriers of differing porosity, the P mobilising strategies of the white clover could be separated and eliminated to analyse their effect on P uptake and growth.

Chapter 5: The Effect of Inter-Species Root Interactions on Growth and P Uptake in Intercropped Clover and Ryegrass

5.1 Introduction

Various studies have highlighted that current fertilisation practices, especially in Europe, are leading to use inefficiency and the build-up of P in the soil that is not readily utilised by crops (known as legacy P) (Powers *et al*., 2016; Menezes-Blackburn *et al.,* 2018; Hallama *et al.*, 2019). Up to half of the P imported by the EU accumulates in agricultural soils after application (van Dijk *et al.,* 2016.) and current fertiliser application practices are creating a cycle where legacy P remains slowly mobilised in the soil and any remaining available P is being used by crops, requiring more fertilisation that in turn leads to more P accumulation through processes such as adsorption and precipitation (Sharpley *et al*., 2013). Furthermore, increasing P fertiliser demand over recent years is leading to increasing fertiliser prices and necessitating the need to develop alternative strategies for meeting this demand or reducing fertiliser use (*Santos et al.,* 2021). One such strategy would be to exploit the pool of legacy P residing in agricultural soils to reduce fertiliser input. Menezes-Blackburn *et al.,* (2018) identified two methods of remobilising legacy P to reduce fertiliser load. The first was by reducing fertiliser application and depleting soil P reserves. This method however, risks yield penalties if soil P reserves are low. The second utilises crop species that are better adapted to scavenging for P in a low P soil, thereby increasing P availability for subsequent crops. Chapter 4 discovered that intercropping with white clover significantly increased P uptake in perennial ryegrass compared to monocropping in a low P soil. Adding P fertiliser increased P uptake in ryegrass even further.

Plant diversity has a positive relationship with productivity in most ecosystems, including anthropogenic ones such as cropping systems (Li *et al*., 2016). Compared to the intensive monocultures employed by modern agriculture, diverse plant communities display greater productivity resulting from facilitative plant–plant interactions and varied resource acquisition strategies (Zhu *et al*., 2022). Grass-legume combinations have been popular in identifying intercropping effects on biomass production and P availability, and agronomic practice in some parts of the world reflects these findings. Mixtures of maize and faba bean are commonly used to improve grain yield and P-use efficiency in areas such as India, Southeast Asia, Latin America, and Africa (Zhang *et al.*, 2016). Many different mechanisms can explain the growth, yield and nutrient uptake advantages provided by intercrop systems, which can broadly be classified as competition, complementarity and facilitation. Competition impedes growth of a neighbouring plant through allelopathic strategies and resource acquisition; complementarity avoids competition through differing resource acquisition or filling separate environmental niches; and facilitation increases growth of another plant by improving environmental conditions and resource availability (Li *et al*., 2016; Zhu *et a*l., 2022).

Plants adopt different P acquisition strategies which may confer complementarity and facilitatory effects on neighbouring species. Spatial adaptations for P acquisition involve altering root architecture for P foraging in the surface on near-surface soil horizons, where P is more plentiful (Lynch and Brown, 2001). This can involve developing shorter basal roots, adventitious rooting, lateral root branching and increasing root hair length and volume and increasing root length density, all of which allow greater volumes of soil to be explored (Pérez-Torres *et a*l., 2008; Sandral *et al*., 2017). Plant roots can exude several compounds that can mobilise P and facilitate uptake. Acid phosphatase can hydrolyse organic P compounds (the most common of which is phytate) to more soluble forms (Feng *et al*., 2003; Ma *et al*., 2004). The dissolution of calcium phosphates can be promoted through rhizosphere acidification resulting from root exudation of H+ and organic anions such as citrate and malate (Hisinger, 2001; Tran *et al*., 2010). Organic anions can also facilitate desorption of P from Al and Fe compounds in acidic soils and thereby increase P mobility in the soil (Richardson *et al.*, 2009). Maize shoots have higher P content when partnered with faba bean (Zhang *et al*., 2016), grass pea (Zhu *et al*., 2022), field pea and white lupin (Nuruzzaman *et al.*, 2015). Moreover, roots of maize avoid other maize roots but proliferate in the presence of faba bean, especially in P rich patches in the soil (Zhang *et al*., 2020). Adding faba bean increased maize yield in spilt pot experiments, even when insoluble P forms ($AlPO_{4-}$ and $FePO_{4-}$) were supplied and when the root systems were separated by a mesh barrier (Li *et al*., 2007). Thus, faba bean could promote P mobilisation through rhizosphere acidification of the insoluble P forms which are then utilised by the maize even when roots of the two species do not come into contact. However, the barriers used in this experiment could not discriminate between the effects of plant exudates and those produced by symbiotic microorganisms such as arbuscular mycorrhizal fungi (AMF) as the mesh size would have permitted access to fungal hyphae (Dodd *et al*., 2000).

AMF colonise around 90% of all vascular plant species (Willis *et al.,* 2013) and are present in the roots of nearly all species in grasslands, even extensively managed ones (Zhu *et al.,* 2000; Mariotte *et al.,* 2012). However, compatibility with AMF is determined by the ability of the fungi to infect the roots of the host and therefore some species, such as white clover are more mycotropic than others such as grasses (Zhu *et al.,* 2000). Colonisation and subsequent symbiosis are driven by root exudates acting as a signal between AMF and the host plant (Ingraffia *et al.,* 2019). Plant associations with AMF confer numerous benefits to the host species and surrounding ecosystem, including increasing the nutritional status (P in particular) of many grassland species (Grimoldi *et al.,* 2005). Low soil P status shown to stimulate root colonisation and AMF can mobilise organic and inorganic forms of through hyphal exudation (Mariotte *et al.,* 2012). Hyphal exudate composition is similar to P mobilising plant species, with phosphatases, carboxylates, amino acids, protons and organic ligands being prevalent (Andrino *et al.,* 2021; Zhang *et al.,* 2021). Fungal mycelia can act as a functional extension of a plant's root system via exchanging acquired P for carbon (Andrino *et al.,* 2021). This hyphal network can be further extended by the fusion of individual mycelia (nastomosis) and is shown to facilitate the transfer of P between individual clover (*Trifolium subterraneum*) plants (Mikkelsen, Rosendahl and Jakobsen, 2008). The P acquisition strategies of the symbiont fungi can then benefit the host plant and its neighbours as it can colonise one plant and then contact the root systems of other plants and transfer P between plant species using this hyphal network (Yao *et al.,* 2003; Dong *et al*., 2008; Ingraffia *et al.,* 2019). Therefore, the formation of associations with AMF provides another mechanism by which growing crops in a polyculture promotes overall productivity. Intercropping wheat and faba bean increase hyphal density and root colonisation of AMF by up to 59% in both species (Wahbi *et al.,* 2016). However, the relationship between host plant and symbiont fungi occurs along a spectrum from mutualism and parasitism, where favourable edaphic conditions (such as high P availability) produce a more parasitic relationship as the AMF can act as a carbon sink and ultimately suppress plant growth (Collins and Foster, 2009). Therefore, AMF associations are less beneficial in cropping systems with higher nutrient inputs.

Intercropping white clover and perennial ryegrass can improve P uptake and productivity of a pasture treated with liming agents (such a cement bypass dust) when no P fertiliser is added via several potential mechanisms. However, the findings from the previous chapter do not provide a mechanistic explanation as to why the growth of the ryegrass was facilitated by the addition of clover or why this arrangement was detrimental to the growth of the clover Previous experiments in maize and grass pea (*Lathyrus sativus* L.) have demonstrated that direct root interactions facilitated intercropped maize growth in P-deficient conditions by using barriers of different porosity (Zhu *et al.*, 2020). Similar methods could be used to address whether intercropping with clover improves ryegrass growth though hyphal plant-to-plant transfer of P or whether the ryegrass could assimilate the P mobilised by clover in a low P soil by occupying the same rhizosphere. Three research questions were formulated to address this:

1. Does root activity by neighbouring clover cause localised changes in soil P availability that promote P uptake and growth of ryegrass?
2. Do the roots of both species need to be in close proximity to each other to modulate plant growth?
3. Do AMF associations facilitate growth and P uptake in the monocrop and intercropped ryegrass-clover systems?

Therefore, a pot experiment used a low P soil and four barrier treatments of decreasing porosity to separate white clover and perennial ryegrass grown as a monocrop or intercrop, to assess whether growth and P uptake changed when root and hyphal interactions between the two species was permitted or prohibited.

5.2 Materials and Methods

5.2.1 Soil Preparation

Soil was sourced from the same location as in Chapter 4, with Table 4.1 documenting its pH and nutrient status. The soil was passed through a 5 mm sieve to remove rocks and plant matter. Lime- free grit sand (Moist Horticultural Sand – BLP205, Boughton Topsoil, Kettering, United Kingdom) was added to the soil at a 1:4 ratio. Lime was added to 10 L batches of the soil: sand mixture and then homogenised in a cement mixture for 5 minutes. The batches were then sealed in polythene rubble sacks and left to incubate for 8 weeks.

5.2.2 Plants, Potting and Sowing

This experiment was conducted using 382 ml pots constructed from PVC pipes (height 11.5, diameter 6.5 cm). The pipes were cut in half to fit a mesh screen to separate the two halves (Figure 5.1b). A wire mesh was attached to the bottom of the pots to allow for drainage. The same cultivars of white clover and perennial ryegrass as in previous chapter were used and sown on the soil surface using forceps. Fifteen seeds were planted on each side of the mesh in four rows (Figure 5.1c). The same method was used in pots where there was no mesh divide.

The soil was watered shortly before sowing to ensure It was wet enough for germination. Watering after sowing would have dislodged the seeds from their positions. The pots were then covered with tinfoil immediately after to reduce evaporation and left this way for two weeks until most seeds had germinated.

5.2.3 Experiment Design

The plants were grown in the greenhouses at Lancaster Environment Centre for six weeks. The pots were laid out in blocks of six across a greenhouse bench and were arranged so that no row in the block had repeats of the same treatment. The pot position was changed after every watering to mitigate any spatial effects on growth. The plants were grown with either their own species or the other species on the other side of the pot separated by one of four barrier treatments. Each side of the mesh/pot only had one species. When combined with the different meshes, there was a total of 12 treatments. Each treatment had 6 replicates, totalling 72 pots. Watering took place every other day and the amount of water used was determined gravimetrically to replace evapo-transpiration. The mean temperature and relative humidity in the greenhouse were 18.6°C and 29.2% respectively and the plants received 16 hours of light per day.

Table 5.1: Treatment combinations of plant species, cropping method and pot barrier (mesh).

Side 1 Plant Species	Side 2 Plant Species	Mesh
Ryegrass	Ryegrass	No Mesh
Clover	Clover	No Mesh
Ryegrass	Clover	No Mesh
Ryegrass	Ryegrass	41 µm
Clover	Clover	41 µm
Ryegrass	Clover	41 µm
Ryegrass	Ryegrass	1 µm
Clover	Clover	1 µm
Ryegrass	Clover	1 µm
Ryegrass	Ryegrass	0 µm
Clover	Clover	0 µm
Ryegrass	Clover	0 µm

5.2.4 Mesh Treatments

Four different barriers were used to separate the two halves of the pot:

- a control with no barrier which would allow the roots to grow freely throughout the pot.
- a 41 µm nylon mesh (Normesh Ltd, Lancaster, United Kingdom) to stop roots, but allow AMF hyphae through (Marian *et al*., 2019; Scrase et al., 2019)
- a 1 µm mesh to prevent passage of AMF hyphae (Dodd *et al*, 2000) but allow flow of nutrients and water.
- a solid polythene sheet (0 µm) to prevent any interaction between the two halves of the pot.

The barrier material was slightly larger than the width and height of the half-pot (Figure 5.1c) to allow it to be stretched tightly across the open part of the pot and secured using duct tape (Shurtape UK Ltd, Hampstead Heath, United Kingdom). Soil was then added to the sealed pots, filling each side individually. Each pot was allocated a number, and the sides of the pot were then labelled either 1 or 2 for ease of identification when conducting soil analysis.

Figure 5.1: Experiment design schematic (a) and photographs of pot construction (b and c).

5.2.5 Harvesting and Tissue Analysis

After 6 weeks of growth the plants were then harvested by cutting 1mm above the soil surface then stored in paper bags and oven dried at 105°C for 24 hours. Each side was harvested and labelled separately. The dried plant matter was then weighed and ground in a ball mill in preparation for nutrient analysis.

The ground plant tissue was analysed for P content using the nitric acid microwave digestion method outline in Chapter 3.2. The digested material was not analysed using ICP-OES in this instance and was instead analysed using a microplate reader (BMG Labtech, Ortenberg, Germany). The digested samples were diluted to 2%, and then analysed according to the methods outlined in Chapter 3, section 3.2.6. The machine was calibrated using standards ranging from 0 – 4 ppm.

5.2.6 Soil Analysis

Soil P availability was assessed using the saturated paste method adapted from Rowell *et al*. (2014, pp.287–288). Air-dried soil (40 g) was placed in a 50 ml centrifuge tube and de-ionised water was added slowly via a syringe until the soil was nearly saturated. The soil was stirred continuously during the process. The tubes were then sealed and incubated for 24 hours. Then any water remaining on the soil surface was removed using a pipette and decanted in to a 0.5 ml microcentrifuge tube and then stored in a freezer at -20°C until analysis. The samples were thawed overnight prior to analysis and then passed through a 0.45 µm syringe filter. The filtered samples were analysed by plate reader (BMG Labtech, Ortenberg, Germany) and via the method outlined in Chapter 3, section 3.2.6. The machine was calibrated using standards ranging from 0.025 – 1 ppm.

5.2.7 Statistical Analysis

Statistical analysis was performed using the R software package (R Core Team, 2018). Differences between treatment responses were analysed using mutli-way ANOVA (using dry weight, shoot tissue P content, species, barrier treatment and cropping method as factors) and means were differentiated using Tukey's honest significance test. Where the data was non-parametric, Kruskal–Wallis test was used and Dunn's test was to compare means. Relationships between factors were analysed using linear regression and Pearson's correlation coefficient.

5.3 Results

5.3.1 Biomass Production

When the clover was grown as a monocrop and was not restricted by a root barrier, it produced the highest biomass of all the different treatment combinations (0.105 g per plant) and 23% more than its intercropped counterpart (0.081 g per plant). In the two monocropped treatments where access to the whole soil volume was restricted but the movement of resources such as water and nutrients was permitted (41 µm and 1 µm), the plants had a higher biomass than ones grown with the solid barrier which prevented any interaction ($p<0.001$). Monocrop plants grown in the pots separated by a 41 µm barrier produced a mean dry weight of 0.079 g per plant and those grown in pots separated by a 1µm barrier produced a dry weight of 0.084 g per plant, whereas those grown in pots separated by the solid barrier (0 µm) produced 0.062 g per plant. Intercropping decreased biomass compared to monocropping across all barrier treatments, with the greatest difference occurring when plants were grown without a barrier. When a barrier preventing interaction between the two pot halves was introduced, there was no significant difference between monocropping and intercropping (Figure 5.2 and Appendix C, Table 1). The 0 µm barrier produced slightly lower biomass than the other three but this was not significant.

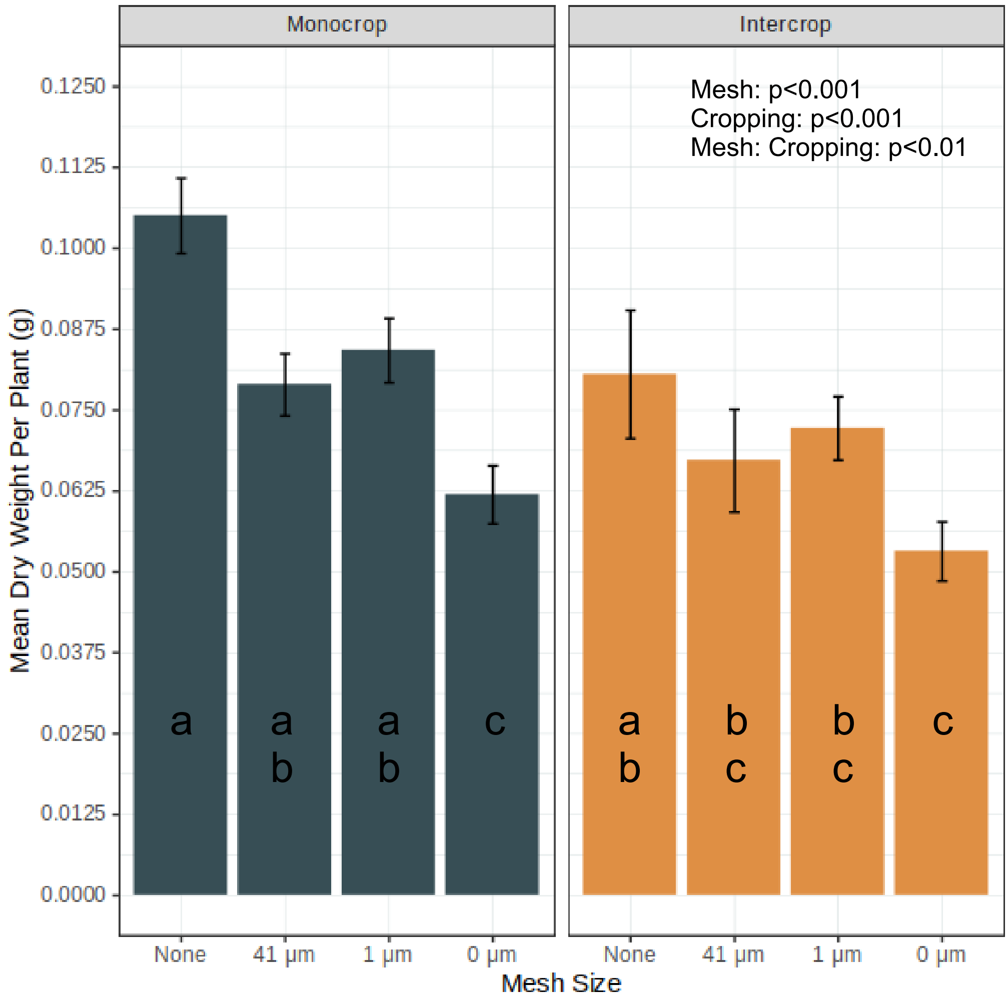


Figure 5.2: Mean dry weight per plant of white clover grown in pots divided by one of four barrier treatments paired with either the same species (monocrop) or perennial ryegrass (intercrop) on the other side of the barrier. Bars are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots). Letters of mean discrimination identify means that differ significantly.

In contrast to clover, intercropping ($p<0.05$) promoted ryegrass growth when the roots of the two species were permitted to occupy the same soil volume (Figure 5.3 and Appendix D, Table 1). The intercropped plants grown in pots without a barrier produced the highest biomass of all the treatments (0.079 g per plant) and 13% more than their monocropped counterpart (0.069 g per plant). Growth was restricted in both cropping systems by the declining permeability of the pot barrier ($p<0.01$). There was also an interaction between cropping method and barrier type ($p<0.05$). When the roots of the two species are prevented from physically touching, but where resources such as soil water and nutrients or micro-organisms such as AMF can cross the barrier (41 µm barrier), the biomass produced was still higher than when only water and nutrients could pass through (1 µm) or when any interaction between the two sides of the pot was prohibited (0 µm). The two cropping methods produced similar biomass when the pots were separated with the 1 µm barrier and the solid barrier (0 µm). Monocropped ryegrass in pots separated by the 1 µm barrier produced a mean dry weight of 0.056 g per plant whereas the intecropped ones produced 0.055 g per plant. The monocropped plants separated by the solid barrier had a mean dry weight of 0.050 g per plant and the intercropped plants 0.049 g per plant.

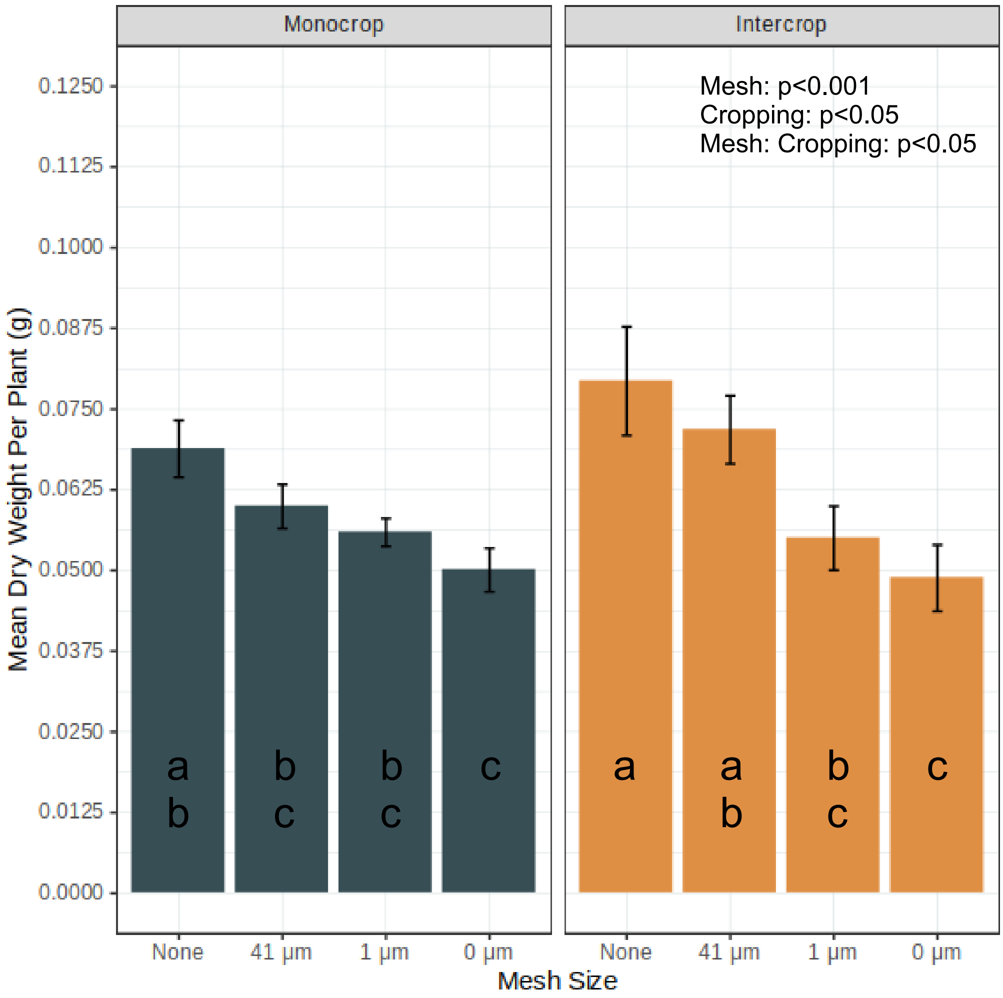


Figure 5.3: Mean dry weight per plant of perennial ryegrass grown in pots divided between one of four barrier treatments paired with either the same species (monocrop) or white clover (intercrop) on the other side of the barrier. Data are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots). Letters of mean discrimination identify means that differ significantly. Analysis was performed on log transformed data.

To determine whether differences in soil volume affected plant biomass, the no barrier treatment was removed from the dataset, which was then re-analysed. In this scenario, all the plants had access to the same soil volume (half a pot) but their access to water and nutrients from the other side of the pot varied. Analysis of the new dataset found that both mesh size ($p<0.001$) and cropping method ($p<0.001$) still had an influence on the biomass production of clover and there was no interaction between the two treatments. Intercropping with ryegrass reduced clover growth regardless of the barrier used. When the clover had access to water and nutrients from both sides of the pot (41 µm and 1 µm meshes), their biomass was higher than the plants which only had access to resources from one side of the pot. The declining mesh porosity also had the same effect on ryegrass when the no-barrier treatment was removed ($p<0.01$) this means that access to resources was more important to growth than soil volume regardless of cropping method in both species.

5.3.2 Soil Water P Concentration

The species present in each pot half had a significant effect on soil water P concentration ($p<0.05$). Pot halves containing ryegrass had a significantly higher concentration at 6.12(±0.3) µg solution-P kg^{-1}, compared to 5.32(±0.3) µg solution-P kg^{-1} found in the pot halves containing clover. Both cropping method and barrier type significantly influenced soil water P concentration in white clover ($p<0.05$ for both) (Figure 5.4, Appendix D, Table 3). However, there was no significant interaction effect between the two factors. Soil water P concentration was significantly higher in pots with intercropped plants across all barrier treatments (5.81 µg solution-P kg^{-1}) when compared to pots with monocropped plants (4.71 µg solution-P kg^{-1}). Soil water P concentration increased as barrier porosity decreased across both cropping methods. The concentration was lowest when there was no barrier separating the two halves of the pot. In monocropped pots the soil water P concentration was 3.62 µg solution-P kg^{-1} and 5.21 µg solution-P kg^{-1} in the intercropped pots. Pots separated by a solid barrier produced the highest concentration at 5.57 µg solution-P kg^{-1} for the monocropped pots and 7.12 µg solution-P kg^{-1} for the intercropped pots. There was no significant difference between the 41 µm and 1 µm barriers.

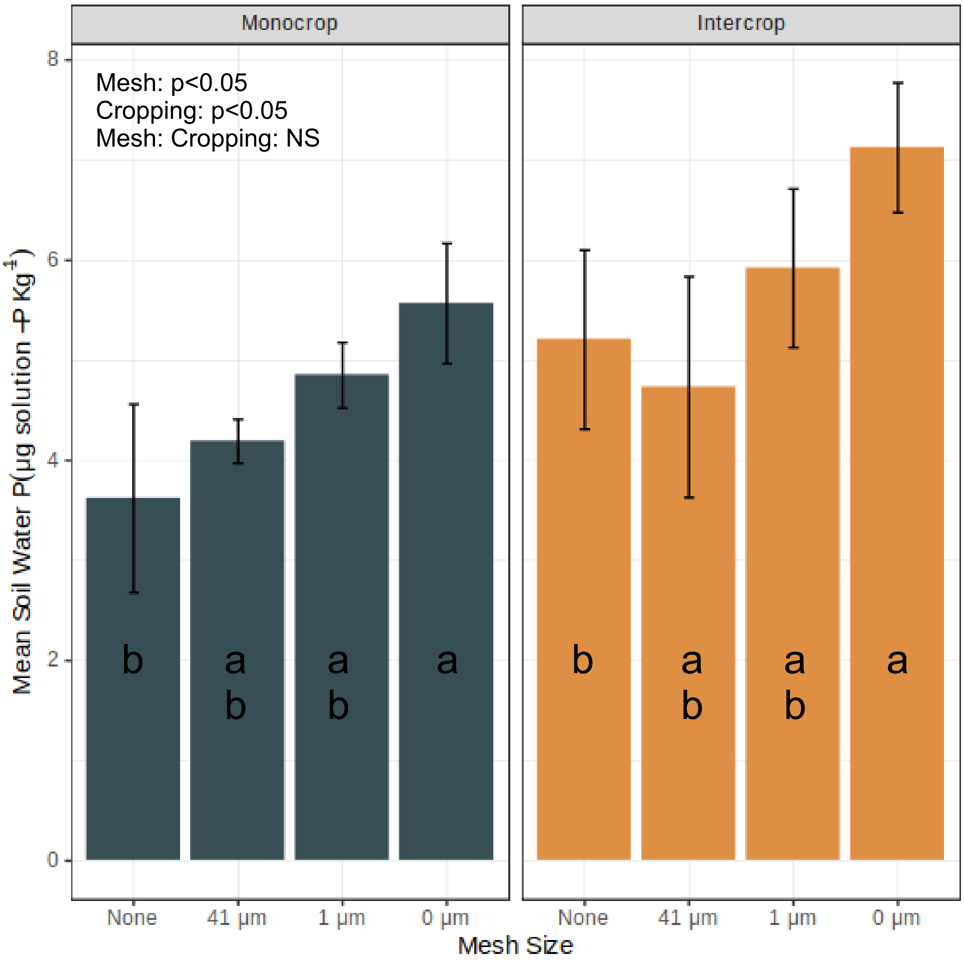


Figure 5.4: Mean soil water P concentration (µg solution-P kg^{-1}) per half pot containing white clover, divided by one of four barrier treatments paired with either the same species (monocrop) or perennial ryegrass (intercrop) on the other side of the barrier. Bars are means ± SE of 6 pots.

The soil water P concentration in pots containing ryegrass was not significantly influenced by barrier type (Figure 5.5, Appendix D, Table 3). Cropping method significantly affected soil water P concentration ($p<0.05$), with monocropping producing the highest concentration at 6.68 µg solution-P kg^{-1} and intercropping producing a concentration of 5.13 µg solution-P kg^{-1} across all barrier treatments. There was no significant interaction effect between cropping method and barrier treatment.

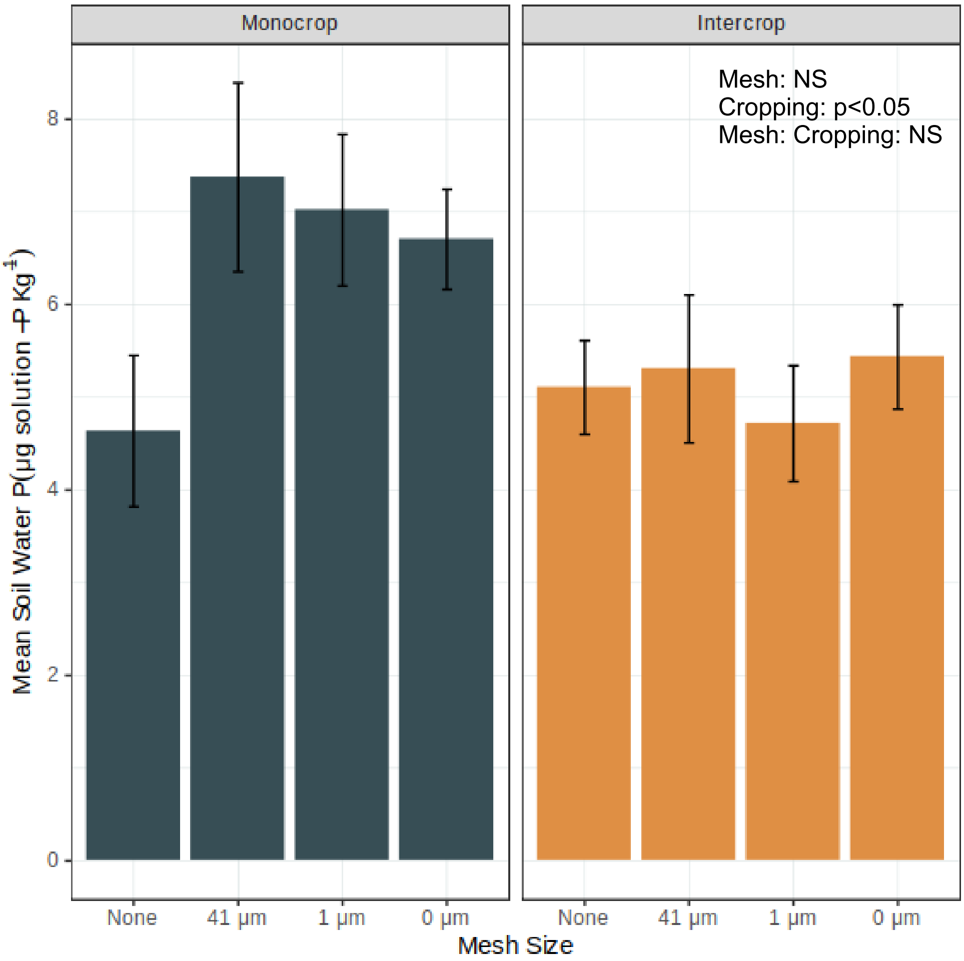


Figure 5.5: Mean soil water P concentration (µg solution-P kg^{-1}) per half pot containing perennial ryegrass, divided by one of four barrier treatments paired with either the same species (monocrop) or white clover (intercrop) on the other side of the barrier. Bars are means ± SE of 6 pots. No method of mean discrimination is displayed as the barrier type had no significant effect.

5.3.3 Shoot Tissue P Concentration

Leaf tissue P concentration (mg g^{-1}) in the white clover was not significantly influenced by barrier type, cropping method or the interaction between the two (Figure 5.6 and Appendix D, Table 5). There was no meaningful difference in P concentration between the different pot barriers in the monocropped plants. The intercropped plants grown in pots separated by the 1 µm and solid barriers had a lower leaf tissue P concentration that those grown without a barrier or separated by the 41 µm barrier, however this difference was not significant. Leaf tissue P concentration had no significant relationship to dry weight production in either cropping method (monocrop: p NS, R^2 2%, intercrop: p NS, R^2 2.4%) (Figure 5.8).

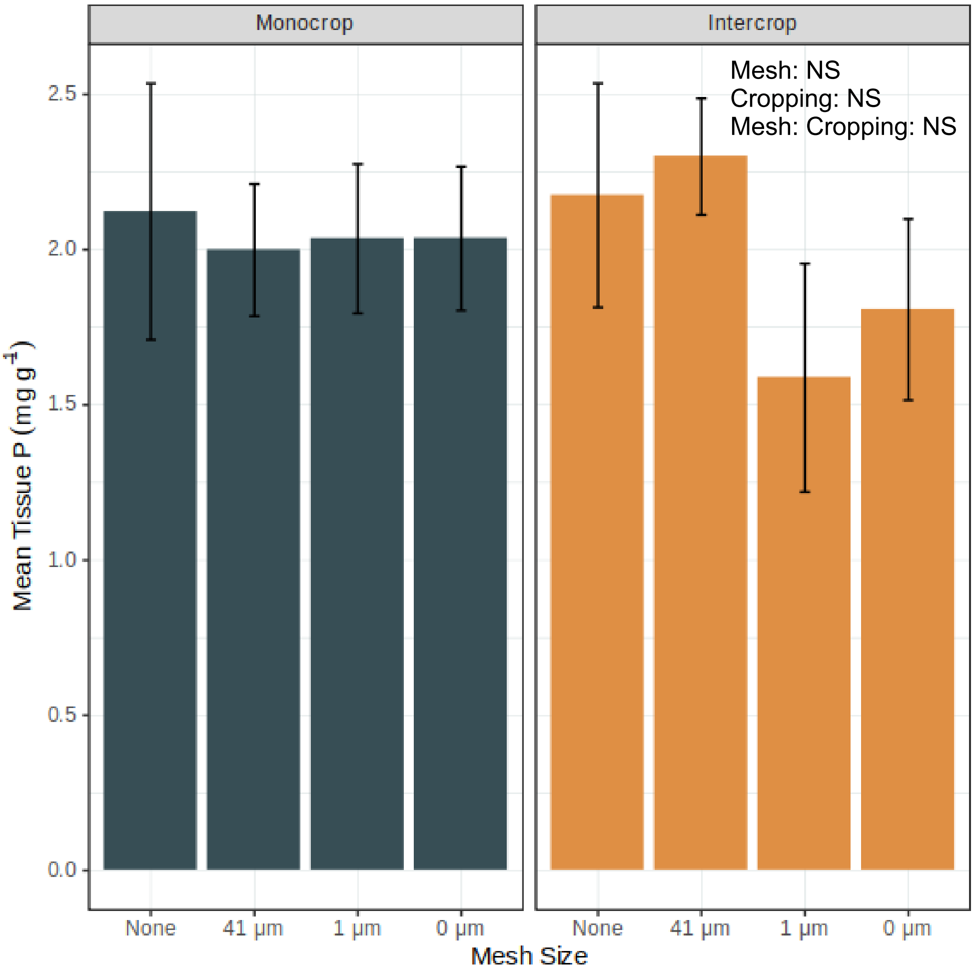


Figure 5.6: Mean tissue concentration (mg g^{-1}) of P in white clover tissue. Data are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots). Nonparametric analysis was used for this dataset due to non-normal distribution.

Cropping method and barrier type also had no significant effect on the leaf tissue P concentration of the perennial ryegrass and the was no significant interaction effect between the two factors (Figure 5.7 and Appendix D, Table 6). As with the white clover, there was little difference between pot barriers in the monocropped plants. The intercropped plants grown with the 41 µm, and solid barrier had lower tissue P concentrations than the no barrier and 1 µm treatments, however this difference was not significant. Leaf tissue P concentration had no significant relationship to dry weight production in either cropping method (monocrop: p NS, R^2 2%, intercrop: p NS, R^2 3%) (Figure 5.9).

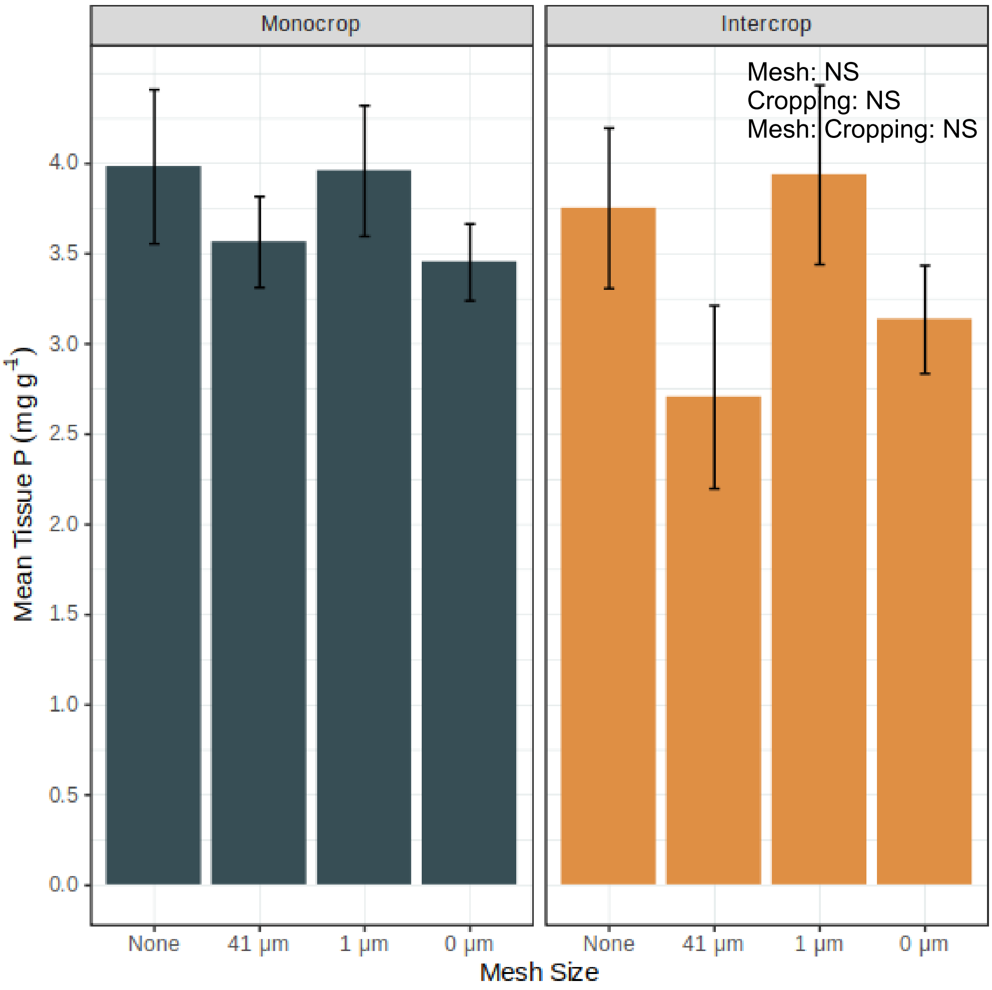


Table 5.7: Leaf tissue P concentration (mg g^{-1}) of perennial ryegrass plants grown as a monocrop or intercrop, separated by one of four barrier treatments. Data are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots).

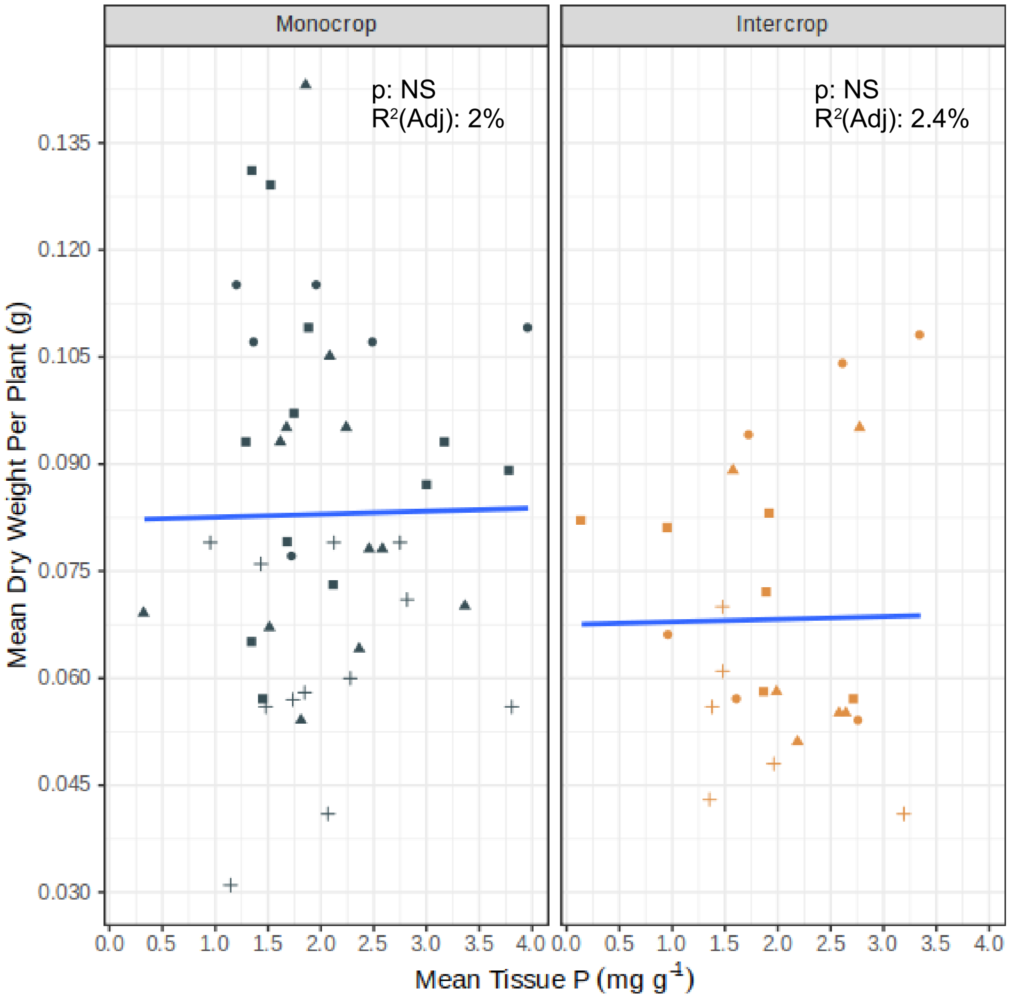


Figure 5.8: The relationship between mean dry weight per plant and mean tissue P concentration (mg g^{-1}) per plant in white clover grown as a monocrop or intercropped with ryegrass. Data are mean weight and tissue concentration per plant across six pots.

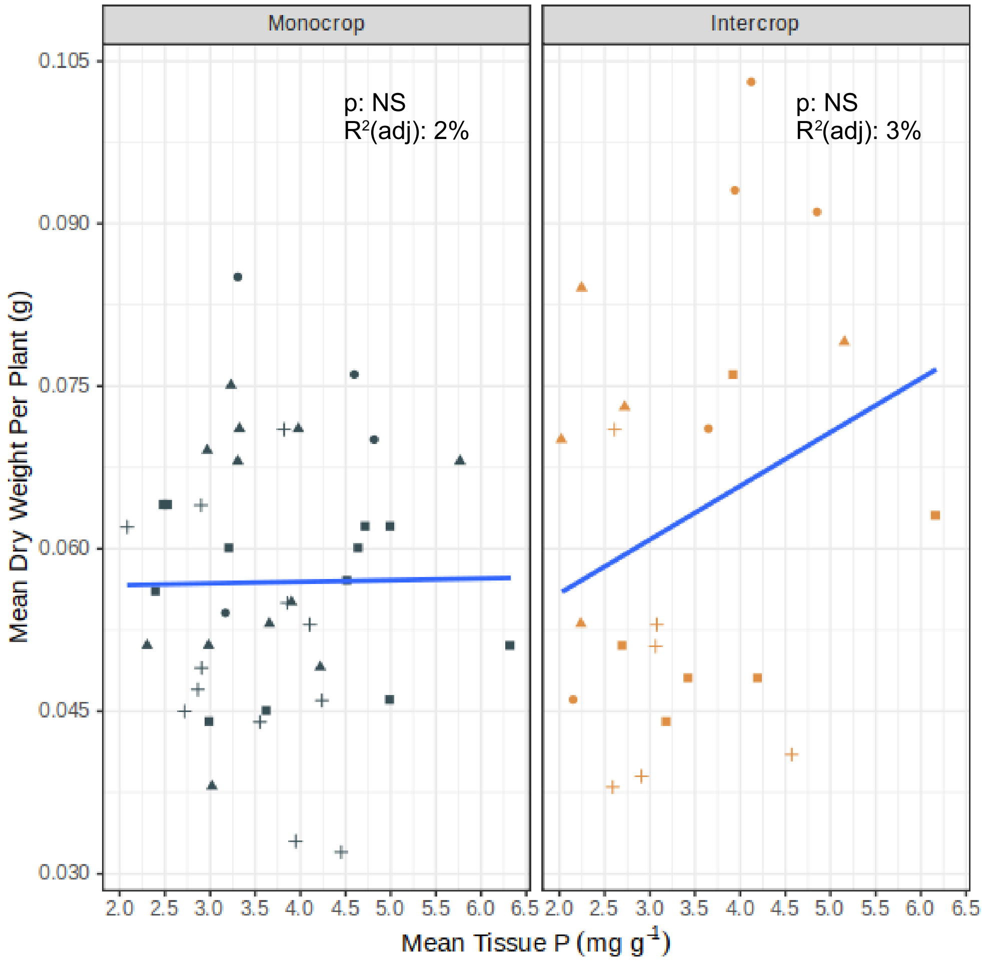


Figure 5.9: The relationship between mean dry weight per plant and mean tissue P concentration (mg g^{-1}) per plant in perennial ryegrass grown as a monocrop (a) or intercropped with white clover (b). Data are mean weight and tissue content per plant across six pots.

5.4 Discussion

Clover and ryegrass growth responded differently to the two cropping systems, with clover responding positively to monocropping, while ryegrass benefited from intercropping. Similar results have been seen in work by Dirks *et al.,* (2021) where perennial ryegrass doubled its biomass production whereas clover's was reduced by three quarters. However, numerous experiments have produced contrasting results, with intercropping being advantageous to clover growth (Saia *et al*., 2016) or both species responding positively to monocropping (Walker and King, 2009, Bacchi *et al*, 2021). Several factors including: clover species used, variability in climatic conditions, soil characteristics, and management practices could explain these differences (Saia *et al*., 2016). As most of these experiments were conducted in the field, environmental conditions and soil nutrient dynamics presumably differed from this glasshouse experiment possibly account for the differences observed (Poorter *et al*., 2016; Schittko *et al*., 2016). Furthermore, the clover could have taken longer to establish, giving the ryegrass a competitive advantage at the early stages of growth that could have been remediated had the experiment run longer and additional harvests taken place (Hauggaard-Nielsen *et al.,* 2012, Bacchi *et al.,* 2021). Shoot competition could also be considered here, as the plants in this experiment were grown close each other and were allowed to interact. In experiments with other clover and grass species (Kura clover (*Trifolium ambiguum*) and meadow bromegrass (*Bromus biebersteinii*), eliminating shoot competition using a barrier had no effect on leaf number, leaf area, or leaf biomass for both species when compared to treatments that permitted shoot competition. The Kura clover increased its canopy height to avoid that of neighbouring bromegrass and therefore mitigate competition for light. Eliminating root competition however increased shoot biomass of both species, implying that root interactions are more likely to be driving the competition effect (Walker and King, 2009).

It is also possible that the differences in soil volume between the no-barrier and solid barrier treatments could impact the growth of the plants in this experiment and explain why the no-barrier plants produced the highest biomass in both species across cropping methods.

Previous observations in experiments investigating root competition have maintained that plants can sense their neighbours and increase root production to achieve a competitive advantage in acquiring resources such as nutrients but at the expense of shoot growth in a phenomenon known as the tragedy of the commons (Hess and De Kroon, 2007). However, a common issue with such experiments is that the addition of other plants often occurs alongside an increase in the total soil volume available to the plants which also increases access to nutrients (Markham and Halwas, 2011; Wheeldon *et al.,* 2020). Previous work using barriers of varying porosity has shown that root and shoot growth response to neighbours is more likely to be a function of pot volume and availability of nutrients throughout the pot rather than root competition, meaning that it is important to separate the effects of root competition, nutrient availability and soil volume (Semchenko *et al.,* 2007). To investigate this potential effect, the no-barrier treatment was removed from the dataset and analysed again. In this analysis all pots had the same soil volume but resources such as water and nutrients could move through the 41 µm and 1 µm mesh barriers but not the solid barrier. When the no-barrier treatment was eliminated, cropping method and mesh size still had a significant impact on clover biomass production ($p<0.001$ for both). Clover grown in pots with the 41 µm and 1 µm mesh barriers had a higher biomass than those grown with a solid barrier regardless of cropping method, meaning that access to resources was more important than soil volume. With the ryegrass, when the no-barrier treatment was excluded from analysis and cropping had no significant effect, but mesh size did, with biomass decreasing with mesh porosity. As seen with the clover, access to resources was more important than soil volume to the ryegrass however these findings also show that growth promoting effects of intercropping with clover were significantly reduced when the roots of the two plants were prevented from occupying the same rhizosphere. This again Indicates that ryegrass roots must be in proximity to clover to gain any beneficial effect.

Cropping method affected soil water P regardless of barrier treatment in pots with either species present (Figures 5.4 and 5.5). Intercropping increased soil water P concentration when compared to monocropping in the pot halves where the clover was grown. The reverse was true for the ryegrass. Soil water P concentration was also consistently higher in the pot halves containing ryegrass. These findings contrast with those in the literature, where the presence of clover increases Olsen-P values (McDowell and Smith, 2023), total P availability and organic P availability (Wang *et al*., 2021). However, the concentration of P in the soil water may have been higher in the presence of ryegrass due to lower uptake by the ryegrass compared to the clover. As this occurred regardless of cropping and barrier method, it may be that the clover simply utilised more of the P available in the soil solution and can partially explain the contrasting findings of this experiment. These discrepancies could also be due to other factors including differences in grass/legume species used and differing experimental methods. The methods used for analysing soil P availability differed between this experiment and the others reviewed, meaning that different fractions of P were measured and therefore making direct comparison difficult. For example, the methods used for this experiment detect soluble reactive P, a form of inorganic orthophosphate (PO_4) (Rowell *et al*., 2014), whereas the other experiments have used Olsen-P, resin-P, and total P to determine soil P availability.

Barrier type only influenced the soil water P concentration in pot halves where clover was grown, with concentration increasing as barrier porosity decreased. This reflects the work of Zhu *et al*. (2022), who found that soil P availability was increased with the addition of a solid barrier, which was attributed to restriction of root activity. Therefore, it appears that clover's ability to forage for P is greatest when the roots can physically explore the soil, suggesting that the ability of root exudates to mobilise P is limited in range. Also, as barrier method had no influence of the availability of P in the pot halves where ryegrass was grown, and there was no interaction between barrier and cropping methods, it indicates that there is no involvement of AMF on the ability of clover to influence P availability in an intercropping scheme. However, to explore this further, plant shoot P content was analysed to assess actual uptake.

As previous research has established that legume species such as clover can increase the growth of neighbouring plants by facilitating P uptake (Yao *et al.,* 2003; Zhang and Li, 2003; Zhang *et al.,* 2016), the P concentration of both species in this experiment was analysed and cropping methods and barrier treatments compared. Cropping method did not affect tissue

P concentration of clover shoot tissue. There was no significant difference between the barrier treatments. Therefore, it appears that the clover required roots to be physically present across the whole soil volume to acquire P. This is surprising since legume species such as clover have several strategies to acquire P that would otherwise remain unavailable. Root exudation of compounds such as acid phosphatase can hydrolyse organic P compounds (e.g phytate) to more soluble forms (Feng *et al.,* 2003; Ma *et al.,* 2004). The dissolution of calcium phosphates (Ca-P) can be promoted through rhizosphere acidification resulting from root exudation of H+ and organic anions such as citrate and malate which can also facilitate desorption of P from Al and Fe compounds in acidic soils (Hisinger, 2001; Richardson *et al*., 2009; Tran *et al*., 2010). As mentioned previously, this suggests that the P mobilisation methods employed by the clover are limited in range, thus requiring the roots to explore the greater soil volume to acquire more P. However, the concentration of solution-P in the soil used for this experiment was very low (Figures 5.4 and 5.5, Rowell *et al*, 2014) and the clover therefore may not have been able to utilise these strategies to mobilise P, so it is difficult to rule this out. Further experimentation with soils of varying P availability is therefore required to fully rule out the role of exudates in promoting P uptake in mixed clover and ryegrass systems.

Shoot P concentration was not associated with biomass production of either species across both cropping methods (Figure 5.8), which indicates that the growth reduction of clover in response to intercropping is not driven by competition from ryegrass for P in the low P soil because shoot P concentration did not differ between cropping treatments. This contradicts studies that suggest ryegrass is a strong competitor for P (Høgh-Jensen and Schjoerring, 2010), however ryegrass has the faster growth rate of the two species and may have produced more root biomass as the clover was still establishing, thereby increasing competition for water and nutrients other than P (Boot and Mensink, 1990; Lu *et al.,* 2020).

Mycorrhizal associations increase growth and P uptake in both white clover and ryegrass (Dong *et al*., 2008; Li *et al*., 2021) by improving P assimilation through hyphal exudates and the creation of mycelial networks connecting multiple individual plants and facilitating the transfer of nutrients such as P (Mikkelsen, Rosendahl and Jakobsen, 2008; Collins and Foster, 2009). White clover is highly mycotrophic in comparison with most grass species due to grasses having heavier roots and more root hairs, which are traits considered to reduce AMF infection (Zhu *et al.,* 2000). Pot and glasshouse experiments report transfer of P and N between plants via hyphal links, with P transfer rates of 5-51% being recorded between white clover and ryegrass (Yao *et al.,* 2003; Li *et al*., 2021). Therefore, it is feasible that fungal connections between the two species (one being highly mycotrophic) in this experiment could be facilitating the transfer of P that is being mobilised by root and hyphal exudates thanks to the presence of the clover. The different barrier treatments aimed to rule out this possibility as the 41 µm barrier excludes roots but permits AMF hyphae whereas the 1 µm excludes both and therefore, if there are differences in the P concentration of plants separated by the 41 µm and 1 µm then hyphal transfer of nutrients may be taking place. In both species there was no significant difference in growth between the 41 µm and 1 µm barrier treatments regardless of cropping method. Therefore, in this instance the diffusion of nutrients and potentially root exudates were more important than mycorrhizal in the facilitative effect of intercropping with clover on the growth of ryegrass. Furthermore, there was no differences in P uptake between the 41 µm and 1 µm barrier treatments in either species. Therefore, it does not explain why intercropping was detrimental to clover in pots with 41 µm and 1µm meshes present and therefore indicates another mechanism such as competition for nutrients that is limiting growth in intercropped clover (Wang *et al*., 2020; Zhang *et al*., 2020, Zhu *et al*., 2022).

However, the methods used for this experiment do not completely rule out the involvement of AMF. The plants were not inoculated with AMF as it was presumed to be present in the soil used for the experiment, which was obtained from a field previously used for grazing and was not sterilised and therefore presumably hosted a microbial community. Lack of time also meant that the roots of either species were not examined for colonization. Further experimentation expanding the methods outlined in this chapter by inoculation with known AMF species would be a more robust approach in defining the role of AMF in the facilitative interactions between these two species. Current research supports this approach as many factors regulate AMF colonisation, such as root density, root exudates, and the availability of nutrients in the rhizosphere (Yao *et al.,* 2003); and the roots of ryegrass not as accommodating for AMF infection as clover (Zhu *et al.,* 2000). Therefore, AMF my have not formed association with the ryegrass or colonisation rates may have been too low to facilitate nutrient uptake/transfer in this experiment. Isotopic studies have previously provided specific evidence of AMF facilitated P transfer and could also be used expand the findings of this experiment further (Yao *et al.*, 2003). Additionally, interactions between AMF and roots can occupy a continuum between mutualism and parasitism and can both increase and decrease competitiveness in either species (Mariotte *et al.,* 2012), ergo the edaphic conditions of this experiment may not have promoted the facilitative relationship between the AMF and ryegrass host if infection did occur.

The findings of this experiment can be summarised as follows: white clover and perennial ryegrass displayed different responses to intercropping, with the growth of ryegrass responding positively at the expense of the growth of the clover. This effect was most apparent when the roots systems could overlap with one another and access the whole pot and indicates that the facilitative interaction is driven by rhizospheric interactions between the two species. As grasses are often more competitive and have higher nutrient requirements than legumes in mixed crop systems (Wang *et al.,* 2020; Zhang *et al.,* 2020, Zhu *et al.,* 2022) it is likely competition for nutrients is negatively affecting the growth of the clover in the intercrop system. However, as there were no differences in P uptake between the two cropping systems in either species, it is likely that competition for other resources such as water or nutrients other than P are likely to be driving this response. As there was no difference growth and P uptake between the 41 µm and 1 µm barrier treatments in either species or cropping method, the diffusion of nutrients and potentially root exudates was more important than mycorrhizal associations in the facilitative effect of intercropping with clover on the growth of ryegrass. Furthermore, above ground competition was not eliminated for this experiment and introducing methods such as an above ground barrier (Walker and King, 2009) to determine the extent in which above ground competition can impact the growth of either species grown as an intercrop. The research outlined in this chapter could be extended further by deliberately inoculating one or both species with AMF species known to colonise these plants and assessing differing pasture species in combination for complimentary traits in terms of nutrient acquisition strategies to mitigate growth penalties and utilise pools of nutrients that may be unavailable to other species and therefore reduce fertiliser input.

CHAPTER 6: GENERAL DISCUSSION

The pressures on our nutrient resources from intensive modern agricultural practices is increasing the need for optimised use of fertilisers (Udeigwe *et al.*, 2015; Kopittke *et al*., 2019). As a result, there is growing interest in alternative nutrient sources and fertilisers, including repurposed industrial wastes (Singh *et al.*, 2021; Mabrouk *et al*., 2023). By products from the cement manufacturing process such as cement by-pass dust (CBD) and cement kiln dust (CKD) contain considerable amounts of K and are highly alkaline, making them suitable candidates as a source of K fertiliser and for modifying soil pH (Adaska and Taubert, 2008). These products are recycled at the source of production until they are no longer useful and then disposed of (Bhatty, 1995; Rodd *et al*., 2010). Diverting them from landfill and repurposing them as agricultural amendments allows nutrients to be recycled through input into soil and off-take through crops and animal produce. They also act as a link between the cement industry (through waste management) and agriculture (through nutrient recycling). Thus, fulfilling three of the four circular economy principles that aim to decouple economic activity from the consumption of finite resources (Baily *et al.*, 2013; Ellen Macarthur Foundation, 2018). CBD and CKD are currently being deployed in Great Britain as soil alkalising agents, however there is little work on their agronomic effectiveness. This thesis aimed to assess their effectiveness as a liming agent and fertiliser and develop strategies to optimise their use.

The pot trial conducted in Chapter 2 found that found CBD applied at rates up to 5 t ha^{-1} increased pH to the same degree as lime, however from 5 - 8 t ha^{-1} lime increased pH more. This was corroborated by the results in Chapter 3 that found at 5 t ha^{-1} CBD application increased soil pH to a similar degree as lime and lime + K fertiliser. Soil pH increased more gradually with CKD application and to a much lesser degree, most likely due to its larger aggregate size decreasing its reactivity (Goulding, 2016). This contradicts the findings of other researchers, who found that CKD was more reactive than lime and increased pH to a similar degree (Dann, Dear and Cunningham, 1989; Rodd *et al*., 2004; Lalande *et al*., 2009). These discrepancies are likely owing the high variability in CKD composition, which can vary between plants and even batches from the same plant (van Lierop, Tran and Morissette, 1982; Bhatty, 1995; Adaska and Taubert, 2008). This is also evidenced in Chapter 2, where the dusts investigated varied in neutralising value (Table 2.2). This highlights the need for further experimentation with the CBD and CKD produced in Great Britain as comparison with other research conducted in other countries and with other sources of cement dust is difficult. Furthermore, in the years following the bulk of the research investigated, CBD has become the predominant waste product produced by cement plants in Great Britain and as its composition differs from CKD, again making comparison difficult. Furthermore, the research in this thesis was limited to two soils obtained from land used for sheep grazing in the North West of England. It is not clear what effect CBD/CKD application would have on more acidic or intensively managed agricultural soils and more experimentation is required to determine their efficacy on such soils and whether a tailored approach should be taken towards their application. Additionally, CBD and CKD are more than just alkalising agents and their potential as a K fertiliser was also explored in this thesis.

Current application practices of CBD/CKD ignore their fertiliser potential and opt on application rates above 5 t ha^{-1} designed to correct soil acidity. However, analysis in Chapter 2 found that at these rates K is being greatly over supplied (Table 2.6). For example, depending on the source of CBD/CKD used, a rate of 6 t ha^{-1} would supply 360^{-1} kg K ha^{-1}, which is almost double the 133 kg k ha^{-1} application recommended for a high demand crop such as oats (AHDB, 2023b). As they are typically used on grassland, supplying at this rate would over supply even on a cropping system with high demand and application was once every three years (Table 2.6). This is an inefficient practice that risks losing much of the K that is supplied through leaching (Kayser *et al*., 2007; Römheld and Kirkby, 2010). As luxury uptake of K can occur in many crop species (Jiang *et al*., 2018 ; Soratto *et al*., 2020), it is doubtful that the amount of K supplied is translated in to a proportional effect on growth and yield. Therefore, the extra added K is effectively useless.

If treated as a K fertiliser, the cement dust produced in the following regions can supply enough K to meet the demands of 7% of grassland or 5% of arable K demand across England and Wales (Figure 2.4). This equates to 147,543 ha and 197,406 ha of farmland respectively (Figure 2.4 and Table 2.9). Considering the economic value of the K present in the CBD/CKD being produced in England and Wales, the approach of applying it as a liming agent is essentially wasting money. Thus £3,150,997 could be saved on fertiliser costs if CBD/CKD is instead treated as a source of K fertiliser. However, CBD/CKD is currently treated as an alkalising agent in Great Britain due to the costs associated with licencing for application on agricultural land. It therefore makes economic sense to apply at rates of 5-6 t ha^{-1} to offset these costs. The licencing requirement stems from the Sludge (Use in Agriculture) Regulations 1989 (Anon, 1989), which is in place to avoid the buildup of Potentially Toxic Elements (PTEs) in the soil. Yet the findings in Chapter 2 illustrate that when CBD/CKD is applied more frequently at a lower rate as a K fertiliser, the amount of PTEs being added is well below the recommended limits.

Further examination of national soil data revealed that just 3% of soils fit the ideal criteria for applying CBD/CKD at a lime rate (Table 2.8). Yet when considered for application at K fertiliser rates CBD is suitable for use on 75% of arable soils and 96% of grassland soils (Table 2.8 a and b). This means that K is being over supplied in almost every instance. The regulations are put in place to promote sustainable agronomic practices, but as evidenced by these findings, the opposite is being promoted. Therefore, it is worth questioning whether alternative approaches to this legislation should be investigated. The findings of Chapter 2 have demonstrated that CBD/CKD have the potential to be used as a K fertiliser and Chapter 3 addresses the reality of applying CBD/CKD at lime rates and whether applying such large amounts of K has any proportional benefits to plant growth.

When applied at lime rates (5 t ha^{-1}) to a ryegrass-based pasture, CBD and CKD produced plant biomass that was comparable to that of K fertiliser rate and greater than lime and lime + K applied at the recommended rates. However, similar work has found that found CBD and CKD at lower application rates to be as effective in other species. CKD applied at 0.5-2 t ha^{-1} increased growth and yield of maize by 15-99% (Lalande *et al.,* 2009). CKD also increased yield of potato, barley and alfalfa yield by 8%, 17% and 14% when compared to control when applied at 200 kg ha^{-1} (Van Lierop *et al*., 1982). These findings again illustrate that rates above 5 t ha^{-1} may not be necessary for improving plant growth and nutrition and lower rates could be sufficient. Chapter 3 also found that CBD/CKD application increased soil K availability by up to 140%. This is supported by previous studies that observed similar increases in soil K (Lafond and Simard 1999; Lalande *et al*., 2009).

CBD and CKD also increased plant uptake of K compared to K and lime + K treatments, but this effect dropped off after the first harvest and was comparable to the other products by the second harvest. This demonstrates that although large amounts of K are being added with CBD and CKD at lime rates, their influence on the K nutrition of plants does not last throughout the growing season is not maintained. However, these findings are contradicted by some of the literature. The growth promoting effects observed by Rodd *et al.* (2010) carried over into the next year with CKD increasing yield compared to the control and limed plots by 38% and 25% respectively (at an average of 7.8 t ha^{-1} across three sites). This is likely due to the differences in the species used, application rates and soil properties. This highlights the need to test products such as CBD/CKD on British soils as it is difficult to extrapolate results from other regions. The plant tissue K results are supported by the Partial Nutrient Balance (PNB) performed on the data. The PNB demonstrated that further application would result in soil build-up of K, meaning the supplied K was not being fully absorbed by the plants. Therefore, risking K leaching (Kayser *et al*., 2007; Römheld and Kirkby, 2010). Furthermore, as there were no differences in biomass production between CBD, CKD, K and lime + K, this extra K is not being translated to any growth advantages over conventional methods. This further supports the notion that lower application rates designed to correct soil K availability instead of pH could be sufficient to meet crop demand. Further work is advised to determine effective rates for using CBD and CKD as K fertilisers in order to make direct comparisons to more conventional sources of K. Additionally, Van Lierop *et al.*, (1982) have demonstrated potential for using CKD and food crops (barley and potato) and Chapter 2 has found that CBD and CKD production from four cement plants could meet up to 5% of arable K demand in England and Wales (Figure 2.4). It is therefore feasible that CBD/CKD could be used as a K fertiliser in regions such as East England and East Midlands where arable farming predominates (Table 2.11). However, more experimentation is required to assess whether CBD/CKD applied at K fertiliser rates is as effective as conventional products across a diverse range of crop species.

As mentioned in Chapter 2, the K present in CBD/CKD is a valuable resource and most soils in England and Wales do not require both the amount of pH and K correction that CBD/CKD at lime rates would supply. Therefore, legislation is promoting an agronomically and economically wasteful practice. Again, these findings question the validity of the (Use in Agriculture) Regulations 1989 (Anon, 1989) if the costs associated with licencing for it are driving wasteful practice which the act is trying to avoid. It is therefore worth questioning whether CBD/CKD should be considered waste at all and instead be treated as a nutrient resource. The regulations are designed to prevent PTE build up in the soils, which could enter the food chain through plant uptake and then animal/human consumption, however Chapter 2 found that CKD and CBD application didn't alter uptake of As, Cd, Cr, Pb and Se compared to the control. It therefore it appears that any PTEs that are being added are not being taken up by the plants when applied at lime rates. These findings are supported by those of Lalande *et al*., (2009) who found that CKD application of up to 10 t ha^{-1} have been found to have no effect on availability of Cd, Cr, and Pb. If CBD/CKD do not increase the availability of PTEs at lime rates, then more regular application at lower rates is less likely to have an effect. This again highlights the paradoxical effect that the legislation is having on practice. A more efficient approach would be to treat CBD and CKD as K fertilisers and combine them with a traditional source of lime to maintain a soil pH above a level that promotes PTE availability (Xian and In Shokohifard, 1989; Eich-Greatorex et al., 2007; Kumar et al., 2022). More work should be undertaken to assess the effects of long-term CBD/CKD application at a range of rates on the build-up and availability of PTEs on agricultural soils, especially as their neutralising effect diminishes in the first year after application (Figure 3.5). This risks increasing availability of these elements and potentially compounding the issue if more CBD/CKD is applied to correct soil acidity in subsequent years (Xian and In Shokohifard, 1989; Eich-Greatorex *et al*., 2007; Kumar *et al*., 2022).

It is also feasible that CBD/CKD application could form part of a complete lime and fertilisation strategy in combination with other fertilisers such as N and/or P. However, CKD has been found to decrease P availability in some cases (Lalande *et al*., 2009; Rodd *et al*., 2010) and lime + P combination can also reduce P availability of added fertilisers through formation of Ca-P complexes (Curtin and Syeres, 2001; Hinsinger, 2001; Bolan *et al*., 2003). Chapter 4 examines whether it is possible to increase P uptake when a liming agent is applied to unfertilised and fertilised soils through intercropping ryegrass with a P mobilising species such as white clover. Legume species such as clover can mobilise soil P through multiple mechanisms. These include rhizosphere acidification, release of exudates such as citrate and malate, alkaline phosphatase (APase) activity and associations with Arbuscular Mycorrhizal Fungi (AMF) (Pypers *et al*., 2007; Wang *et al*., 2020; Chaoui *et al.*, 2023). As this mobilised P can be absorbed by neighbouring plants, they have been historically used in intercropping systems to reduce N and P inputs (Dai *et al*., 2019; Carton *et al*., 2020).

The addition of white clover improved P uptake of the ryegrass grown alongside it (evidenced by the increased leaf tissue P concentration. See Figure 3.5) at both levels of P and lime supply. Intercropping plus P application produced the highest P concentration in ryegrass leaf tissue when compared to the control. Therefore, P application combined with intercropping improves P uptake in ryegrass more than if no P was added. As this effect occurred in both limed, CBD and control mesocosms, intercropping with white clover can increase P uptake in limed and un-limed soils regardless of P fertilisation. However, intercropping was detrimental to clover growth and was not remediated by P application. Despite the reduction in clover growth, intercropping was the more productive system across all lime and P treatment combinations. This is evidenced by the fact that the Land Equivalent Ratio (LER, Table 4.3) exceeded 1.0. Therefore, intercropping with clover and ryegrass can enhance growth and enhance P uptake in limed pastures. This means that this cropping method could be used to offset any reductions in P availability from CBD/CKD application without the need for further P input (Lalande *et al*., 2009; Rodd *et al*., 2010). However, it is unclear from this experiment what mechanisms were behind the facilitative and competitive relationship between the two plants.

Chapter 5 addressed the level of root interaction between clover and ryegrass required for the facilitation and competition effects to take place. Plant response to the two cropping systems mirrored the findings of Chapter 4, with intercropping increasing ryegrass growth and reducing that of clover. The effect was most present when root exploration was not restricted by a barrier, where growth was increased by 13% in ryegrass. Thus, root contact between the two species is required for both the facilitation of ryegrass by the clover and for ryegrass to gain the competitive advantage. Similar interactions have been observed in other grass or cereal and legume systems. Eliminating direct root contact using pot barriers reduces facilitative effect of intercropping in maize/grass pea intercrops by up to 15% (Zhu *et al*., 2022) and in kura clover/meadow bromegrass intercrops by 100% (Walker and King, 2009). Previous work has determined that facilitative effects of clover are due to their ability to mobilise soil P and the competitive effects of ryegrass are due to its faster establishment making it a strong competitor for P (Boot and Mensink, 1990; Høgh-Jensen and Schjoerring, 2010; Lu *et al*., 2020). However, this was not observed in this experiment. The lack of differences in soil P availability and uptake between barrier treatments in either species indicate that the facilitative and competitive effects of intercropping on the two species were not due to changes in P availability. Furthermore, the different pot barriers used failed to determine whether association with AMF had any influence on growth or P uptake in the intercropped pots. Experimental limitations meant that it was difficult to rule out AMF association altogether and more extensive work is required to determine if AMF association has any influence on plant-to-plant facilitation in clover/ryegrass cropping systems. The pot barrier system used in Chapter 5 could be used in conjunction with direct inoculation with known AMF species in a doer-receiver system like the work of Mikkelsen *et al*., (2008). These methods could be used with a range of P mobilising and non-mobilising species to determine the extent in which root-to-root contact, exudate production and AMF play in modulating plant-to-plant P transfer in various intercropped systems.

The use of alternative sources of fertiliser such as CBD and CKD can relieve some of the pressures on food production resulting from intensive agricultural practices. These products can increase growth and K uptake in ryegrass pastures to the same degree as lime and K fertiliser. Their use could aid in closing the loop of nutrient flow by diverting a waste product rich in K from landfill and back into the food system (Sreekrishnavilasam *et al*., 2017). However, using products that are high in Ca can result in decreased P uptake from applied fertilisers in some cases. Intercropping with white clover can be used in combination with CBD/CKD and/or P fertiliser to improve pasture productivity in terms of growth and P efficiency. This cropping system is overall more efficient than monocropping. This effect is best facilitated by root contact of the plants and therefore further work in assessing different planting densities in combination with lime and P fertilisers is needed to determine the most effective approach. However, chapter 2 and 3 illustrate that the current practice of using CBD/CKD is wasting K as the amount of K being applied is not leading to proportional improvements in biomass production. Therefore, lower rates are more efficient. However, as current practice is constrained by licencing fees associated with the Sludge (Use in Agriculture) Regulations 1989 (Anon, 1989), this thesis questions whether this act is useful in its aims to reduce agricultural waste and build-up of PTEs in soil. Especially as application of CBD/CKD was found to not affect plant uptake of PTEs in chapter 3. Further work is needed to address the agronomic efficacy of applying CBD at lower rates in order to fully answer this question.

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APPENDIX A: SOILS USED FOR EXPERIMENTATION

Table 1: Background data on the soils used for the experiments in this thesis.

	Soil 1	**Soil 2**
Source Location	Morton House Farm, Clitheroe, Lancashire, UK	Pikeber Farm, Skipton, North Yorkshire, UK
Chapters Used	3	2, 4 and 5
OM	2.8%	1.2%
Clay %	24.7	5.84
Sand %	38.25	77.2
Silt %	37.05	16.96
Texture	Clay Loam	Sandy Loam
C (%)	4.0	2.9
N (%)	0.4	0.2
C:N	1:11	1:13

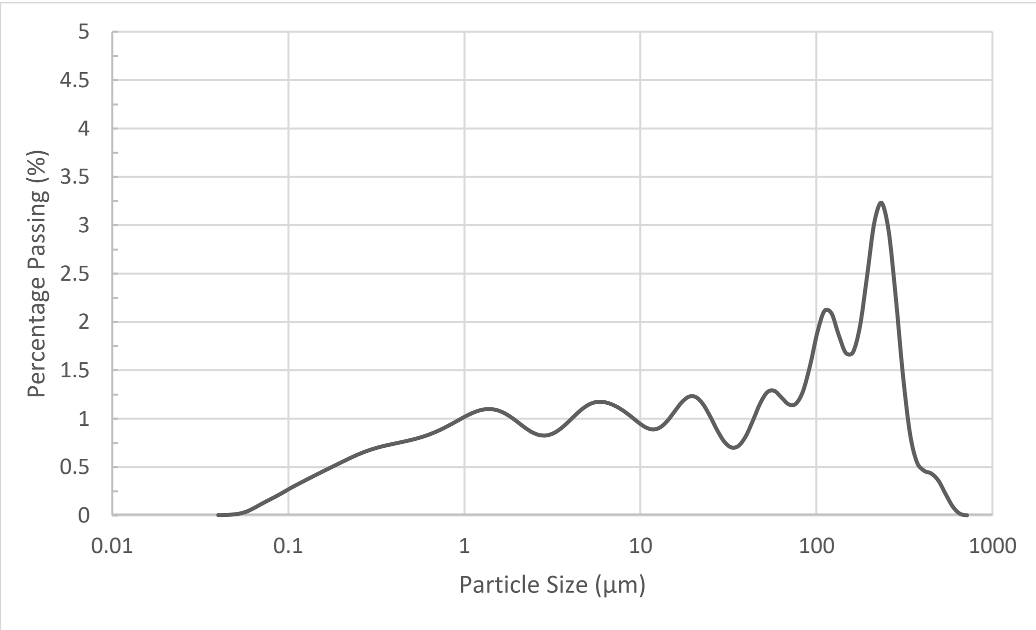

Figure 1: Particle size distribution for soil #1 (see Table 1).

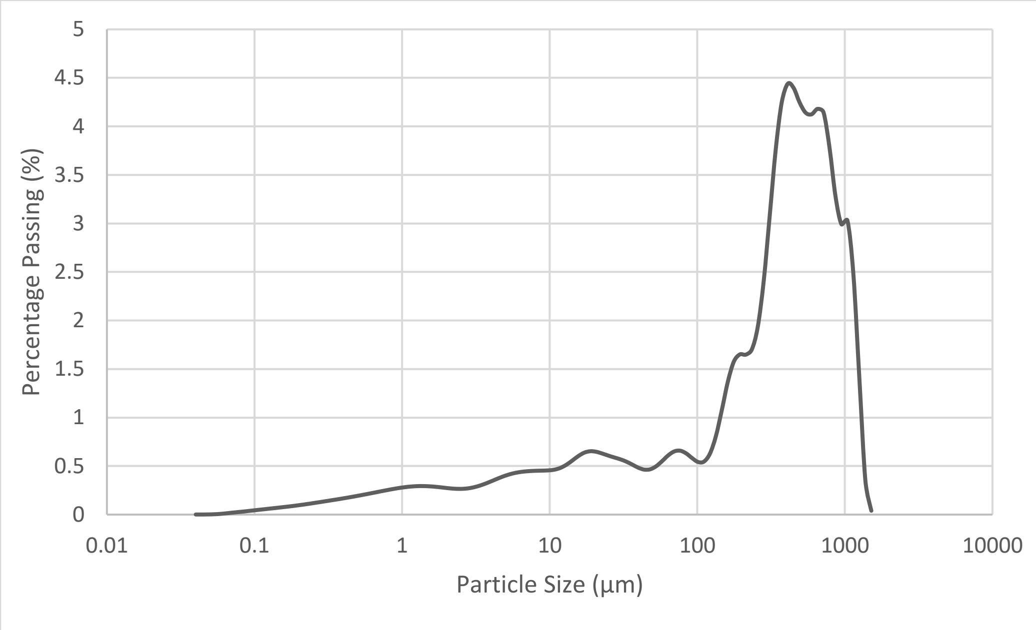

Figure 2: Particle size distribution for soil #2 (see Table 1).

Materials and Methods for Supplementary Soil Data

Soil Sampling and Preparation

Sampling was carried out in the same manner as in section *3.2.3*. The soil samples were air-dried (at 27°C, until constant weight) and sieved to 2mm and stored in plastic zip-lock bags. For C:N analysis the samples were further processed by filling half a 2ml Eppendorf microtube and grinding through a ball mill (Retsch GM400, Verder Scientific, USA) for one minute at 30.0 Hz until the sample was a fine powder. The samples were then dried further for an hour at 80°C. For all analyses, three replicates were used.

Estimation of Organic Matter by Loss-On-Ignition

Organic matter was estimated using the Loss-On-Ignition Method (Rowell *et al.*,2014, pp.48). Five grams of the air-dired soil was weighed into a glass crucible and left in a drying oven overnight at 105°C to remove water. After this the crucibles and soil were weighed before being heated in a muffle furnace (Carbolite CWF 1300, Carbolite, UK) 550°C for 12 hours to remove organic matter. Weight of the crucibles without soil, with soil after drying and after organic matter removal was recorded and used to estimate organic matter content using the following calculation:

$$OM(\%) = \frac{W_{dry} - W_{OML}}{W_{dry}} \times 100$$

Where OM(%) is the percentage of organic matter as a percentage of dry soil, W_{dry} is the weight of the dried soil and W_{OML} the weight of the soil after organic matter is removed.

Particle Size Distribution Analysis

The method used for was based on those established by on Gale & Hoare (1991).

Two grams of the air-dried sample was digested in a 250 ml glass beaker with approximately 20 ml hydrogen peroxide (H_2O_2) and then heated on a hot plate to 75°C once visible reaction subsided. The sample was then cooled and H_2O_2 was added until no more reaction occurred. After this 1 ml of 10% Calgon (= 10 % w:v sodium exametaphosphate ($(NaPO_3)6$) was added, the mixture stirred and then left over night. Sample analysis was performed in triplicate using a LS13320 Particle Size Analyzer (Beckman Coulter) with the laser set to 780 nm and the PIDS set to 462, 604 and 900. Samples were run for 90 seconds with the power set to 8 and then sonicated for 30.

C:N

Dried and milled samples were analysed using a Elementar Vario EL Cube CN analyser (Elementar, Germany).

APPENDIX B: CHAPTER 3 SAMPLING SCHEMATIC AND RESULTS DATA

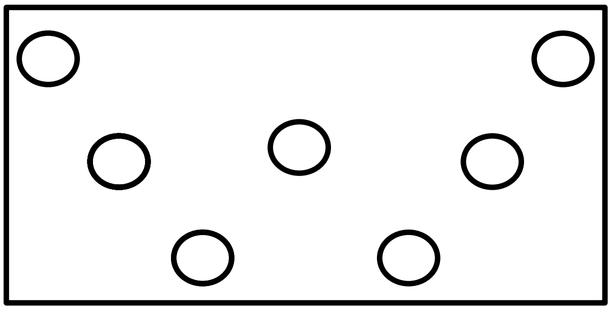

Figure 1: The schematic for taking soil samples from each field trial plot. Seven cores (denoted by the circles in the image) were taken from each plot (denoted by the rectangle) in a 'W' shaped pattern. The six samples were amalgamated for analysis.

Table 1: The effect of the different soil amendments on the biomass production (measured as dry weight in g m^2) of perennial ryegrass (*Lolium perenne* L.) grown in the field. Data are means ± SE of 3 plots.

	Mean Dry Weight (g m^2)			
	05/06/19	**30/08/19**	**16/07/20**	**22/09/20**
Control	409.67 ± 38.2	139.24 ± 13.0	68.27 ± 15.8	50.60 ± 2.4
K Fertiliser	552.62 ± 80.1	173.27 ± 12.5	77.43 ± 0.9	49.44 ± 7.3
Lime	487.06 ± 31.3	124.43 ± 9.2	67.63 ± 14.1	66.74 ± 6.5
Lime + K	647.52 ± 109.2	138.15 ± 11.0	91.83 ± 8.5	60.60 ± 3.8
CBD	661.48 ± 23.2	146.85 ± 8.9	85.33 ± 6.8	71.15 ± 5.5
CKD	645.86 ± 42.4	176.11 ± 43.4	82.16 ± 2.9	59.85 ± 3.2

Table 2: The effect of the different soil amendments on soil pH over 6 sampling dates. Data are means ± SE of 3 plots.

	Mean Soil pH					
	03/01/19	05/06/19	30/08/19	01/02/20	16/07/20	22/09/20
Control	5.84 ± 0.1	6.35 ± 0.2	5.80 ± 0.1	5.26 ± 0.3	5.64 ± 0.0	5.79 ± 0.1
K Fertiliser	5.77 ± 0.1	6.13 ± 0.1	5.61 ± 0.0	5.03 ± 0.1	5.42 ± 0.2	5.70 ± 0.1
Lime	5.72 ± 0.1	6.52 ± 0.1	5.42 ± 0.0	5.45 ± 0.0	5.38 ± 0.1	5.90 ± 0.2
Lime + K	5.68 ± 0.1	6.59 ± 0.1	5.52 ± 0.1	5.16 ± 0.2	5.61 ± 0.1	5.95 ± 0.1
CBD	5.59 ± 0.1	6.61 ± 0.2	5.53 ± 0.1	5.34 ± 0.2	5.36 ± 0.1	5.57 ± 0.1
CKD	5.57 ± 0.1	6.39 ± 0.0	5.61 ± 0.1	5.42 ± 0.2	5.75 ± 0.1	5.89 ± 0.0

Table 3: The effect of the different soil amendments on soil K availability over 4 sampling dates. Data are means ± SE of 3 plots.

	Mean Soil K (mg kg^{-1})			
	05/06/19	30/08/19	16/07/20	22/09/20
Control	78.56 ± 10.9	102.06 ± 10.5	87.41 ± 10.4	39.95 ± 7.7
K Fertiliser	147.90 ± 64.2	117.24 ± 38.0	103.09 ± 5.2	72.16 ± 16.3
Lime	87.60 ± 13.1	92.95 ± 9.1	82.19 ± 13.8	45.81 ± 2.9
Lime + K	114.74 ± 10.9	141.53 ± 38.8	82.19 ± 5.2	66.31 ± 10.6
CBD	153.93 ± 23.5	241.72 ± 55.7	87.41 ± 10.4	60.45 ± 8.8
CKD	123.78 ± 45.0	153.67 ± 21.3	123.98 ± 23.9	57.52 ± 7.7

Table 4: The effect of the different soil amendments on soil P availability over 4 sampling dates. Data are means ± SE of 3 plots.

	Mean Soil Olsen P (mg kg $^{-1}$)			
	05/06/19	**30/08/19**	**16/07/20**	**22/09/20**
Control	33.89 ± 1.1	25.17 ± 1.6	38.77 ± 5.3	10.75 ± 1.6
K Fertiliser	35.36 ± 1.2	28.70 ± 3.2	24.62 ± 11.6	8.96 ± 1.4
Lime	32.13 ± 2.5	33.14 ± 4.3	29.11 ± 4.9	22.10 ± 10.7
Lime + K	37.38 ± 1.3	29.67 ± 1.7	32.99 ± 7.2	14.50 ± 5.0
CBD	44.01 ± 2.7	28.37 ± 1.1	36.19 ± 4.8	11.89 ± 3.7
CKD	35.76 ± 4.7	38.03 ± 3.3	33.47 ± 2.8	14.31 ± 3.6

Table 5: The effect of the different soil amendments on leaf tissue Ca concentration over 4 sampling dates. Data are means ± SE of 3 plots.

	Mean Tissue Ca (mg g $^{-1}$)			
	05/06/19	**30/08/19**	**16/07/20**	**22/09/20**
Control	9.40 ± 0.4	9.85 ± 0.9	4.02 ± 0.1	3.73 ± 0.1
K Fertiliser	4.24 ± 0.4	9.31 ± 1.0	4.53 ± 0.3	3.37 ± 0.1
Lime	13.44 ± 0.2	9.76 ± 0.6	4.68 ± 0.1	3.20 ± 0.3
Lime + K	2.77 ± 0.6	9.30 ± 1.4	4.54 ± 0.4	3.63 ± 0.1
CBD	9.23 ± 0.2	7.08 ± 0.9	4.39 ± 0.3	3.37 ± 0.2
CKD	8.28 ± 0.3	8.06 ± 0.2	4.40 ± 0.3	3.10 ± 0.2

Table 6: The effect of the different soil amendments on leaf tissue K concentration over 4 sampling dates. Data are means ± SE of 3 plots.

	Mean Tissue K (mg g $^{-1}$)			
	05/06/19	**30/08/19**	**16/07/20**	**22/09/20**
Control	8.31 ± 1.7	7.37 ± 1.5	7.58 ± 0.2	6.80 ± 0.5
K Fertiliser	11.97 ± 2.9	6.78 ± 1.6	10.59 ± 1.2	9.20 ± 0.7
Lime	10.57 ± 1.2	4.51 ± 0.2	6.48 ± 0.7	6.30 ± 1.1
Lime + K	5.19 ± 0.7	7.86 ± 1.5	8.77 ± 1.4	8.93 ± 1.3
CBD	31.42 ± 0.8	5.93 ± 1.9	10.02 ± 1.2	8.80 ± 0.5
CKD	33.79 ± 1.8	6.54 ± 0.2	11.80 ± 0.9	10.17 ± 0.3

Table 7: The effect of the different soil amendments on leaf tissue Mg concentration over 4 sampling dates. Data are means ± SE of 3 plots.

	Mean Tissue Mg (mg g $^{-1}$)			
	05/06/19	**30/08/19**	**16/07/20**	**22/09/20**
Control	4.02 ± 0.1	2.54 ± 0.2	2.52 ± 0.2	1.93 ± 0.0
K Fertiliser	2.27 ± 0.9	2.33 ± 0.2	1.83 ± 0.1	1.67 ± 0.0
Lime	5.35 ± 0.3	2.39 ± 0.2	2.09 ± 0.1	1.80 ± 0.1
Lime + K	1.02 ± 0.0	2.30 ± 0.2	1.97 ± 0.1	1.90 ± 0.3
CBD	2.65 ± 0.0	1.54 ± 0.2	1.90 ± 0.0	1.73 ± 0.1
CKD	2.43 ± 0.1	1.58 ± 0.0	1.68 ± 0.3	1.43 ± 0.3

Table 8: The effect of the different soil amendments on leaf tissue P concentration over 4 sampling dates. Data are means ± SE of 3 plots.

	Mean Tissue P (mg g $^{-1}$)			
	05/06/19	**30/08/19**	**16/07/20**	**22/09/20**
Control	4.12 ± 0.40	2.76 ± 0.35	3.12 ± 0.28	2.40 ± 0.06
K Fertiliser	1.74 ± 0.25	2.34 ± 0.26	2.69 ± 0.27	2.30 ± 0.10
Lime	5.72 ± 0.68	2.51 ± 0.18	2.92 ± 0.08	2.33 ± 0.13
Lime + K	1.11 ± 0.06	2.52 ± 0.17	2.67 ± 0.27	2.77 ± 0.33
CBD	3.56 ± 0.12	1.69 ± 0.40	2.50 ± 0.16	2.27 ± 0.09
CKD	3.53 ± 0.26	1.85 ± 0.06	2.82 ± 0.37	2.33 ± 0.26

APPENDIX C: CHAPTER 4 RESULTS DATA

Table 1: Mean dry weight of white clover per pot across product application, cropping method and harvest date. Data presented is the mean ±SE of 3 mesocosms.

	Monocrop Mean Dry Weight (g per pot)		
Product	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	102.42 ± 14.9	42.41 ± 7.6	15.09 ± 2.6
Lime	79.45 ± 4.3	57.1 ± 6.8	21.48 ± 1.0
CBD	99.25 ± 20.6	60.46 ± 5.3	18.7 ± 3.3

	Intercrop Mean Dry Weight (g per pot)		
Product	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	52.62 ± 3.8	72.62 ± 8.1	58.64 ± 2.3
Lime	29.95 ± 8.3	18.15 ± 2.9	30.89 ± 11.1
CBD	10.81 ± 4.0	10.69 ± 7.9	7.55 ± 3.0

Table 2: Mean dry weight of perennial ryegrass per pot across product application, cropping method and harvest date. Data presented is the mean ±SE of 3 mesocosms.

	Monocrop Mean Dry Weight (g per pot)		
Product	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	22.36 ± 1.1	24.54 ± 0.6	14.17 ± 2.4
Lime	24.51 ± 1.8	27.77 ± 1.7	22.74 ± 3.2
CBD	20.33 ± 1.3	27.33 ± 1.8	21.08 ± 3.9

	Intercrop Mean Dry Weight (g per pot)		
Product	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	18.38 ± 1.8	30.35 ± 6.8	28.70 ± 5.1
Lime	16.1 ± 1.7	40.57 ± 5.7	43.60 ± 2.8
CBD	14.14 ± 2.0	39.46 ± 9.3	36.6 ± 6.0

Table 3: Soil pH of mesocosms receiving either no product application, lime application or CBD application across 2 cropping methods and 4 sampling dates. Data are means ± SE of 3 mesocosms.

	Monocrop Mean Soil pH			
Product	**02/05/19**	**22/07/19**	**14/10/19**	**12/10/20**
None	5.6 ± 0.1	6.2 ± 0.1	6.1 ± 0.1	6.2 ± 0.1
Lime	5.7 ± 0.0	6.4 ± 0.1	6.6 ± 0.1	6.9 ± 0.1
CBD	5.7 ± 0.0	6.6 ± 0.1	6.8 ± 0.1	6.8 ± 0.1

	Intercrop Mean Soil pH			
Product	**02/05/19**	**22/07/19**	**14/10/19**	**12/10/20**
None	5.6 ± 0.1	6.3 ± 0.1	6.1 ± 0.1	6.2 ± 0.1
Lime	5.7 ± 0.0	6.1 ± 0.1	6.6 ± 0.1	6.7 ± 0.1
CBD	5.7 ± 0.1	6.9 ± 0.1	6.6 ± 0.1	6.8 ± 0.1

Table 4: Soil P availability of mesocosms receiving either no product application, lime application or CBD application across 2 levels of P application, 2 cropping methods and 3 harvest dates. Bars are means ± SE of three mesocosms.

		Monocrop Mean Soil Olsen P (mg kg^{-1})		
Product	**P Addition**	**22/07/19**	**14/10/19**	**12/10/20**
None	No Added P	25.16 ± 4.7	18.33 ± 2.8	11.00 ± 2.1
Lime	No Added P	22.71 ± 3.7	22.20 ± 6.4	4.11 ± 1.9
CBD	No Added P	23.16 ± 3.8	30.42 ± 3.1	9.74 ± 3.9
None	Added P	23.67 ± 5.2	35.05 ± 5.7	17.64 ± 2.9
Lime	Added P	27.69 ± 6.6	32.30 ± 6.8	11.81 ± 3.1
CBD	Added P	17.79 ± 3.9	24.45 ± 6.3	5.17 ± 2.1

		Intercrop Mean Soil Olsen P (mg kg^{-1})		
Product	**P Addition**	**22/07/19**	**14/10/19**	**12/10/20**
None	No Added P	15.56 ± 3.1	10.70 ± 0.4	2.92 ± 1.1
Lime	No Added P	14.93 ± 1.1	25.26 ± 3.4	8.87 ± 2.6
CBD	No Added P	31.53 ± 6.1	10.19 ± 0.0	10.94 ± 4.1
None	Added P	22.98 ± 2.3	30.76 ± 2.5	12.78 ± 1.7
Lime	Added P	28.55 ± 5.4	28.25 ± 2.0	8.77 ± 1.6
CBD	Added P	16.43 ± 1.5	11.67 ± 3.2	2.95 ± 1.1

Table 5: Incremental changes in leaf tissue P concentration of white clover across different cropping dates, cropping systems, P fertiliser and lime treatments. The results presented are normalised to the untreated, monocropped plants (1.0) which acted as a control. Data are means ± SE of 3 pots.

		Monocrop Relative Leaf Tissue P		
Product	**P Addition**	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	No Added P	1.00 ± 0.0	1.00 ± 0.0	1.00 ± 0.0
Lime	No Added P	0.85 ± 0.0	0.96 ± 0.1	0.99 ± 0.2
CBD	No Added P	0.66 ± 0.1	0.94 ± 0.1	0.82 ± 0.1
None	Added P	0.77 ± 0.0	1.00 ± 0.1	0.96 ± 0.1
Lime	Added P	0.88 ± 0.2	0.93 ± 0.1	0.90 ± 0.1
CBD	Added P	0.70 ± 0.2	1.00 ± 0.0	1.09 ± 0.0

		Intercrop Relative Leaf Tissue P		
Product	**P Addition**	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	No Added P	0.80 ± 0.1	0.50 ± 0.0	0.65 ± 0.0
Lime	No Added P	0.55 ± 0.0	0.63 ± 0.1	1.09 ± 0.0
CBD	No Added P	0.53 ± 0.1	0.61 ± 0.0	0.79 ± 0.0
None	Added P	0.80 ± 0.1	0.82 ± 0.1	1.15 ± 0.0
Lime	Added P	1.07 ± 0.2	0.93 ± 0.1	1.13 ± 0.1
CBD	Added P	0.76 ± 0.1	0.75 ± 0.1	0.91 ± 0.1

Table 6: Incremental changes in leaf tissue P concentration of perennial ryegrass across different cropping dates, cropping systems, P fertiliser and lime treatments. The results presented are normalised to the untreated, monocropped plants (1.0) which acted as a control. Data are means ± SE of 3 pots.

		Monocrop Relative Leaf Tissue P		
Product	**P Addition**	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	No Added P	1.00 ± 0.0	1.00 ± 0.0	1.00 ± 0.0
Lime	No Added P	0.82 ± 0.2	0.56 ± 0.1	0.83 ± 0.1
CBD	No Added P	1.01 ± 0.1	0.91 ± 0.0	0.89 ± 0.1
None	Added P	0.63 ± 0.1	0.79 ± 0.2	0.99 ± 0.1
Lime	Added P	0.85 ± 0.1	0.94 ± 0.1	1.24 ± 0.1
CBD	Added P	0.76 ± 0.1	0.67 ± 0.1	1.03 ± 0.2

		Intercrop Relative Leaf Tissue P		
Product	**P Addition**	**22/07/2019**	**14/10/2019**	**12/10/2020**
None	No Added P	0.95 ± 0.3	0.90 ± 0.3	0.94 ± 0.1
Lime	No Added P	1.19 ± 0.2	1.01 ± 0.2	0.93 ± 0.1
CBD	No Added P	1.25 ± 0.2	0.71 ± 0.1	0.83 ± 0.2
None	Added P	1.36 ± 0.0	1.13 ± 0.1	0.96 ± 0.1
Lime	Added P	1.32 ± 0.1	0.98 ± 0.1	1.19 ± 0.1
CBD	Added P	1.13 ± 0.0	0.94 ± 0.1	1.03 ± 0.1

Appendix C: Chapter 5 Results Data

Table 1: Mean dry weight per plant of white clover grown in pots divided by one of four barrier treatments paired with either the same species (monocrop) or perennial ryegrass (intercrop) on the other side of the barrier. Data are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots).

Mesh Size	Mean Biomass (g per plant)
Monocrop	
None	0.105 ± 0.01
41 µm	0.079 ± 0.00
1 µm	0.084 ± 0.00
0 µm	0.062 ± 0.00
Intercrop	
None	0.081 ± 0.01
41 µm	0.67 ± 0.01
1 µm	0.072 ± 0.00
0 µm	0.053 ± 0.00

Table 2: Mean dry weight per plant of perennial ryegrass grown in pots divided between one of four barrier treatments paired with either the same species (monocrop) or white clover (intercrop) on the other side of the barrier. Data are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots).

Mesh Size	Mean Biomass (g per plant)
Monocrop	
None	0.069 ± 0.00
41 µm	0.060 ± 0.00
1 µm	0.056 ± 0.00
0 µm	0.050 ± 0.00
Intercrop	
None	0.079 ± 0.01
41 µm	0.072 ± 0.01
1 µm	0.055 ± 0.00
0 µm	0.049 ± 0.01

Table 3: Mean soil water P concentration (µg solution-P kg^{-1}) per half pot containing white clover, divided by one of four barrier treatments paired with either the same species (monocrop) or perennial ryegrass (intercrop) on the other side of the barrier. Data are means ± SE of 6 pots.

Mesh Size	Mean Soil P (µg solution-P kg^{-1})
Monocrop	
None	3.62 ± 0.9
41 µm	4.19 ± 0.2
1 µm	4.85 ± 0.3
0 µm	5.57 ± 0.6
Intercrop	
None	5.21 ± 0.9
41 µm	4.73 ± 1.1
1 µm	5.92 ± 0.8
0 µm	7.12 ± 0.6

Table 4: Mean soil water P concentration (µg solution-P kg^{-1}) per half pot containing perennial ryegrass, divided by one of four barrier treatments paired with either the same species (monocrop) or white clover (intercrop) on the other side of the barrier. Data are means ± SE of 6 pots.

Mesh Size	Mean Soil P(µg solution-P kg^{-1})
Monocrop	
None	4.63 ± 0.8
41 µm	7.37 ± 1.0
1 µm	7.02 ± 0.8
0 µm	6.70 ± 0.5
Intercrop	
None	5.11 ± 0.5
41 µm	5.31 ± 0.8
1 µm	4.72 ± 0.6
0 µm	5.43 ± 0.6

Table 5: Mean tissue concentration (mg g^{-1}) of P in white clover tissue. Data are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots). Nonparametric analysis was used for this dataset due to non-normal distribution.

Mesh Size	Mean Tissue P (mg g^{-1})
Monocrop	
None	2.12 ± 0.4
41 µm	2.00 ± 0.2
1 µm	2.04 ± 0.2
0 µm	2.04 ± 0.2
Intercrop	
None	2.17 ± 0.4
41 µm	2.30 ± 0.2
1 µm	1.59 ± 0.4
0 µm	1.81 ± 0.3

Table 6: Leaf tissue P concentration (mg g^{-1}) of perennial ryegrass plants grown as a monocrop or intercrop, separated by one of four barrier treatments. Data are means ± SE of 90 plants (15 plants per half pot with each treatment consisting of 6 pots).

Mesh Size	Mean Tissue P (mg g^{-1})
Monocrop	
None	3.98 ± 0.4
41 µm	3.56 ± 0.3
1 µm	3.96 ± 0.4
0 µm	3.45 ± 0.2
Intercrop	
None	3.75 ± 0.4
41 µm	2.71 ± 0.5
1 µm	3.94 ± 0.5
0 µm	3.14 ± 0.3