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The Use of Rockdust and Composted Materials as Soil Fertility Amendments

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Abstract

This thesis aims to investigate the use of two materials: rockdust and greenwaste compost for use as soil fertility amendments. A field trial was conducted over three years to investigate the impact these materials had on plant yield, plant nutrient content, soil chemistry and soil microbial communities in direct comparison with chemical fertilizer and farmyard manure. There were annual applications of compost, manure and chemical fertilizer in spring with one rockdust application in the autumn prior to the first year of the trial. Two harvests were carried out each year in summer and autumn to determine differences in plant yield. The soil was analysed prior to applications to determine the baseline chemical status then was analysed at two more points through the trial.

Results from the field trial showed clear effects of organic amendments on plant yield that were attributed to nitrogen addition by compost and manure. NPK chemical fertilizer produced a yield effect at an earlier point in the trial compared to manure and compost. This, and the chemical analysis of the materials showed that the organic materials required a period of mineralization of organic-N in order to replenish soil available nitrogen.

The results from the field trial also showed differences in plant nutrient content (as a measure of plant quality). The organic treatments were shown to generally produce higher plant nutrient content than the NPK fertilizer showing that the increased yields of the inorganic fertilizer treatment impacted negatively on the nutrient content.

No yield effects due to rockdust addition were apparent after 3 years of the field trial. In addition, rockdust did not impact on plant nutrient content nor did it affect the soil chemistry despite 3 years of weathering that was considered sufficient time to release nutrients to the soil.

Samples of soil were taken in the summer after the final year of the field trial to determine long-term changes in the soil microbial communities between the treatments. Results showed that there were fewer long-term changes than were initially expected in soil microbial communites at the end of a 3 year trial of these materials.

Short-term greenhouse pot trials were also conducted using 3 different test crops to investigate the use of greenwaste compost and various types of rockdust for use as growth media in comparison with a peat based control. Results showed that while greenwaste compost supported plant growth as well as the peat based media, no rockdust type increased plant growth beyond the yield in a greenwaste compost control. The short-term supply of nitrogen in greenwaste compost was as good as that of the peat based control and while the phosphate supplied by the peat based control was shown to give excessively high plant P content. Results from the pot trials showed that greenwaste compost could wholly or partially replace peat in plant growth media without negatively impacting on plant yield or quality.

The likely effects of various types of rockdust on soil chemistry were investigated by carrying out nutrient extractions using increasing extractant 'strength'. Nutrient extractions showed that a high degree of rock weathering was required to release small quantities of trace elements from rockdust samples. Sodium, calcium and to a lesser degree potassium, magnesium, iron and phosphate were supplied in greatest quantities from most rockdust samples with basic rocktypes releasing highest quantities of nutrients.

As a result of the work carried out in this thesis, it is concluded that composted greenwaste could be a valuable addition to agricultural soil and that it could replace peat in some plant growth media. There are some implications to the use of composted materials – transport and application costs and the potential addition of potentially toxic elements to soil; however the potential nutrient addition and improved plant quality could make it an attractive fertility amendment in some organic farming techniques.

It was concluded that rockdust was not shown to influence plant yield or quality in the agricultural setting of the field trial, nor was it shown to be a useful addition to plant growth media. Therefore rockdust could not be proven to be a useful soil fertility amendment.

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Author's Declaration

I declare that the work described in this thesis has been carried out by myself, except where otherwise acknowledged. It is entirely of my own composition and has not, in whole or in part, been submitted for any other degree.

Nicola Campbell

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Chapter 1: Introduction

The work presented in this thesis will investigate the use of rockdust and composted materials as agricultural soil amendments and as horticultural growth media. The main focus will be on the SEER Centre field trial of rockdust and organic amendments while further work will investigate the nutrient availability from rockdust. Composted greenwaste materials will be examined within the context of both agricultural and horticultural applications.

1.1 Introduction to rockdust materials

Rockdust is a by-product of quarrying operations that extract and screen rock for the aggregate industry. Rock particles larger than 6 mm are generally used in asphalt production with a current high demand for 10 mm single-sized aggregate. Large stock piles of less economic fine grade ‘rockdust’ can be generated. Other descriptors of this product include rock powder, rock fines, mineral fines and quarry tailings. Rockdust may be further processed to generate very fine grade material or used in the state that they are produced (a mix of very fine and coarser particles).

1.1.1 The quarrying process

During rock quarrying, explosive charges are fired in holes drilled into the rock face. The blasted rock is then taken to a primary jaw crusher that breaks the rock down to smaller sizes. The rock from the primary crusher is processed several more times by hammer crushers and screened to different particle sizes. Crushed aggregates are stored in separated size grades for different uses. At every stage in the process, rock fines are produced and stored on-site. The type of rock quarried can influence the amount of fines generated during the extraction and screening process. Generally, coarse grained rocks (e.g. granite) will produce fewer fines than fine grained rock (e.g. basalt) due to the mineral particle sizes in the rock. Some quarries extracting rock types that produce fewer quantities of fines may actually need to import fines from other operators for use in asphalt production (MIRO/Leeds University, 2008).

The single-size aggregate produced during the screening process can be further processed at the quarry in asphalt production. During this process, the aggregate is coated with bitumen as the binding agent. There are tight regulations on the aggregate sizes used in asphalt production for various uses that are detailed in BS 594 and BS EN 13043 (British Standards Institution 2005a; 2002). BS 594 details the proportions of coarse aggregates (greater than 2 mm), fine aggregates (less than 2 mm) and fines (less than 63 μm) permitted in asphalt mixtures for different applications. Many asphalt producers have developed their own brand named mixes for different uses. A portion of rock fines can be added to the asphalt mixtures as long as they conform to BS EN 13043. This document details the maximum content of fines less than 63 μm in aggregates for bituminous mixtures.

Another on-site use for rock fines is to use them in sand and gravel operations. Rock fines are washed and coarse material is settled out by sedimentation. These coarse grains can be used instead of importing sand and gravel from other quarries. The very fine material less than 63 μm is removed in suspension to settling lagoons.

Despite the uses of fines in asphalt production and sand and gravel, the demand for high specification aggregates in asphalt production means that large stockpiles of fine aggregates and rock fines can be produced at quarries. It is these mixed fine aggregates and rock fines less than 6 mm that will be investigated in this thesis.

1.1.2 Possible effects of use of rockdust materials

The claims made about the benefits of using rockdust in agriculture originate from the work of Hamaker (1982) who promoted ‘remineralization’ of the soil using glacial rockdust. This was reported to increase soil mineral content, increase plant quality and Hamaker believed that this material could have far-reaching global implications on climate change by reducing atmospheric CO_2 levels. While the effects of rockdust materials on climate change are beyond the scope for this thesis; the effects on plant and soil will be investigated.

Szmidt and Ferguson (2004) reviewed some replicated trials of various types of rockdust at varying rates of application. A great deal of these rockdust trials were reported in 'Remineralize the Earth' magazine. These included trials using a wide range of crops including vegetables and trees. Results were variable with some authors stating that rockdust application led to increased yields, plant growth or reduced disease incidence. Other effects reported included: increased soil moisture infiltration; increased soil nutrients and improved plant nutrient uptake. However, some other authors could not find any benefits from rockdust compared to controls. Many of the trials reported in 'Remineralize the Earth' magazine were not statistically validated or peer-reviewed. The experiments were, in some cases, poorly designed. Reported rates of rockdust application ranged from 7.4 t ha^{-1} to as high as 124 t ha^{-1} with roughly 25 t ha^{-1} as a preferred rate (Szmidt and Ferguson, 2004). Although there were many potential advantages to the use of rockdust reported in 'Remineralize the Earth' magazine, replicated and statistically validated trials are necessary to prove the benefits of rockdust use. Of the few statistically valid experiments reviewed by Szmidt and Ferguson (2004), rockdust was shown to function most effectively on low fertility soil. For example, Blum *et al*. (1989b) showed that long-term additions could raise the cation exchange capacity and acid neutralising capacity of poor soils. Another example given was that of Szmidt (2004) where rockdust application to a low nutrient, highly organic soil resulted in plant survival where otherwise they all died. Szmidt and Ferguson (2004) suggested that, as with inert material such as sand, rockdust could affect (either positively or negatively) soil physical properties such as density, moisture holding capacity or air porosity.

Van Straaten (2006) reviewed the advantages and disadvantages of using rock fertilizers in agriculture. The advantages were discussed as the possibility of multi-elemental release; high pH; possible improvement to the acid neutralization capacity of some soils; or changes to the cation exchange capacity of some soils. The disadvantages were identified as the low solubility and slow nutrient release; large application rates required and that a large portion of the rock could be minerals with no nutrient value.

1.1.3 Rockdust as potassium fertilizers

As igneous rocks contain high quantities of potassium bearing minerals such as feldspars and micas, a major area of research into the use of rockdust has been on the potential of this material as potassium fertilizers.

Some studies e.g. Coroneos *et al*. (1996) aimed to show that potassium supplied by rockdust application resulted in extra plant growth. At 7 weeks clover showed a significant growth response to granite application, ryegrass growth was systematically higher but not significant. They concluded that there must have been release of non-exchangeable K from granite either by root-assisted dissolution of mica or by soil-mediated granite dissolution. This was supported by Wang *et al*. (2000) who concluded that mineral K could be mobilized and utilised by some plants when assessing K release from gneiss (where K bearing minerals are likely to be feldspar, muscovite and biotite). However, Sanz Scovino and Rowell (1988) showed that plant growth and uptake of K from pure mineral feldspar application were not significant despite an apparent upward trend. The indication from lab experiments that showed K could be released in significant amounts over long periods of time was not proven in the field experiments.

Bakken *et al*. (1997b) tested adularia rock dust, mine tailings, carbonatite and epidote schists in plant growth experiments with *Lolium multiflorum* in 3 soil types and with 6 harvests. They concluded that almost all feldspar-K applied in adularia and mine tailings was unavailable to plants whereas rocks containing biotite and/or nepheline could supply considerable amounts of potassium. However, a rock containing carbonate minerals would dissolve faster than those containing silicate minerals leading to more exposed minerals and more weathering of K-bearing minerals and therefore more plant-available K. A similar conclusion was reached by Bakken *et al*. (1997a) who found that adularia and microcline gneiss did not supply significant amounts of K to plants during a plant growth experiment. The potassium supplied by rocks that contained nepheline, biotite and carbonatite supplied potassium to plants in higher quantities than rocks containing feldspar. Again, Bakken *et al*. (2000) concluded that the weathering rate of adularia was not high enough to cover plant K-demand. This is because the main K-bearing mineral in adularia is feldspar. Biotite and nepheline disintegrate more readily and release K at higher rates than feldspar. However, they also state "even the most soluble rocks weather too slowly to replenish the native pool of plant available K in a short time scale". So it can be seen that the mineral source of potassium in a rockdust sample is very important when determining the potential effectiveness of a crushed rock product as a potassium fertilizer; but that rockdust may not be an effective potassium fertilizer.

Other studies have focused on the effect of rockdust application to the soil e.g. Hinsinger *et al*. (1996) who showed an increase in exchangeable K in 9 out of 20 acid, highly weathered soils from Western Australia treated with granite after 60 days incubation with 4 out of 20 of the soils exhibiting a doubling in exchangeable K. They also suggested that higher plant yields produced by granite application may be due to K supplied by the rock since Na, Ca and Mg did not change significantly. Hildebrand and Schack-Kirchner (2000) showed that basalt rockdust may be a useful long-lasting K fertilizer. In percolation experiments, 20 % of added K was transported to the mineral soil after 1000 mm percolation volume. Conversely, Gillman *et al*. (2002) concluded that finely ground basalt rock would not be expected to be a long term source of K due to high leaching losses of exchangeable K in a short period of time from amended soils. In the 3 years following application of phonolite rockdust to an acidified glacial loam, potassium did not increase in soil solution (von Wilpert and Lukes, 2003). They suggested the reasons for this were low solubility rates of K bearing minerals in phonolite rock in addition to plant uptake of what little potassium became available.

Research into rocks and minerals as potential potassium fertilizers has also investigated the mode of potassium release from minerals. Hinsinger and Jaillard (1993) aimed to show the transformation of phlogopite (trioctahedral mica) into a vermiculite clay mineral in relation to K-depletion in the rhizosphere and subsequent release of interlayer K from the mica. They showed a significant release of interlayer K and parallel vermiculitization due to plant roots after 8 days of cropping which greatly increased after 32 days. The absence of any mica alteration products at the end of a plant growth experiment by Gilkes and Young (1974) indicated that only minor stratification had occurred. They found that the least oxidised biotite samples were most effective as potassium fertilizers. Highly oxidised biotites released K at a slower rate, similar to that of dioctahedral micas such as muscovite. In agreement with these findings, Wentworth and Rossi (1972) showed that phlogopite and muscovite additions at a variety of rates produced potassium deficient plants. This was also true for low level additions of biotite and illite. Vermiculite was the only mineral to supply K at levels high enough to produce 'normal' plant uptake when applied at high rates. Potassium release from layer silicates was shown to be most easily released from vermiculite followed by illite, biotite, phlogopite then muscovite. The order could change due to levels of F in the trioctahedral micas which could inhibit K release.

1.1.4 Effect of rockdust on soil pH

Amongst the possible advantages to rockdust use, liming effects have been widely examined. Hinsinger *et al*. (1996) showed a significant increase in pH after a 60 day incubation in 6 out of 20 acid, highly weathered soils from Western Australia treated with granite. However the liming effect was much lower than that of crushed limestone. Silva *et al*. (2005) agreed that granite powder could correct the acidity of various materials due to its high pH, although larger quantities would be required compared with other common liming materials. In contrast, Coroneos *et al*. (1996) concluded that application of granite did not give any clear liming effect when added to a sandy, acid podzol.

von Wilpert and Lukes (2003) stated a positive pH response of 1 pH unit in an acidified glacial loam below the humus layer treated with phonolite rockdust (a volcanic silicate rock with hydrothermal minerals). This effect lessened with depth to less than 0.5 units at 20cm depth. A positive pH effect was also shown by von Mersi *et al*. (1992) who showed that addition of a basalt/diabase/bentonite powdered rock mixture to acid forest soils could lead to higher soil pH. This could also lead to increased nitrification due to a stimulation of microbial activity. For very acid soils, a much higher dose of rock powder was required since a rate of 4.7 t ha^{-1} showed no effect on microbiological activities.

Gillman (1980) found that soil pH was raised with increasing application rates of crushed basalt to a highly weathered soil. Finer ground material and longer incubation times enhanced this effect. Gillman *et al*. (2002) also showed that increasing application rates of crushed basalt on highly weathered (low pH) soils steadily raised the soil pH, although high application rates above 25 t ha^{-1} were required in most instances to raise the pH above 5. There was a simultaneous reduction in reserve acidity in treated soils.

Bakken *et al*. (2000) stated that soil pH was not affected by fertilizer treatment when adding adularia, mine tailings epidode schists, biotite and carbonatite to grassland sites at a rate of 50 kg ha^{-1} potassium equivalent to rockdust application rates of between 75 and 227 t ha^{-1}.

These previous studies clearly show that the effect of rockdust on soil pH seems to be limited to very poor, low pH soils such as highly weathered soils or forest soils. The effect was consistently much lower than that of traditional liming materials. It is unlikely, therefore that rockdust materials would have an effect on the pH of agricultural soil.

1.1.5 Effect of rockdust on plant growth

The response of plants to rockdust application has been widely investigated in the literature using a variety of plants and a range of rock types.

Hinsinger *et al*. (1996) reported that wheat did not respond to diorite application whereas it did respond to K from granite application. At 5 t ha^{-1} the yield in granite treated pots was significantly higher than in the control. The concentration of K in plant tissue also increased with rate of granite application while it did not with diorite application. Their results indicated that the increased plant growth was due to potassium supplied by granite rockdust as the concentrations of other macro-nutrients in plant tissue were not affected.

Plant growth effects were also shown by Weerasuriya *et al*. (1993) who found that acidulated mica chips gave significant increases in panicle number and seed weight of rice compared to a muriate of potash control. They concluded that the acidulated mica must add elements and trace elements other than potassium since the potash control added 4 times as much K. Kahnt *et al*. (1986) found positive effects on plant growth when various rock powders were mixed with sandy soil. They found that 10 % (w/w) additions gave greater shoot dry matter yields than 20 % (w/w) additions. A spring barley grain yield increase of 67 % on the control was found when basalt rock powder was added to sandy soil at a rate of 10 % (w/w).

Rockdust applications in addition to other fertilizing materials have also been tested. These have included NPK fertilizer and composted materials. Leonardos *et al*. (1987) showed that the highest yield of beans was found in treatments of NPK with various types of rockdust (basalt and phonolite, mica-schist or micronutrients) which also had a better residual effect than NPK alone. They reported results of another experiment where rockdust addition of 3 – 5 t ha^{-1} to low nutrient, lateritic soil produced dry matter yield gains in grass of 10 – 29 %. Hartmann *et al*. (1999) applied N-enriched rock powder (containing apatite, biotite, kolemanite and dolomite) to poor sandy soils and showed that it stimulated microbial activity and soil organic matter formation. N-free rock powder and N-containing rock powders were also shown to influence the production of field layer vegetation and stimulate the mineralization process. An overall increase in plant growth using glacial silt/quartz dolerite rockdust was shown by Szmidt (2004) when added to 3 different soil types (with and without composted materials). However, rockdust may only be a valuable soil amendment on nutrient poor soils. This was shown in a highly organic soil, where addition of rockdust ensured plant survival where otherwise all plants died. There was no consistent effect on plant available nutrients across the other soil types.

Phosphate rock was shown by Msolla *et al*. (2007) to give positive responses on maize growth when applied to acid soil. There was also a better residual effect than triple superphosphate due to solubilization of the rock over time in acid soil and lower plant uptakes of phosphate during the first harvest period. However, only a small amount of applied apatite-containing rock powder (high in phosphate) was shown by Hartmann *et al*. (1999) to be taken up by forest vegetation in the first year of application. This was thought to be partly due to low solubility at high pH and also due to high Ca^{2+} in solution leading to fixation as calcium phosphates.

1.1.6 Comparisons of rockdust with soluble fertilizers

Some trials of rockdust materials have involved a direct comparison with traditional, soluble fertilizers. The conclusion for many of these experiments showed that rockdust would not be an appropriate short-term substitute for inorganic fertilizers. For example, Hinsinger *et al.* (1996) stated that granite rockdust would only be an alternative to soluble fertilizers when leaching was expected to be high. However, this was based on short-term experiments comparing ground rock with soluble K fertilizer. The long term effects would need examining. Similarly, von Wilpert and Lukes (2003) suggested that the slower reaction of phonolite compared to dolomite (lime) could mean that it was an alternative where the risk of nitrate mobilization is high. Nitrate mobilization was noticed as a result of the increase in soil pH brought on by dolomite application.

However, in most applications, rockdust could not compete with soluble fertilizers. Bolland and Baker (2000) found that high applications of granite rockdust actually reduced yields of wheat grown in sandy soils compared to the control treatment. Potassium limited the yield of wheat but this was only improved by adding soluble K fertilizer. They concluded that granite rockdust does not supply potassium at the rate required to meet the demands of wheat.

While Bakken *et al.* (1997a) found that considerable amounts of potassium could be taken up by plants grown in soils treated with rockdust containing nepheline or biotite, they would need further processing to be suitable long-term K fertilizers. In short term pot trials, plants grown on KCl treated soil produced greater plant matter than those grown on rockdust treated soil. However, after 23 weeks, there were no yield differences between the KCl treatment and plants grown on rockdusts with high proportions of carbonatites, nepheline and biotite. Those with high concentration of potassium feldspar were amongst the least effective as potassium fertilizers due to the low solubility of the mineral. Supanjani *et al.* (2006) found that the combined application of phosphate and potassium rock powder with P and K solubilising bacteria increased plant yields similarly to those gained using soluble fertilizers. This treatment also increased P and K availability in treated plots to the same level as soluble fertilizer. The addition of rock solubilising bacteria to the P and K rock meant that these rocks were converted to more plant available forms quickly and was shown to be a sustainable alternative to industrial fertilizers for hot pepper production.

The use of rockdust as phosphate fertilizer was also examined by Gillman *et al.* (2002) who concluded that amending soils with finely ground basalt could reduce phosphate requirements in the short-term only, due to the low P content of basalt. Despite increased levels of extractable P after application of basalt fines, there was a finite limit of 3 kg P per tonne applied.

These trials all showed that rockdust could not replace inorganic fertilizers. Rather, they could be alternatives in sensitive areas where leaching of added nutrients could be a problem or applied as a supplement to soluble fertilizer. The mineral source of plant nutrients is also of importance since research has shown that some forms can be very resistant to weathering and therefore release of nutrients.

1.1.7 Nutrient release from rockdust

The release of nutrients from rockdust is an important area of research into the possible benefits to its use. The factors influencing mineral dissolution were investigated by Harley and Gilkes (2000) who stated that it would be dependant on the soil environment including: pH, redox, soil solution compostion and temperature. Decreased soil pH increases silicate dissolution; localised reducing conditions could increase Fe in solution; diffusion gradients in the soil solution could accelerate rock weathering; and mineral dissolution occurs faster at higher temperatures. The soil is a complex system where many different weathering reactions can occur simultaneously making it difficult to predict how a mineral will dissolve. Plant roots can reduce the concentration of ions in the soil solution (near to the roots) so that rockdust weathering in this region could be enhanced due to the diffusion gradient (Harley and Gilkes, 2000). The greatest potential for rockdust dissolution would be when nutrients are removed (i.e. by plants) and by action of organic acids added by mycorrhiza. The role of plant roots in rock weathering was further investigated by Meheruna and Akagi (2006) who used a hydroponic system to show decreasing pH in planted pots compared to the control that had no plants. There was a concurrent release of nutrients from crushed andesite rock. Most of the elements released were accumulated in the plant tissue. Where there was a high nutrient demand, calcium and manganese were shown to be released in higher amounts when plant roots were in direct contact with rock particles. The hydroponic system was also used by Akter and Akagi (2005) with crushed basalt rock. The highest elemental release from basalt was shown in the crop that produced the most vigorous growth and therefore had higher nutritional requirements. In crops with high nutrient requirements, the proximity of fine roots on nutrient release from basalt rock would be of greatest importance. Bakker *et al*. (2004) showed that weathering of powdered plagioclase could be stimulated by plants although mineral dissolution was primarily due to geochemical (pH) effects. This was supported by Hinsinger *et al*. (2001) who showed a small decrease in solution pH due to H-ion release from plant roots. This decrease in pH also resulted in enhanced basalt dissolution rates. There was a consistent, positive effect on rate of basalt weathering in the presence of plants. They concluded that rock weathering in the rhizosphere could be fast enough so that crushed silicate rocks or parent rocks rich in primary minerals could be potential nutrient sources for soil fertility. Wang *et al*. (2000) also postulated that root induced acidification may have influenced the release of mineral K from gneiss rockdust.

Huang and Kiang (1972) investigated the dissolution of plagioclase minerals. They found that there was a rapid dissolution stage followed by a step with a reduced rate of dissolution (when all easily soluble cations from broken bonds or highly disordered sites are used up). They reported that sodium-rich plagioclase dissolves more readily than calcium-rich plagioclase in deionised water. However, calcium is more soluble than sodium from all plagioclase minerals. Increasing extraction of cations from the plagioclase minerals by organic acids was due to complexing capacities of the acids as opposed to dissociation of the acid. So the composition of soil solution could be an important factor that could determine weathering rates of rocks and minerals. Hinsinger *et al*. (2001) showed that the incongruent dissolution of basalt weathered plagioclase minerals (releasing calcium and sodium) faster than ferromagnesian silicates. Similarly, a crushed basalt amendment was able to provide substantial amounts of basic cations (especially calcium and magnesium) to highly weathered soils (Gillman *et al*., 2002). However, only a small fraction of the total cations was released and it was unknown if further release following plant uptake would occur.

Blum *et al.* (1989b) showed that rock powders could be used in the long term to increase CEC in poor soils but commented that these are usually forest soils and not used for agricultural purposes. They decided that rock powders with high carbonate contents would be best for improving poor soils but those high in silicate minerals would have little effect. Investigations into silicate minerals have shown that sheet silicate minerals such as mica are more susceptible to acid attack (and therefore weathering) than framework silicates such as feldspars. As the release of magnesium from phlogopite mica required irreversible weathering of the silicate structure (Hinsinger *et al.*, 1992); uptake by ryegrass roots remained lower than release of Mg from rockdust. XRD analysis showed no evidence of weathering of the phlogopite. Conversely, interlayer potassium could have been released and slight vermiculitization of the mica was shown (Hinsinger *et al.*, 1992). Weerasuriya *et al.* (1993) reported that fresh phlogopite mica released more bases into solution than weathered phlogopite. Hence the rate of nutrient release from rockdust samples is very dependant on the mineral composition of the rock used and also the degree of weathering. Low soluble and extractable nutrient contents were found in granite, diabase, basalt and volcanic ash rock powders investigated by Blum *et al.* (1989a). Any differences between rock powders were attributed to differences in mineralogy as opposed to total nutrient content. Because of the low nutrient content and high transportation costs, these authors did not recommend use of rock powder in agriculture.

Other research has investigated the most soluble cations from rockdust. For example, Gillman (1980) found that only a small fraction of the cations applied as crushed basalt scoria was mobilized in incubation experiments. However, crushed basalt addition did result in an increased level of exchangeable cations. Silva *et al.* (2005) showed that the most soluble elements from granite powder were calcium and magnesium, not potassium as had been extensively studied in the literature. High amounts of sodium were released by phonolite rock powder (von Wilpert and Lukes, 2003) with 30% of the total sodium appearing in soil solution of an acidified glacial loam after 1 year. They also reported a 2 – 5 mg l^{-1} increase in calcium below the humus layer after 1 year. The increase in the exchangeable calcium pool was highly significant down to 10 cm depth. A highly significant increase in base saturation in phonolite treated plots was shown although it was less than in lime treated plots.

1.1.8 Micro-nutrients from rockdust

Although there have been many studies on the macro-elemental release from rockdust, the potential for these materials as micro-nutrient fertilizers has not been widely investigated. Leonardos *et al*. (1987) suggested that ground rocks of various composition could be used to supply the variety of both macro and micro-elements that are normally present in soil but are absent in lateritic soil systems. Van Straaten (2006) agreed that multi-elemental release could be an advantage of rockdust use. O'Brien *et al*. (1999) investigated changes in a range of extractable nutrients from a plant growth medium treated with either basaltic or glacial rock fines. Most nutrients were significantly affected by fines addition although the increases were most marked in macro-nutrients such as Ca and Mn. Szmidt *et al*. (2004) also investigated the effect of rockdust amendment on substrate element availability but could find no consistent effect on macro or micro-element availability. Harley and Gilkes (2000) reviewed the distribution of plant nutrients (K, Ca, Mg, P, S, B, Cl, Cu, Fe, Mn, Mo, Ni, Zn, Co, Na and Si) in igneous and metamorphic minerals. Most trace elements exist in minerals as inclusions or 'foreign' ions as opposed to main structural elements and are likely to be available in lesser quantities than macro-nutrients. Despite the range of elements present in quarry fines, Vetterlein (2004) stated that most of the nutrients are not readily available. He *et al*. (2005) stated that the easily weathered constituents of basaltic rocks can contain Cu, Zn, Co and Mn. Release of Si, Al, Ca, Mg, Fe and Mn in the presence of plant roots from andesite was investigated by Meheruna and Akagi (2006) and from basalt by Akter and Akagi (2005). Weerasuriya *et al*. (1993) stated that one of the potential benefits of rockdust was the possibility of multi-elemental release when compared to conventional fertilizers. To improve the effectiveness when applying rockdust materials to soil, they pre-treated mica and feldspar with acid and determined the water soluble bases. As expected, low mica to acid ratios increased the water soluble concentrations of K, Mg, Fe, Zn, Mn and Cu due to the leaching of interlayer cations and degradation of mica to kaolinite.

1.1.9 Effect on physical and biological properties of soil

Most research into the effects of rockdust has focused on the effects on chemical properties of soil. Limited research exists on the effects of rockdust on the physical and biological properties of soil. Kahnt *et al.* (1986) found that rockdust addition to sandy soil increased the field capacity by 12 – 23 % compared to the control. Short term growth experiments showed that five test crops responded mostly positively to rockdust addition to sandy soil; while in clay soil, the effect was slightly negative. Szmidt (2004) commented that rockdust, as with other inert mineral materials such as sand, could have effects on physical properties of plant growth media. Effects could occur on density, moisture holding capacity and air porosity.

Some effects have been shown on the biological activity of soil. For example, von Mersi *et al.* (1992) showed a significant effect on protease activity. They suggested that applications of rockdust could increase C and N mineralization which could affect mineral nutrient turnover in forest ecosystems in the long-term. Effects on the microbial population of soil could be due to indirect effects of rockdust on the soil chemistry or physical properties giving rise to more favourable conditions for microbial activity. They could also be caused by soil microbes directly metabolising rockdust materials. However, Szmidt and Ferguson (2004) acknowledge that there is limited evidence to support this theory. Harley and Gilkes (2000) reviewed some evidence of the ability of rhizosphere micro-organisms to release soil minerals or increase trace element mobility. Micro-organisms have been shown to alter biotite (Berthelin and Belgy, 1979). Microbes could also accelerate weathering by the mass action effect of absorption of elements (Barker *et al.*, 1997) or by increasing carbonic acid in soil by respiration.

1.1.10 Effect of grain size of rockdust

Wang *et al.* (2000) showed a significant increase in plant growth when using fine particle size (1-2 mm) gneiss compared to coarse size (2-5 mm). This was attributed to some physical or chemical effect other then K since no difference in response to the supply of K was found between the two size fractions. The effect of grinding basalt rockdust was investigated by Blum *et al.* (1989a) who showed that reducing particle size from 100% passing a 2 mm sieve to 100% passing a 200 µm sieve doubled the amount of easily soluble elements. Gillman (1980) reported a high correlation between cation exchange capacity and the amount of applied rockdust material passing the 125 µm sieve. Although it is expected that smaller grain size would lead to greater reactivity of rockdust due to greater exposure of the reactive surface of minerals, Harley and Gilkes (2000) reviewed some articles where this was not always the case. Grains larger than 2 mm were suggested as a nutrient reservoir and some studies reviewed showed that smaller grains may not have greatest dissolution rates.

1.1.11 Use of rockdust and compost

The use of compost with rockdust has been investigated in the literature including a range of possible benefits to the use of rockdust in the composting process. Garcia-Gomez *et al.* (2002) stated an increase in microbial respiration, which was shown by a loss in biomass and increased carbon dioxide production, when using a blend of glacial silt and quartz dolerite in the composting of spent mushroom substrate (SMS). They also postulated that rockdust could have improved the physical properties of SMS allowing 'faster surface reactions, gas exchange and spatial effects'. Sikora (2004) aimed to show that addition of basaltic mineral fines to an animal manure composting mixture could stimulate biological activity and improve compost quality by reaching higher temperatures during the process. However, despite apparently higher temperatures after mixing at six weeks, there was no statistical difference between the unamended control and the rockdust amended treatment.

Another area in this research is in blending rockdust with composted materials in the manufacture of growth media. Mitchell *et al.* (2004) found that growth media manufactured from compost and quarry fines would need to be supplemented with fertilizer to establish plants and produce good growth in the medium-term. Artificial soils manufactured from these materials were also shown to support grass and tree growth at the level of 'economy grade' soil. Guillou and Davies (2004) combined various composts with 4 types of rockdust and showed that the best soil substitutes were formed using greenwaste compost with any type of rockdust or kerbside collection compost with basalt rockdust. Blending various composts with rockdust had no detrimental effects on acceptability to the consumer of tomato fruit with differences in tomato yield due only to compost type used. Guillou and Davies (2004) also showed that larger rock particles could improve the drainage of some composts. Very fine (< 75 µm) particle size rock fines gave higher bulk densities in compost/rockdust blends. This could have an impact on the acceptability of compost/rockdust growth media as alternatives to peat based media.

Vetterlein (2004) explained that the greater transportation costs relative to competing products would have the greatest impact on viability of compost and quarry fines blends. This is due to the high bulk density of quarry fines. Transport costs of a blended product are likely to be similar to the cost of transporting topsoil but up to 10 times the cost of transporting peat. As well as analysis of total elemental compositions in a compost and quarry fine blended product, water extractable and plant available nutrients and trace elements should be analysed since most nutrients in quarry fines are not readily available (Vetterlein, 2004).

1.2 Introduction to composted materials

1.2.1 The composting process

Zucconi and de Bertoldi (1987) defined compost as 'the stabilized and sanitized product of composting which is beneficial to plant growth. It has undergone an initial rapid stage of decomposition and is in the process of humification (stabilization stage)'. The composting process was defined as a 'controlled bio-oxidative process'. They identified the following stages in the process:

- Incorporation of a heterogeneous organic substrate in the solid state
- Transition through a thermophilic stage (also called "active stage") and temporary release of phytotoxins
- Production of carbon dioxide, water, minerals and stabilized organic matter (compost)

During the process of composting, there is a decrease in ammonium and an increase in nitrate (Garcia *et al*., 1991). This is because, at the end of the active stage in composting, temperatures decrease and nitrifying bacteria are able to convert ammonium to nitrate (Sánchez-Monedero *et al*., 2001). The process of nitrification is carried out by two groups of bacteria as described below:

- $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O$ (*Nitrosomonas* bacteria)
- $2NO_2^- + O_2 \rightarrow 2NO_3^-$ (*Nitrobacter* bacteria)

Sánchez-Monedero *et al*. (2001) also explained that nitrification in compost is limited due to organic-N mineralization rates.

Because the mineralization potential in composted materials is so low, Sullivan *et al*. (2004) looked at indicators of mineralization potential of fresh yard trimmings. They showed that a large initial C: N, high organic-N content, low lignin (high carbohydrate and hemicellulose) content and high rates of CO_2 evolution were all good indicators of high N mineralization rates from fresh wastes.

During composting, organic N increases as carbon dioxide is evolved and the C: N ratio decreases (Bernal *et al.*, 1996). There is a reduction in inorganic N due to immobilization or volatilization. Garcia *et al.* (1991) showed that there is an increase in cation exchange capacity (CEC) and there are more functional groups per unit organic carbon. Bernal *et al.* (1996) also found an increase in CEC of the organic matter during composting which was attributed to humification during composting (humification gives rise to functional groups). Grey and Henry (1999) showed that more humified compost (due to a longer maturation period) has a greater capacity to hold and release nutrient cations (Ca^{2+}, Mg^{2+} and K^{+}).

Vermicomposting has been shown to give a higher organic matter content in the finished product along with higher total nitrogen and available nutrients (Tognetti *et al.*, 2007). They stated that this was due to a shorter thermophilic stage along with enhanced microbial activity leading to mineralization.

The composting process can take several months to produce a stable composted product. Aerobic digestion may reduce the composting period significantly (Hoitink and Poole, 1980) to 2 weeks of active stage followed by 1 month stabilization. Although forced aeration needs to be closely controlled to maintain high moisture contents to avoid low decomposition rates. Decomposition of compost in bioreactors was also shown by Cambardella *et al.* (2003) to be limited by low or high moisture contents leading to less stable compost products. They also stated however, that increasing composting times could compensate for the effects of moisture limitations. Hoyle and Mattingly (1954) showed that increasing periods of aeration led to increased losses of N from wheat straw and sewage sludge compost. They also showed that the optimum range for initial-N levels was between 1.35 and 1.97 %. Increasing the initial-N beyond 2 % was not recommended since it did not increase soluble-N significantly but did increase losses of N substantially.

Sullivan *et al.* (2004) showed that hemicellulose in grass clipping samples decreased and lignin increased with increasing storage time. This showed that the samples were becoming more resistant to decomposition with increasing storage. The available N from grass clippings added to soil also decreased as the age of the material increased. Composted wastes are more stable and are less microbially active (Ayuso *et al.*, 1996) and contain 'better quality' organic matter (fewer labile fractions and more polymerized fractions) than fresh wastes. Keeling *et al.* (1995) showed a gradual increase in pH and a decrease in conductivity with increasing composting time. Younger compost contained significantly more protozoan biomass and had a higher microbial productivity than more stable compost.

1.2.2 Compost stability and maturity

It is important to distinguish between the terms 'compost maturity' and 'compost stability'. Compost maturity refers to the potential for plant growth or micro-organism re-colonization after peak heating whereas compost stability is the degree of decomposition undergone and can be determined by measuring microbial activity rates (Iannotti *et al.*, 1993). These workers found that measuring oxygen consumption in a flask containing a compost sample gave a good indication of the degree of compost stability. Bernal *et al.* (1998a) found that the most suitable parameter for measuring the maturity of compost was its water soluble organic carbon to organic nitrogen ratio. They also showed that water soluble carbon and fulvic acid carbon contents along with lignin concentration best defined compost stability. Compost stability was characterised by Hue and Liu (1995) using a number of measurements but they recommended water soluble carbon: total organic nitrogen as a quick and simple method. A CO_2 production rate less than 120 mg CO_2 kg^{-1} hr^{-1} was also stated as the value after which composts can be deemed stable.

1.2.3 Benefits of compost use

There have been a number of reported benefits to the use of compost both as container media and as agricultural amendments. Material used in these trials have ranged from greenwaste compost, food waste compost and composted biosolids from the wastewater treatment industry. Bugbee (2002) reported increased plant growth of flowering annuals and herbaceous perennials when biosolids compost was added at 50 – 100 % (vol) rates in a mix of biosolids compost, bark, peat and sand. There were no adverse effects of increasing compost additions on aeration, moisture retention or bulk density. Ozores-Hampton *et al.* (1999) showed that tomato transplants grown in media containing yard trimming/biosolids compost had greater leaf area and shoot weight than those grown in a peat/vermiculite media. They recommended that compost quality must be addressed prior to its usage in vegetable transplant media. Mathur and Voisin (1996) found that addition of food and wood waste compost to peat based growth media at rates of 40 % (v/v) and 75 % (v/v) in some instances increased yields of Clematis plants compared to peat alone. Some of the Clematis plants grown in compost amended peat had higher nutrient contents than plants grown in peat based growth medium alone. One of the conclusions of this report was that good quality compost could 'substantially replace peat in container growth media' due to (amongst other reasons) the increased plant growth and increased water-supplying capacity of these mixtures. Another consideration that must be made if compost is to be used as a container media growth medium is that the pore size should be small enough for handling but large enough to assure a high porosity. The fine content is necessary to raise CEC and moisture capacity of the final product (Hoitink and Poole, 1980). Also if compost was to be packaged, they stated that the moisture content should be less than 40 %. The bulk densities of composted materials are much higher than peat based growing media (approximately 3 times) which can have a significant impact on the transport costs (Vetterlein, 2004). Sánchez-Monedero *et al.* (2004) mixed compost samples with a commercial growing substrate and peat and assessed germination, plant growth and nutrient effects on 3 plant species. Mixing compost with peat resulted in lower bulk density and higher porosity and water holding capacities along with lower salinities and electrical conductivities. Sánchez-Monedero *et al.* (2004) attributed a reduction in seed germination to the high electrical conductivity of compost samples. However, plant growth in mixtures containing compost could be enhanced depending on individual plant salt tolerances. This was due to high nutrient contents in compost-containing mixtures that coincided with high nutrient content in seedlings grown in compost mixtures. These authors concluded that compost could be used in vegetable transplant production; however, liquid feeding regimes at nurseries would need to be adjusted on a crop-by-crop basis.

Agassi *et al.* (2004) showed that the beneficial yield affect gained by annual mulching of agricultural soil with composted municipal solid wastes were due to reduced evaporation since those plots treated had a higher soil water content than control plots. These annual applications also eliminated the need to fertilize the crop. A rate of 100 m^3 ha^{-1} (40 t ha^{-1}) was recommended to provide these benefits without any negative effects of increasing of soil salinity or heavy metal content. Annual applications of composted municipal solid wastes were shown by Hadas *et al.* (2004) to replace the need for P fertilization. They also reported a continuous increase in soil organic matter each year in the top 5 cm of soil after surface applications of compost. Chen *et al.* (1996) also found that composted materials were an excellent source of P for plant growth and that N and P did not limit ryegrass growth at rates of addition of biosolids compost greater than 2 % (w/w). There was a positive effect of increasing rates of biosolids compost and cow manure compost application on cumulative dry matter yields of ryegrass. Cow manure compost was shown to limit ryegrass growth by lack of available N, but could potentially provide N as a slow-release fertilizer. Bernal *et al.* (1998b) found that while plant N uptake was highest in compost treatments, plants grown in soil treated with mature sewage sludge compost did not give a statistically higher yield than soil treated with inorganic fertilizer. Mature sewage sludge compost could be used as N fertilizer due to the level of nitrate formed during the maturation stage of composting (Bernal *et al.*, 1998b). The fertilizer value of composts prepared from other sources (i.e. greenwaste compost) would be lower due to the nitrogen content of the starting materials. Garcia (1991) showed that the agronomic value of NPK in compost is 16 – 18 % of mineral fertilizer.

The effect of one-time high rate applications of compost were studied by Sullivan *et al.* (2003) using a rate of 155 t ha^{-1} tilled-in compost. The plots received annual fertilizer-N applications and were compared to a fertilizer only (no compost control). An increase in soil mineralizable-N was shown at years 3 and 6 after compost application. All compost treatments increased grass yields from year 2 onwards (until at least year 7). Compost also increased N uptake in grass compared to the fertilizer only control. Food waste and yard trimmings compost produced highest yields and N uptakes. Soumaré *et al.* (2003) showed that mineral fertilizer in combination with compost significantly increased dry matter yield of ryegrass. The compost used was shown to increase plant available K, Fe, Mn, Zn and Cu in the soil although, due to low dry matter yields, trace metal uptake by plants after compost application alone was not significantly affected. They recommended compost application in combination with NPK fertilizer.

Svensson *et al.* (2004) also recommended that compost application is complemented with mineral-N additions but, due to increases in N mineralization with repeated compost applications, after some time a reduction in mineral-N applied could be made. Soils with regular compost additions would have an increased N delivering capacity over time also. An increase in mineralization after 7 years of a 10 year agricultural trial of compost was shown by Erhart *et al.* (2005) which led to higher spring nitrate concentrations. The value of using compost is therefore long-term for supplying slow release N for crop growth. Yield responses due to compost application were low at the beginning of the trial but increased with time. Compost at an application rate of 23 t ha^{-1} y^{-1} was shown to increase yields 10 % on average over 10 years compared to the control.

As long as nitrate and calcium levels in compost are low, the water soluble phosphate content of compost will be high and it could have a similar fertilizing effect to super-phosphate (Jakobsen, 1995). Soil available P was maintained at 'high' levels throughout a trial of urban compost applications at a rate of 14 t ha^{-1} by Cabrera *et al.* (1989). Soil available K also slightly increased in compost applications. Guidi *et al.* (1983) showed that levels of K in composted urban refuse and aerobic/anaerobic sludge were not high in terms of crop requirement and that deficiencies might be seen in crops with high potassium requirements.

1.2.4 Problems of compost use

While there are many possible benefits to the use of composted materials in agriculture and horticulture, there can also be some problems associated with its use. Ozores-Hampton *et al.* (1999) found that yard trimming/biosolids compost had to be mixed with peat and vermiculite for use in pot trials. This was due to the initial high electrical conductivity of the compost that could adversely affect percentage germination and plant growth.

In agricultural applications, annual high application rates of compost were seen as unacceptable by Hadas *et al.* (2004). The heavy N load led to large N losses in the soil and possible groundwater contamination. To lower losses of nitrate, Tognetti *et al.* (2007) found that adding woodshavings to municipal organic waste would increase TOC/TN favouring immobilization of nutrients. Gerke *et al.* (1999)

showed that only long-term excessively high compost application rates; or applications of compost in combination with mineral N fertilizer could possibly lead to high nitrate leaching exceeding critical levels on a loam soil. The combination of compost at 10 t ha^{-1} y^{-1} with mineral N at 20 kg ha^{-1} y^{-1} gave highest crop yields with lowest average nitrate in drainage waters.

Agassi *et al.* (2004) was concerned that addition of composted municipal solid waste could lead to high salinity at the root zone and a build up of sodicity, however only a high application of 120 t ha^{-1} and not a lower application rate of 40 t ha^{-1} did so. This did not affect crop yield but it could have a negative effect on sensitive crops. The lower rate was recommended since similar yields were obtained at both rates while the lower rate had a lesser effect on soil salinity.

Another possible negative aspect of compost applications is the possible addition of heavy metals to soil. Cabrera *et al.* (1989) showed that compost treatments at rates of 14 t ha^{-1} led to increases in total copper and zinc in soil after 2 years of applications. This could be of concern at higher application rates or in the longer term. Svensson *et al.* (2004) also expressed concern that compost amended plots received high doses of heavy metals (especially lead) compared to those supplied with mineral fertilizer only.

Some of the problems associated with compost application to agricultural land are the result of application of poorly matured material. However, while composted materials may require a period of time to supply nutrients to soil, fresh urban wastes contain higher N, P and K levels (Ayuso *et al.*, 1996) although fresh wastes are not suitable for soil preservation applications due to high microbial activities. Non-mature compost should not be applied to soil unless a safety period is incorporated (Bernal *et al.*, 1998b). This was because a degree of immobilization was encountered when adding incompletely composted samples to soil leading to plant nutrient deficiencies when compared to matured compost. This view was supported by Ramunni *et al.* (1987) who found positive effects on root and cotyledon growth only after a period of 2 years had elapsed since uncomposted farmyard manure was added to poor volcanic soil. Uncomposted waste was also shown by Garcia *et al.* (1991) to have a depressive effect on yield at the first harvest although this effect diminished with time until the phytotoxic effects disappeared. They agreed that uncomposted waste must be added prior to sowing and left long enough to avoid the depressive yield effect. The depressive effect on seed germination was shown by Ayuso *et al*. (1996) where uncomposted municipal solid waste and uncomposted sewage sludge produced germination indices of 20 % or less. Composting these wastes resulted in germination indices of 80 % or more; this was due to degradation of phytotoxic low molecular weight organic acids during the composting process. For this reason Ayuso *et al*. (1996) recommended that composts and not fresh wastes should be applied to agricultural soils. If fresh yard trimmings were to be used in agriculture, Bary *et al*. (2005) explained that on farm management practices would need to be employed to minimise ammonia losses and encourage organic-N mineralization. Frequent analysis of Total-N, NH_4-N and C: N in the material would be necessary if seasonal differences in the proportion of grass clippings in fresh yard trimmings were anticipated. Jakobsen (1995) also noted phytotoxic effects when adding non-matured compost to soil however, 1 month later the crop had recovered. Gerke *et al*. (1999) showed that the long term differences in nitrogen turnover between mature vs. non-mature composts were small compared to site specific properties and management practices and went on to suggest that non-mature compost could be an economically interesting alternative to composted material. Keeling *et al*. (1995) showed a high level of available-N in all compost samples aged from 1 week – 4 weeks. The initial availability fell for some time as it was taken up by plant growth before being replaced by a period of increasing N mobility in all composts (although this occurred earlier in younger composts).

There are other alternatives to the application of composted wastes to agricultural soil. Trials have included applications of biosolids from the wastewater industry that can have been treated in a number of ways including aerobic/anaerobic digestion, dewatering, drying or composting. Composting of this material was seen by Guidi *et al*. (1983) to be an effective means of managing possible water contamination (eutrophication) since the maximum nitrate and phosphate pollution hazard came from aerobic sludge while composting this material with urban refuse led to decreases in concentration of these nutrients. The high electrical conductivity of uncomposted aerobic sludge may also inhibit germination. The effect of 7 years biosolids application to grassland was investigated by Cogger *et al*. (2001) who showed increased yields and nitrogen uptakes with increased application rates. Due to surface accumulation of phosphorus and the cumulative effect on soil available-N, high application rates were recommended in the short term only. There was an increase in surface soil organic C in biosolids treatments compared with fertilizer-N and no-N treatments. Heavy metal accumulation in soil and in plants was well below toxic levels and therefore not a concern.

Henry *et al*. (2000) showed little difference in N mineralization from wet or dried biosolids although dried biosolids produced less variable effects. Cogger *et al*. (2004) showed that heat-dried biosolids had a greater early availability of N although, after an initial fast rate of N release, subsequent N release was slower. Gilmour *et al*. (2003) showed that there was a good relationship between biosolids total-N and observed plant available-N. They stated that N-mineralization could be categorised only in biosolids that have been stabilized (i.e. in long-term lagoons or by composting). Cogger *et al*. (2004) and Gilmour *et al*. (2003) showed that stabilized biosolids decompose much more slowly and have lower levels of plant available N than non-stabilized biosolids.

Hence, it can be seen that composting of organic wastes including biosolids is a very effective treatment to stabilize the wastes and minimise potential pollution problems. Although available nutrients can be higher in uncomposted wastes, there are more risks associated with the application of these types of materials to agricultural land. Composted wastes are lower in available nutrients but are stabilized products with lower microbial activities that should not impact the land negatively if applied according to current guidelines.

1.3 The SEER Centre

The SEER Centre is a registered charity located in Perthshire, Scotland. It was established in 1997 by Cameron and Moira Thomson as a demonstration of the effects of rockdust on plant growth. They believe that rockdust can have many important effects including increased plant growth, increased nutritive content of plants, higher trace element content of soil and improved microbial activity. They also believe that rockdust could have global implications on carbon sequestration and climate change. Developments at the SEER Centre have included digging a terraced-bed system that was subsequently filled with various rockdust and greenwaste compost mixtures. These beds were planted with a range of crops and ornamental plants to show plant growth effects. Greenhouses and a large polytunnel were also erected to house year-round horticultural crops, again using compost and rockdust as the growth medium.

The SEER Centre also sells rockdust in 20 kg bags for horticultural use and encourages application to agricultural soil. In partnership with Angus Horticulture Ltd, they have developed two compost/rockdust mixtures for use as soil top dressing or as a plant growth medium. The plant growth medium uses the same ratio of compost and rockdust as used in the deep-bed system at the SEER Centre. The high ratio of 4 compost to 1 rockdust used in the terrace system at the SEER Centre has been described as 'soil formation' rather than a soil amendment.

While the deep-bed system and covered systems could show the effects of using these materials, they did not show possible agricultural benefits. The SEER Centre obtained funding from Entrust in 2003 to establish agricultural field trials of rockdust and organic materials. These trials were to be managed in a more scientifically valid manner than the original bed system in order to quantify the effects on plant growth. The SEER Centre directors organised a steering group for the field trial project that included consultants from the composting and horticultural industries, an ex-manager from the quarrying industry and academics in the areas of geology and environmental chemistry. Initial decisions on the direction of the research project were decided upon by the steering group in consultation with the SEER Centre directors. Chapter 6 describes the field trial that was central to the funding obtained by the SEER Centre. SEER Centre staff maintained the field trial plots on a day-to-day basis and were responsible for labour for the amendment applications, soil sampling and harvesting plant material. The University of Glasgow was responsible for the analysis of amendment materials, soil samples and plant material collected at the harvests. Extra research into nutrient release from rockdust; an investigation into the horticultural applications of different rockdust types; and research into the use of composted materials was also carried out to be detailed in this thesis in addition to the field trial work.

1.4 Aims and objectives

The work presented in this thesis will aim to test several hypotheses. The first hypothesis is that application of rockdust, either alone or together with organic materials or inorganic fertilizers to agricultural soil will lead to:

- increased harvested plant yields
- increased plant quality indicated by increased plant nutrient content
- increased levels of soil nutrients (including trace elements)
- changes to the soil microbial community

These effects will be measured by measuring plant dry matter yield in an agricultural scale field trial of rockdust, organic and inorganic fertilizer. The nutrient content of the harvested material will also be analysed. In addition, soil samples will be taken from the field trial at regular intervals for nutrient analysis. Soil microbial communities will be assessed on samples from the field trial using a physiological profiling technique. This will aim to determine long-term changes in the microbial community in the soil as a result of application of the above materials.

A second hypothesis is that the use of composted greenwaste material, either alone or in combination with various types of rockdust, as plant growth media for several types of crops will lead to:

- increased plant yields
- improved plant quality indicated by increased plant nutrient content

Plant growth media will be manufactured using one greenwaste compost source and various rockdust types for use in a greenhouse pot trial. Plant dry matter yield will be used to assess the effectiveness of the mixtures compared to growth in a peat based media. The plant quality will also be measured by analysis of the nutrient content of harvested material. This trial will also measure the effectiveness of greenwaste compost alone as a horticultural growth medium in direct comparison with peat.

A final hypothesis is that the possible beneficial effects gained from rockdust use are a result of:

- the macronutrient content of rockdust
- the micronutrient content of rockdust
- the high pH of rockdust materials

To assess these possible benefits, a suitable procedure for the analysis of extractable plant nutrients from rockdust will be developed. Various rockdust samples will be analysed using the nutrient extraction technique and comparisons made on the potential nutrient supply from different types of rockdust.

Overall, this thesis aims to show the potential benefits of the use of rockdust and organic materials (primarily composted materials) in both an agricultural and horticultural context.

Chapter 2: Routine Methods

2.1 Measurement of pH

2.1.1 General pH meter setup

All pH measurements were performed using an Orion model SA 720 pH meter calibrated using pH 4.0 and 7.0 buffer solutions. The buffer solutions were prepared by dissolving 1 buffer tablet in 1 litre deionised water. A gel-filled combination electrode (Thermo Electron Corporation) was used for all measurements.

2.1.2 Soil pH measurement

Soil: water 1: 2.5 (v/v)

A 30 ml scoop was overfilled with sample and struck level avoiding further compaction of the material. The sample was transferred to a 100 ml glass jar and 75 ml deionised water added by dispenser. The samples were shaken on an end-over-end shaker for 15 minutes then mixed briefly prior to pH measurement.

2.1.3 Rockdust pH measurement

Rockdust: water 1: 5 (v/v)

An 8 ml scoop was overfilled with sample and struck level avoiding further compaction of the material. The sample was transferred to a 100 ml glass jar and 40 ml deionised water added by dispenser. The samples were shaken on an end-over-end shaker for 1 hour then left to settle for 1 hour before briefly mixing prior to pH measurement.

2.2 Measurement of conductivity

All conductivity measurements were carried out using a Jenway 4070 conductivity meter and glass conductivity probe.

2.2.1 Compost conductivity

Compost: Water 1: 2.5 (v/v)

A 30 ml scoop was overfilled with sample and struck level avoiding further compaction of the material. The sample was transferred to a 100 ml glass jar and 75 ml deionised water added by dispenser. The samples were shaken on an end-over-end shaker for 15 minutes then filtered through Whatman No.2 filter paper prior to conductivity measurement.

2.3 Soil moisture content

2.3.1 Fresh soil

Approximately 20 g of fresh soil was weighed into a pre-weighed empty porcelain basin. The sample was then dried in the oven at 110 °C for 48 hours. Once dry, the samples were cooled in a desiccator for 30 minutes before reweighing.

2.3.2 Air dry soil

Approximately 10 g of air dry soil was weighed into a pre-weighed empty porcelain basin. The sample was then dried in the oven at 110 °C for 48 hours. Once dry, the samples were cooled in a desiccator for 30 minutes before reweighing.

2.3.3 Calculation of moisture content

Moisture content (dry mass basis) is calculated as below:

$$W_{H2O} = \frac{m_1 - m_2}{m_2 - m_0} \times 100$$

Dry matter content is calculated as below:

$$W_{DM} = \frac{m_2 - m_0}{m_1 - m_0} \times 100$$

Where:
W_{H2O} = moisture content (%)
W_{DM} = dry matter content (%)
m_0 = mass of empty porcelain basin (g)
m_1 = mass of basin plus fresh or air dry soil (g)
m_2 = mass of basin plus oven dry soil (g)

2.4 Soil organic matter content

Loss on ignition provides an estimate of soil organic matter and has been carried out at a variety of temperatures by different workers. Ball (1964) compared two ignition techniques: 850 °C for half an hour and 375 °C for 16 hours with organic C values (using the dichromate method). He found that the 375 °C method gave greater accuracy compared to the 850 °C method as there were fewer non-organic material losses. Non-organic material losses can be due to: loss of carbonates in calcareous soils; loss of elemental carbon; and loss of structural water in clay minerals.

The influence of loss on ignition temperature and heating time on the ash content of compost and manure was investigated by Matthiessen *et al*. (2005) who found that temperatures lower than 550 °C could underestimate LOI (%). Increasing heating time at 400 °C lead to increases in LOI (%) but could not compensate for the low temperature used. At 550 °C heating times between 8 – 24 h did not lead to any significant differences in LOI (%) for compost or manure samples.

The heating time of 16 h as required in the recommended soil methods in Ball (1964) and Matthiessen *et al*. (2005) with low temperatures of 375 – 400 °C were not suitable due to safety concerns. As a compromise, organic matter content of soil samples was measured using the loss on ignition method at 550 °C for 8 hours. Approximately 10 g oven dry soil was weighed into a pre-weighed silica or porcelain basin. The samples were placed in a muffle furnace and the temperature set to 550 °C. The furnace was switched on for 8 hours then left to cool overnight. The samples were reweighed and LOI (%) calculated as below:

$$\text{LOI (\%)} = \frac{W_o - W_i}{W_o - W_b} \times 100$$

Where:
W_o = Weight of basin plus oven dried soil (g)
W_i = Weight of basin plus ignited soil (g)
W_b = Weight of dry basin (g)

2.5 Soil textural classification: particle size fractionation by mechanical analysis

The soil structural peds were broken down to release the primary particles by destroying the organic matter then deflocculated and dispersed to break down the bonds causing aggregation.

2.5.1 Method

The following particle size distribution method was modified from BS 7755-5.4 (British Standards Institution, 1998).

2.5.1.1 Soil dispersion

10 g air dry soil (< 2 mm sieved) was accurately weighed into a 400 ml beaker. 50 ml 6 % hydrogen peroxide was added by tilt dispenser followed by two drops of anti-foaming agent. Once any initial reaction subsided, the beakers were heated gently on a steam bath with occasional stirring using a glass rod. If the reaction became too vigorous, the beaker was removed from the heat and more anti-foam added as required. Heating continued until the reaction ceased. Once cool, a further 50 ml 6 % hydrogen peroxide was added and the beaker was washed down with distilled water. The beaker was further heated until the reaction subsided. When no further reaction occurred with further portions of hydrogen peroxide, and to ensure complete destruction of the organic matter, a final 15 minutes of heating was carried out.

The dispersing agent was prepared by dissolving 57 g of sodium hexametaphosphate in 1 litre deionised water. Once the soil/peroxide mixtures were cool, 10 ml 5.7 % Sodium hexametaphosphate was added and the beakers placed in an ultrasonic bath for 10 minutes to disperse the soil.

2.5.1.2 Particle size separation

A 1 litre graduated cylinder was set-up with 180 μm and 53 μm brass sieves in a large funnel in the neck. The dispersed soil was tipped into the larger sieve and quantitatively transferred using deionised water and a glass rod. The soil was washed through the sieves with plenty deionised water until the two sand fractions appeared clean. The sand fractions were recovered by washing them quantitatively into pre-weighed porcelain basins. Excess water was removed by evaporation in a steam bath then the sand was dried in an oven at 110 °C before reweighing. The cylinder was made up to 1 litre volume. The two sand fractions were calculated as a percentage of oven dry mineral soil.

Silt and clay particles were measured using a pipette method based on the sedimentation rates of particles. All particles with a greater settling velocity than the fraction sought will settle below the point of withdrawal after the corresponding time. Stokes Law describes the relationship between the radius of a particle and its settling velocity in a medium of given viscosity:

$$V = \frac{g\ (\sigma - \rho) * d^2}{18\ \eta}$$

Where:

V = settling velocity (cm s^{-1})
g = acceleration due to gravity (981 cm s^{-2})
σ = density of settling particle (2.65 g cm^{-3})
ρ = density of water (0.988 g cm^{-3} at 20 °C)
d = diameter of particle (equivalent settling diameter, cm)
η = viscosity of water (0.010 g s^{-1} cm^{-1} at 20 °C)

Particles are assumed to be regular spheres of density = 2.65 g cm^{-3}. Sedimentation times were calculated for silt plus clay at a depth of 20 cm and clay only at a depth of 10 cm at various temperatures.

The temperature of the suspension was taken to calculate the required settling time (approximately 1 minute) for only the silt plus clay fraction to be removed. The cylinder was shaken thoroughly for approximately 1 minute to ensure all particles were in suspension. Timing began once the cylinder was placed back onto the pipette stand. The pipette was lowered 20 cm into the suspension and, at the calculated time, a 50 ml sample was removed. The sample was run into a pre-weighed porcelain basin and placed in a steam bath to evaporate off excess water, then placed in an oven at 110 °C before reweighing. Duplicate samples were taken.

The clay fraction required over 7 hours settling time (calculated using the water tank temperature). The cylinders were shaken in the morning and left to settle in a water tank at room temperature. Just before sampling time, the cylinders were removed from the water tank carefully to avoid disturbing the sedimentation and placed on the pipette stand. The pipette was lowered 10 cm into the suspension and, at the appropriate time, a 25 ml sample was removed. The sample was run into a pre-weighed porcelain basin and placed in a steam bath to evaporate off excess water, then placed in an oven at 110 °C before reweighing. Duplicate samples were taken.

2.5.1.3 Calculation of particle size fractionation

The weight of salts in the dispersing agent was removed from the fraction weight using the following equation:

$$\text{Weight of dispersant (g)} = \frac{0.57 * \text{volume of pipette}}{1000}$$

Silt plus clay in the mineral soil was calculated using the following equation:

$$\text{Silt plus clay \%} = \frac{(\text{wt. fraction} - \text{wt. dispersant}) * \text{vol. cylinder} * 100}{\text{wt. oven dry mineral soil} * \text{vol. pipette}}$$

Clay in the mineral soil was calculated using the following equation:

$$\text{Clay \%} = \frac{(\text{wt. fraction} - \text{wt. dispersant}) * \text{vol. cylinder} * 100}{\text{wt. oven dry mineral soil} * \text{vol. pipette}}$$

The silt fraction was calculated by subtraction. Percentage recovery was determined by summing the fractions. This was then corrected to a 100 % recovery.

The 3 percentages were then plotted on a soil textural diagram (Figure 2-1) to determine soil classification.

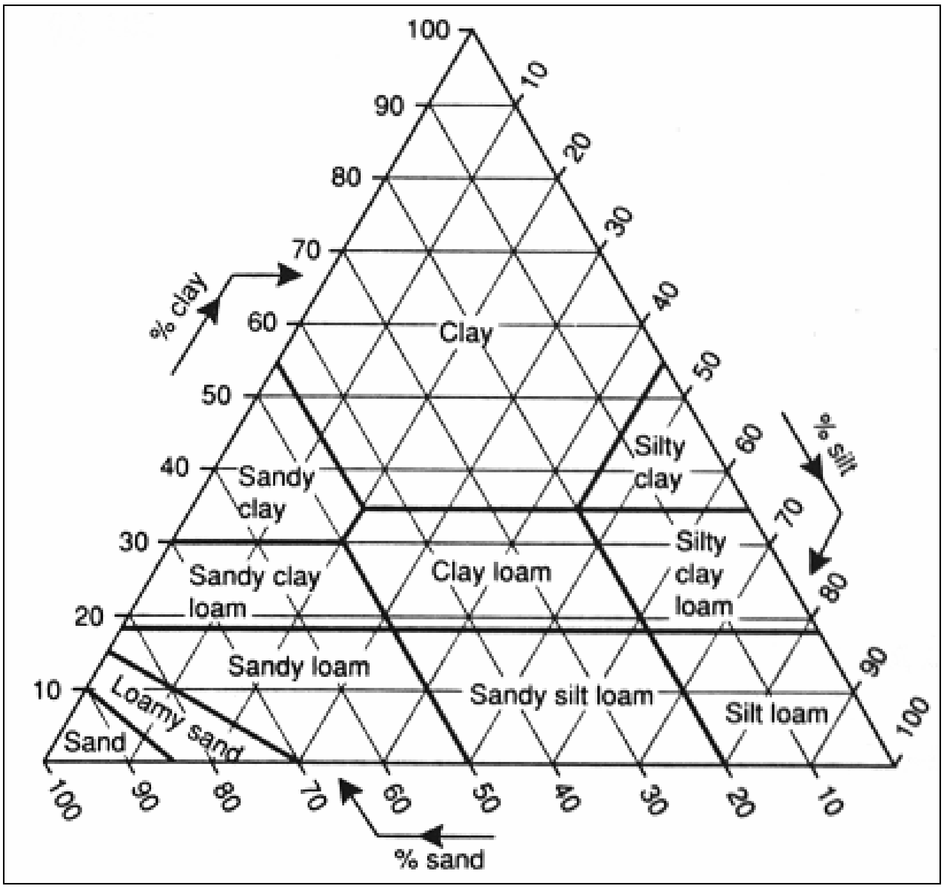


Figure 2-1 Soil textural diagram: Rowell (1994)

2.6 Particle size distribution of rockdust

This method was adapted from BS EN 933-1 (British Standards Institution, 1997). In order to calculate the particle size distribution of rockdust samples, a test portion of rockdust was washed of fine material (< 75 µm). The coarse material retained was then oven dried and passed through a series of dry sieves.

2.6.1 Washing and sieving method

An oven dried test portion of rockdust (approximately 150 g) was weighed (M1) into a 1 litre beaker and sufficient water added to half fill the beaker. The contents were agitated so that particles smaller than 75 µm were completely separated from coarser particles.

Both sides of a 75 µm test sieve were wetted and a nesting guard sieve (2 mm) fitted on top. The suspension of fine solids was poured on to the guarded 75 µm test sieve, allowing the fines < 75 µm to be run to waste. Further water was added into the beaker and the particles again agitated to wash off the fines before again passing the suspension through the sieves (running material < 75 µm to waste).

Washing of the rockdust sample continued until no more fines could be washed from the sample in the beaker and the water passing the test sieve ran clear. The residue from the beaker and that retained on the test sieve (and guard sieve) were washed into a large pre-weighed porcelain basin. Excess free water was removed from the basin by careful decantation through the 75 µm test sieve, avoiding transfer of solids. The coarse residue was dried in the oven at 105 °C until constant mass was achieved. The porcelain basin and contents were cooled and weighed. M2 (weight of dry coarse residue > 75 µm) was calculated as the difference between the empty porcelain basin and the porcelain basin plus dried residue.

The mass of material < 75 µm was determined as M1 – M2 (the difference between initial weight of rockdust and the weight of washed residue > 75 µm).

2.6.2 Sieving the dried residue

A set of clean, dry sieves were used to separate the sample into individual size fractions. The coarse sample collected in the porcelain basin was placed on the coarsest sieve and shaken for at least 2 minutes over a clean base until no more material passed. The material passing the coarse sieve was then placed on the next sieve in the order with another clean base to collect the material passing. The material retained on each sieve was weighed. The sieves were shaken with a varied motion without forcing material through. Gentle brushing was permitted.

2.6.3 Calculation and expression of results

The mass retained on each sieve was calculated as a percentage of the original dry mass (M1). For the mass of material passing the finest sieve, the mass found during dry sieving was added to the weight that passed during washing (M1 – M2).

The mass passing each sieve was expressed as a cumulative percentage of the total sample mass. The sieve sizes used were:

6 mm
4 mm
2.8 mm
2 mm
1 mm
500 μm
300 μm
150 μm
75 μm

Some rockdust samples were also analysed by Collace quarry laboratory according to BS EN 933-1 (British Standards Institution, 1997). The sieves used were:

5 mm
2 mm
1 mm
500 μm
250 μm
125 μm
63 μm

2.7 Soil extractions

2.7.1 Extractable nitrogen in soil samples: 0.5 M K_2SO_4 extraction

Nitrate and nitrite are not held by soil and can be quantitatively extracted by shaking for short periods with water or aqueous solutions (Bremner and Keeney, 1966; Dick and Tabatabai, 1979). Contrary to these findings, Black and Waring (1978) showed that aqueous extracts did not quantitatively recover nitrate in subsoil samples. Exchangeable ammonium in soil is extractable by a neutral K solution (Keeney and Nelson, 1982). Bremner and Keeney (1966) recommended an extractant solution with equivalent to 20 mmol K per gram of soil for quantitative ammonium extraction.

Potassium sulphate was chosen as the extractant rather than the more widely used potassium chloride extractant (Bremner and Keeney, 1966; Keeney and Nelson, 1982; Adamsen *et al*., 1985) because chloride is known to retard nitrate reduction during colorimetric measurements (Sah, 1994; Lambert and Dubois, 1971). However, sulphate displaces organic carbon from adsorption sites on soils (Kalbitz *et al*., 2000) resulting in higher dissolved organic carbon in soil extracts which can also interfere with colorimetric determinations (Sah, 1994; Rowland *et al*., 1984). This is less of a problem in soil extractions compared to compost and manure extractions since the organic matter content is much lower in soils.

Fresh soils were used since air drying or oven drying can result in increased inorganic-N contents in most soils (Nelson and Bremner, 1972) due to sorption of atmospheric ammonia. They recommended extraction and filtration of samples as soon as possible after sampling and storage of extracts below 5 °C.

2.7.1.1 0.5 M K_2SO_4 preparation

Potassium sulphate was dried in an oven set to 80 °C for 1 hour and cooled in a desiccator. 87.15 g was dissolved per litre deionised water to make a 0.5 M K_2SO_4 solution.

Since the extracting solution could be contaminated with ammonium as part of the manufacturing process, a purification step was employed. The pH of the solution was raised to 11 using 1 M KOH before boiling for 15 minutes to release ammonia gas. The solution was then cooled and the pH brought back to about 6 before making back up to volume to account for any water lost during the boiling process.

2.7.1.2 Removal of ammonium from filters

Before using the Whatman No.2 filter paper, ammonium had to be removed by washing them with 2 x 25 ml aliquots of 0.05 M H_2SO_4 (see Section 2.8.1.2 for preparation of acid solution) then rinsing them thoroughly with deionised water. They were dried in the oven at 80 °C before use.

2.7.1.3 Extraction procedure

Approximately 2.5 g fresh soil was weighed accurately to 2 decimal places in to 4 oz glass jars and 50 ml 0.5 M K_2SO_4 solution added by dispenser. The jars were shaken on a reciprocal shaker for 2 hours in the cold room at 4 °C. The samples were then filtered through the ammonium-free filter papers and stored in plastic bottles at 4 °C for analysis.

2.7.2 Extractable phosphate and potassium in soil: modified Morgan's solution extraction

2.7.2.1 Modified Morgan's solution preparation

27.5 ml concentrated acetic acid was dissolved in approximately 900 ml deionised water in a 1 litre volumetric flask. 38.55 g ammonium acetate was dissolved in approximately 500 ml of the acetic acid solution, returned to the flask and made up to 1 litre with deionised water. The pH was adjusted to 4.8 with concentrated HCl.

2.7.2.2 Extraction procedure

Approximately 5 g air-dried soil was weighed accurately to 2 decimal places in to 4 oz glass jars and 50 ml modified Morgan's solution added by dispenser. The jars were shaken on an end-over-end shaker for 1 hour then filtered through Whatman No.2 filter paper and stored in plastic bottles at 4 °C for analysis.

2.7.3 Extractable metals in soil: EDTA extraction

2.7.3.1 0.05 M ammonium EDTA (pH 7) preparation

8 ml ammonia solution (35 % m/m) was dissolved per litre deionised water and 14.6 g ethylene diamine tetra-acetic acid was dissolved into the resulting solution. Upon complete dissolution of the EDTA, the pH was adjusted to pH 7 with ammonia solution (35 % m/m).

2.7.3.2 Extraction procedure

Approximately 5 g of soil sample was accurately weighed to 2 decimal places into a 4 oz glass jar. 50 ml 0.05 M NH_4EDTA (pH 7) was added by dispenser and the glass jars were shaken on an end-over-end shaker for 1 hour. The samples were then filtered through Whatman No.2 Filter paper and collected and stored in plastic bottles at 4 °C until analysis.

2.8 Compost and manure extractions

Plant available nitrate-N, ammonium-N, phosphate-P and potassium were determined in compost and manure samples after extracting with 0.05 M H_2SO_4. As compost tended to be a more homogeneous mix, a small sample could be used in the extraction. A larger sample of manure was necessary due to greater sample variability.

2.8.1 Extractable nitrogen, phosphate and potassium in compost and manure

2.8.1.1 0.05 M H_2SO_4 extraction

Dilute acid was used as the extractant for these high organic matter content samples because soluble organic species have been shown to interfere with colorimetric determinations, especially of nitrate (Sah, 1994). These organic species would be soluble in neutral salt solutions traditionally used as extractants (Keeney and Nelson, 1982) but are insoluble in dilute acid due to a high degree of protonation (Tipping and Hurley, 1988). Hoyle and Mattingly (1952) used 0.1 N HCl to extract 'soluble' nitrogen although dilute sulphuric acid was used in this case due to chloride interferences in the nitrate colorimetric method.

2.8.1.2 0.05 M H_2SO_4 preparation

2.73 ml concentrated sulphuric acid was dissolved per litre deionised water.

2.8.1.3 Removal of ammonium from filters

Before using the Whatman No.2 filter paper, ammonium had to be removed by washing them with 2 x 25 ml aliquots of 0.05 M H_2SO_4 then rinsing them thoroughly with deionised water. They were dried in the oven at 80 °C before use.

2.8.1.4 Extraction procedure

An appropriate weight of material (see below) was weighed into glass jars and the corresponding volume of 0.05 M H_2SO_4 added.

- Compost 2.5 g fresh sample to 100 ml 0.05 M H_2SO_4

- Manure 25 g fresh sample to 500 ml 0.05 M H_2SO_4

The samples were shaken on a reciprocal shaker in the cold room at 4 °C (to minimise changes in N) for 2 hours. The samples were filtered through the ammonium-free filter papers into plastic bottles and stored at 4 °C until analysis.

2.9 Organic amendment and plant material digestion

2.9.1 Kjeldahl digestion

Nitrogen content of compost and manure and nitrogen (and phosphorus) content of plant material samples were measured using a Kjeldahl block digestion technique. This method involved heating a sample with sulphuric acid in a catalysed reaction on a block digester. Bremner and Breitenbeck (1983) used the digestion tubes connected to traditional steam distillation apparatus for measurement of ammonium-N only. However, this method allows colorimetric determination of both ammonium-N and phosphate-P (see Sections 2.11.4 and 2.11.5).

2.9.2 Reagents

Concentrated sulphuric acid (Fisher Scientific, Loughborough, Leicestershire) was used to digest the samples.

Kjeldahl digestion tablets (Thomson and Capper Ltd, Runcorn, Cheshire) were used to catalyse the reactions. The Kjeltabs consist of:

Potassium sulphate	100 parts
Copper (II) sulphate	6 parts
Selenium	1 part

2.9.3 Digestion procedure

Approximately 0.2 g (dry weight) organic amendment or plant material was weighed accurately to 4 decimal places into a digestion tube. Half a catalyst tablet (2.5 g) was added to each digestion tube. This operation was carried out in a fume cupboard wearing gloves. Using a dispenser, 5.0 ml concentrated sulphuric acid was added to each tube. The tubes were left overnight to allow initial reactions to subside.

The digestion block was set up in a fume cupboard along with its own fume extraction system and the fume cupboard set on high. The rack of tubes was heated gently at first until the initial frothing subsided. Once the initial carbonisation was complete, the temperature was increased to 375 °C and heating continued until the digests cleared. The baffle was placed on the front of the rack to promote refluxing higher up the tubes thereby washing material down into the tubes. Once this was complete the baffle was removed and heating continued for a further 2 hours.

The tubes were removed from the block and allowed to cool until just warm to the touch. About 10 ml deionised water was added quickly from a wash bottle, being careful to avoid any vigorous reaction. All tubes were diluted while still warm to avoid solidification of the digest.

The digests were filtered quantitatively through Whatman No.2 filter paper into 100 ml volumetric flasks with at least three more washings. The digests were made up to volume, transferred to plastic bottles and stored at 4 °C until analysis.

2.10 Plant material digestion

2.10.1 Nitric acid digestion

Plant material collected from all field trial harvests was digested with concentrated nitric acid (BDH, Poole, Dorset) on a Tecator digestion block.

2.10.2 Digestion procedure

Approximately 0.2 g (oven dried) plant material was weighed accurately to 4 decimal places into digestion block tubes. 5 ml concentrated HNO_3 was added and the tubes left to pre-digest overnight. The samples were boiled for 3 hours at 120 °C with baffles on the system to promote refluxing conditions and ensure complete digestion. 10 ml deionised water was added after cooling and the sample was filtered quantitatively with washings through Whatman No.50 filter paper into 100 ml volumetric flasks and made up to volume with deionised water. The final concentration of nitric acid in the flasks was therefore approximately 3.4 %. The samples were stored in plastic bottles at 4 °C until analysis.

2.11 Colorimetric analysis

2.11.1 Ammonium-nitrogen

Ammonium was determined in an automated system by a modification of the indophenol green method using a complexing reagent to prevent interferences due to the precipitation of hydroxides in the reagent system. The sensitivity of the method was improved by use of a sodium nitroprusside catalyst (Weatherburn, 1967) such that ammonium nitrogen could be determined in the range 0 to 2.5 mg l^{-1} and as little as 0.1 mg l^{-1} could be readily determined (Brown, 1973).

2.11.1.1 Reagents

Alkaline phenol

20 g of sodium hydroxide was dissolved in approximately 900 ml of deionised water in a 1 litre dark glass bottle. When the solution has cooled to room temperature 45 g of phenol was weighed in the fume cupboard into a 1 litre beaker. Approximately 500 ml of the sodium hydroxide solution was added and stirred carefully with a glass rod to dissolve the phenol. The solution was returned to the bottle and degassed in an ultrasonic bath for 10 minutes. The solution was made up to 1 litre with degassed water and mixed gently.

Complexing reagent

50 g of sodium citrate was dissolved in approximately 900 ml deionised water in a 1 litre bottle and degassed. 0.5 g of sodium nitroprusside was weighed into a 100 ml beaker and dissolved in 50 ml degassed water by gently mixing on a magnetic stirrer. This solution was added to the citrate solution and degassed in the ultrasonic bath for 10 minutes. 1 ml of 15 % Brij-35 solution was added and the reagent made up to 1 litre using degassed water.

Sodium hypochlorite solution (approximately 0.5 % available Cl)

50 ml of sodium hypochlorite solution (10 % w/v available chlorine) was added to 1 litre of degassed water and mixed gently.

Ammonium-N standard stock solution (1000 mg l^{-1})

Ammonium sulphate was dried in the oven at 105 °C for 1 hour and cooled in a dessicator. 4.717 g of ammonium sulphate was dissolved per litre deionised water. Working standards were prepared by dilution using the appropriate extracting solution.

2.11.1.2 Procedure

The manifold could be used for determination of ammonium in water, 2 M and 1 M potassium chloride, 0.5 M potassium sulphate and several other extractants. The extracts were analysed along with standards, blanks and zeros. The samples were run at the rate of 50 per hour or 40 per hour where in-line dilution was required. The colour intensity was measured at 650 nm. The ammonium calibration graph was linear in the range 0 to 2.5 mg l^{-1}.

Complexing reagent	0.60 ml min^{-1}
Alkaline phenol	0.60 ml min^{-1}
Sample	0.32 ml min^{-1}
Hypochlorite	0.16 ml min^{-1}

Sample rate	50 per hour
Sample rate with diluter	40 per hour
Wavelength	650 nm
Waterbath temperature	37 °C
Calibration range	0 – 2.5 mg l^{-1}

The air was cleaned of atmospheric ammonium by bubbling through 5 % sulphuric acid solution.

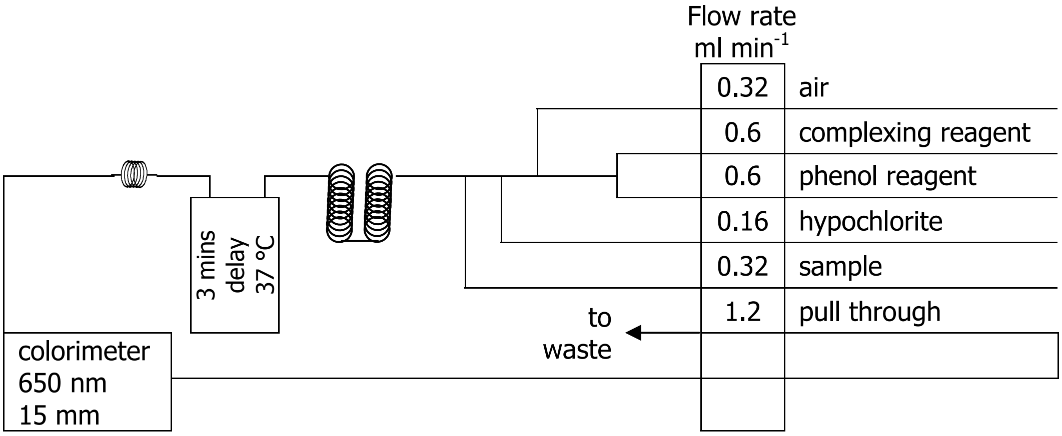


Figure 2-2 Standard ammonium-N system

2.11.2 Nitrate-nitrogen

This automated system was based on the method of Best (1976) and involves a modification of the Greiss-Ilosvay method whereby NO_3–N is reduced to NO_2–N followed by diazotization and coupling with an aromatic amine, forming an azo dye (Keeney and Nelson, 1982). The pH was closely controlled between 9.5 and 9.7 (by use of a buffer solution) to prevent precipitation of calcium and magnesium salts which inhibit the reduction (Henriksen, 1965; Best, 1976). The absorbance of the azo dye could be measured colorimetrically at 520 nm. The method measured the combined total of nitrate plus nitrite. Nitrite could be measured on the same manifold by omitting the reduction reagents; although levels in well aerated systems were likely to be very low (Henriksen, 1965). Nitrate-N was determined by difference.

Organic carbon is known to interfere with the reduction stage in this method (Rowland *et al.*, 1984). However, these workers were able to alleviate the problem by ensuring the final Cu^{2+} concentration in the catalyst solution was at least 1 mg l^{-1} and by running samples with a high dilution. The combination of these two measures was enough to improve the reduction efficiency of the system. Rowland *et al.* (1984) also suggested that the organic carbon interferences could be minimized by using a high solution to soil ratio and using a salt solution rather than water as the extractant.

High levels of calcium and magnesium were shown by Ananth and Moraghan (1987) to interfere with nitrate reduction in the hydrazine sulphate method. They recommended use of a cation exchange resin or switching to the copperized-cadmium method since these methods gave good agreement with steam distillation techniques.

Other workers have also used a copperized-cadmium column for reducing nitrate to nitrite (i.e. Wood *et al.*, 1967). Henriksen and Selmer-Olsen (1970) showed a good recovery of added NO_3-N in soils containing humic acids using copperized cadmium as the reductant rather than hydrazine. However, turbid or highly coloured samples required the use of a dialyser to prevent clogging of the reductor column. Hydrazine was preferred since a liquid reductant could be added in the same state of activity for all samples (Best, 1976) and because preparation of copperized cadmium columns was time consuming. Lambert and DuBois (1971) explained that a uniform copperized cadmium column was difficult to prepare and that too much precipitated Cu could lead to low nitrate results as it could be reduced to a lower oxidation state than nitrite. They also showed that chloride could have a significant effect on the reduction step although there was no effect on diazotization or coupling stages in the colorimetric determination of nitrite.

The precision of the cadmium-reduced system was shown by Adamsen *et al.* (1985) to be slightly lower than expected due to sample crossover in the reductor column. High samples were shown to affect low samples that followed. There was however, good agreement between the system and the traditional steam distillation method.

Other methods for measuring nitrate in soil extracts include steam distillation (Keeney and Nelson, 1982) and dual-wavelength UV spectrophotometry (Norman *et al.*, 1985). UV spectrophotometry involves measuring absorbance of soil extracts at 210 nm and 270 nm with and without removal of nitrate using Raney-Nickel treatment. Norman *et al.* (1985) advised caution when using this method for soils high in heavy metals or those treated with manure or sewage sludge since the background intensity would be high. Hence this method was not employed for measurement of nitrate.

2.11.2.1 Reagents

Buffer solution

22.5 g of sodium tetraborate and 2.5 g sodium hydroxide were dissolved in 900 ml deionised water and made up to 1 litre. The solution was degassed for 10 minutes in the ultrasonic bath.

Greiss reagent

Working in a fume cupboard, 100 ml concentrated hydrochloric acid was added into approximately 800 ml of deionised water and degassed for 10 minutes in an ultrasonic bath. The solution was cooled overnight in the refrigerator at 4 °C. 10 g sulphanilamide and 0.5 g N-(1-naphthyl)-ethylenediamine dihydrochloride were weighed into a 1 litre beaker. 500 ml of the acid solution was added carefully and the contents were stirred gently using a magnetic stirrer. The solution was made up to 1 litre with degassed deionised water and the bottle mixed gently.

Reducing reagent

0.075 g hydrazine sulphate was weighed into a small beaker. The contents were transferred carefully into a 250 ml volumetric flask containing approximately 200 ml of degassed deionised water. The hydrazine sulphate was dissolved using a magnetic stirrer keeping the top of the flask closed to prevent access of oxygen and the volume was made up to the mark with deionised water. Hydrazine sulphate is an oxygen scavenger and its nitrate reducing power would be diminished if allowed to come into contact with oxygen during mixing (Kempers and Luft, 1988). 1 ml of 15 % Brij-35 solution was added to the solution and mixed gently.

Catalyst solution

1 ml 2.47 % copper sulphate solution and 1 ml 15 % Brij-35 solution were added to 1 litre of degassed deionised water and the contents mixed gently.

Nitrate-N standard stock solution (1000 mg l^{-1})

Sodium nitrate was dried at 105 °C for 1 hour and cooled in a desiccator for 30 minutes. 6.068 g of dried sodium nitrate was dissolved per litre deionised water. The solution was stored at 4 °C. Matrix matched working standards were prepared by dilution using the appropriate extracting solution.

Nitrite-N standard stock solution (1000 mg l^{-1})

Sodium nitrite was dried at 105 °C for 1 hour and cooled in a desiccator for 30 minutes. 4.936 g of dried sodium nitrate was dissolved per litre deionised water.

The solution was stored at 4 °C. Matrix matched working standards were prepared by dilution using the appropriate extracting solution.

2.11.2.2 Procedure

The solutions were analysed for nitrate along with standards, blanks and zeros. The samples were run at the rate of 50 per hour or 40 per hour where in-line dilution was required. Nitrate was reduced to nitrite by adding the reducing agent and catalyst solution as it passed through a water bath set at 37 °C. The colour intensity was measured at 530 nm. This was followed by a run to measure nitrite only where the reducing reagents were replaced with deionised water containing 1 ml l^{-1} 15 % Brij-35 solution.

Buffer solution	0.32 ml min^{-1}
Greiss solution	0.32 ml min^{-1}
Reducing reagent	0.42 ml min^{-1}
Copper catalyst	0.42 ml min^{-1}
Sample	0.16 ml min^{-1}

Sample rate	50 per hour
Sample rate with diluter	40 per hour
Wavelength	530 nm
Waterbath temperature	37 °C
Linear range	0 – 2.0 mg l^{-1} nitrate 0 – 4.0 mg l^{-1} nitrite

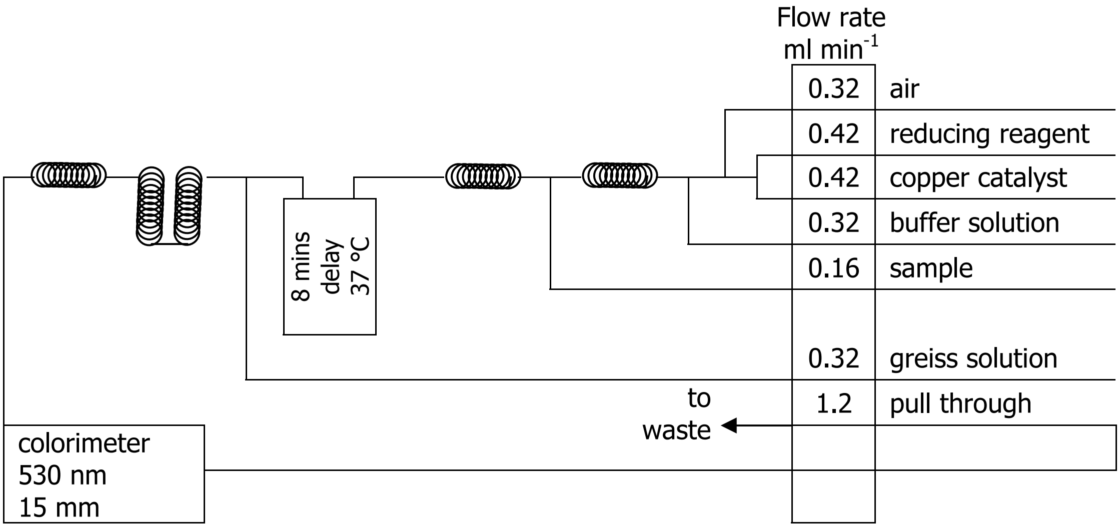


Figure 2-3 Nitrate-N standard system

2.11.3 Phosphate: molybdenum blue ascorbic acid method

The method was based on formation of a phosphomolybdate complex using antimony to accelerate formation of the faintly yellow coloured product. Reduction of the coloured product using ascorbic acid gives a more intense blue colour, which could be measured at 880 or 660 nm. Warrell and Moody (1984) found the automated method gave statistically the same results as the manual method when testing calcium chloride soil extracts. The automated system could be used for determination of phosphate in water, acetic acid, acetate buffers and several other extractants by modifying the ratio of sample uptake to diluent water uptake because the colour stability is highly dependent on acidity (John, 1970). Acetate buffer extracts at sample flow rates greater than 0.23 ml min^{-1} had to be run with sulphuric acid in the diluent water line to counteract the neutralising effect of ammonium acetate. Many other ionic interferences were found by John (1970) who concluded that although these interfering ions could be present in soil and plant extracts, a small sample volume would be sufficient to avoid interference.

2.11.3.1 Reagents

Acid molybdate solution

60 ml of concentrated sulphuric acid was added to approximately 700 ml deionised water in a 1 litre brown glass bottle. When cooled to room temperature, 5.2 g ammonium molybdate was added to the solution and dissolved by stirring. 0.1 g antimony potassium tartrate was dissolved in approximately 50 ml of deionised water in a small beaker. This solution was added to the acid solution with mixing to avoid the formation of a precipitate. The reagent was degassed for 10 minutes in an ultrasonic bath and the volume made up to 1 litre.

Ascorbic acid

0.75 g ascorbic acid was dissolved in 100 ml degassed deionised water and dissolved by stirring gently on a magnetic stirrer. This reagent is unstable and had to be prepared on the day of use.

Dilution water

0 – 1 mg P per litre range

1 ml 1 % aerosol-22 wetting agent was added to 1 litre degassed water and mixed gently.

0 – 5 mg P per litre range

0.5 ml 1 % aerosol-22 wetting agent was added to 1 litre degassed water and mixed gently.

Phosphate-P standard stock solution (1000 mg l^{-1})

Potassium dihydrogen phosphate was dried at 105 °C for 1 hour and cooled in a desiccator for 30 minutes. 4.394 g of dry potassium dihydrogen phosphate was dissolved per litre deionised water. Working standards were prepared by dilution of the stock solution using the appropriate extracting solution.

2.11.3.2 Procedure

The samples were run at the rate of 50 per hour or 40 per hour where in-line dilution was necessary. The colour was developed in a water bath at 37 ºC. The colour intensity was measured at 690 nm. The phosphate calibration graph was linear in the range 0 to 5.0 mg l^{-1} in the standard configuration but linearity was reduced as sample uptake rate increased.

Acid molybdate solution	0.32 ml min^{-1}
Ascorbic acid	0.32 ml min^{-1}
Diluent (water)	0.80 ml min^{-1}
Sample	0.16 ml min^{-1}

Sample rate	50 per hour
Sample rate with diluter	40 per hour
Wavelength	690 nm
Waterbath temperature	37 °C
Standard linear range	0 – 5.0 mg l^{-1}

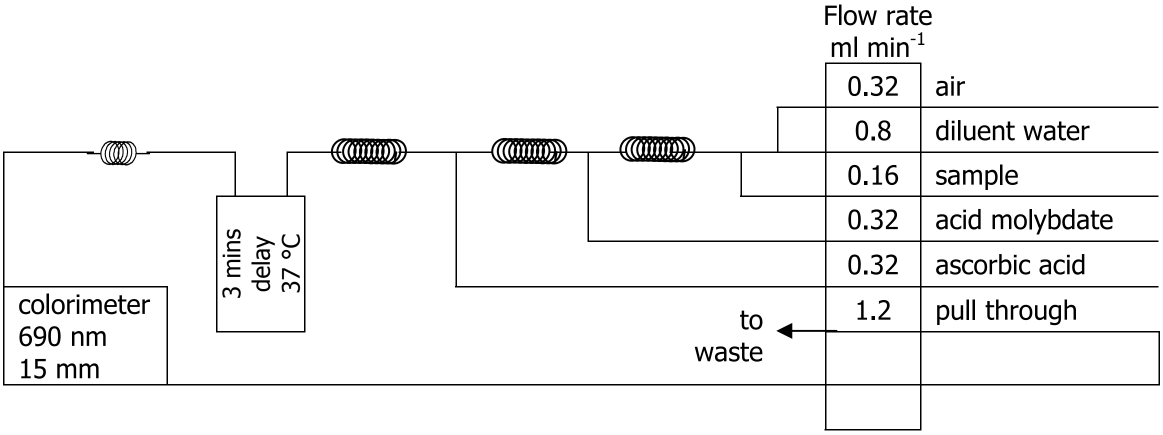


Figure 2-4 Phosphate-P standard system

2.11.4 Determination of Kjeldahl-N

Ammonium was determined by a modification of the indophenol green method using a complexing reagent to prevent interferences due to the precipitation of hydroxides in the reagent system. No interference due to Cu in Kjeldahl digests was reported by Searle (1975) although a higher pH was required to neutralise the digests. The automated system gave values that were highly correlated to standard distillation procedures. See Section 3.2.8 for method development for this system.

2.11.4.1 Reagents

Alkaline phenol

20 g of sodium hydroxide was dissolved in approximately 900 ml of deionised water in a 1 litre brown glass bottle. When the solution has cooled to room temperature 45 g of phenol was weighed in the fume cupboard into a 1 litre beaker. Approximately 500 ml of the sodium hydroxide solution was added and stirred carefully with a glass rod to dissolve the phenol. The solution was returned to the bottle and degassed in an ultrasonic bath for 10 minutes. The solution was made up to 1 litre with degassed water and mixed gently.

Complexing reagent

50 g of sodium citrate was dissolved in approximately 900 ml deionised water in a 1 litre bottle and degassed. 0.5 g of sodium nitroprusside was weighed into a 100 ml beaker and 50 ml degassed water added. The solution was stirred gently using a magnetic stirrer. The solution was added to the citrate solution and degassed in the ultrasonic bath for 10 minutes. 1 ml of 15 % Brij-35 solution was added and the reagent made up to 1 litre using degassed water.

Sodium hypochlorite solution (approximately 0.25 % available chlorine)

25 ml of Sodium hypochlorite solution (12 % w/v available chlorine) was added to 1 litre of degassed water and mixed gently.

Ammonium nitrogen standard stock solution (1000 mg l^{-1})

Ammonium sulphate was dried at 105 °C for 1 hour and cooled in a desiccator. 4.717 g of dry ammonium sulphate was dissolved in per litre deionised water. Working standards are prepared by dilution in blank digest solution.

Ammonium standard 100 mg l^{-1}

5 ml concentrated sulphuric acid and half a Kjeldtab were added to a digestion tube and heated to dissolve the catalyst tablet. When cool, the solution was carefully diluted and transferred to a 100 ml volumetric flask. 10 ml of the 1000 mg l^{-1} stock ammonium standard was added and the solution made up to 100 ml with deionised water.

Standard 0 mg l^{-1}

5 ml concentrated sulphuric acid and half a Kjeldtab were added to a digestion tube and heated to dissolve the catalyst tablet. When cool, the solution was carefully diluted and transferred to a 100 ml volumetric flask and made up to volume.

Kjeldahl neutralising solution (~ 4 % NaOH)

3.6 g NaOH was dissolved in a litre of deionised water. 1M NaOH was added until the solution was able to neutralise the Kjeldahl digests.

Wash chamber solution (5 % H_2SO_4)

50ml concentrated sulphuric acid was dissolved in about 800 ml deionised water, cooled and made up to 1 litre.

2.11.4.2 Procedure

The dilution coil was used for simultaneous dilution and neutralisation of Kjeldahl digests. The system was run at a rate of 40 samples per hour and ammonium measured at a wavelength of 650 nm.

Complexing reagent	0.60 ml min^{-1}
Alkaline phenol	0.60 ml min^{-1}
Sample	0.16 ml min^{-1}
Hypochlorite	0.32 ml min^{-1}

Sample rate with diluter	40 per hour
Wavelength	650 nm
Waterbath temperature	37 °C
Calibration range	0 – 100 mg N l^{-1}

The air was cleaned of atmospheric ammonium by bubbling through 5 % sulphuric acid.

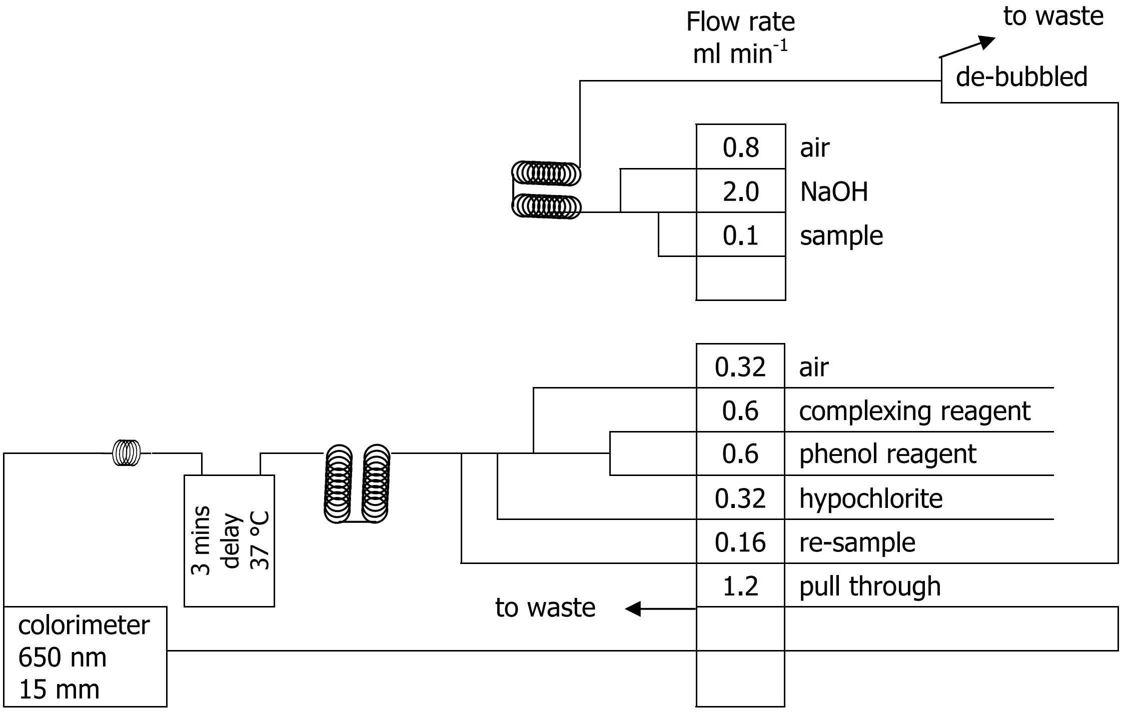


Figure 2-5 Kjeldahl-N ammonium system

2.11.5 Determination of Kjeldahl-P: phosphovanadate method

Phosphate was determined as the yellow phospho-vanado-molybdate complex which could be measured at 420 nm (Varley, 1966) in the range 0 – 50 mg P l^{-1}. A modification to the standard method (which uses 1.0 N HNO_3) to a lower concentration of nitric acid was possible due the acid content of Kjeldahl digests (Karbasi, 2002).

2.11.5.1 Reagents

Ammonium molybdate-ammonium metavanadate

25 g Ammonium molybdate and 1.25 g ammonium metavanadate were dissolved in approx 900 ml deionised water and made up to 1 litre in a brown glass bottle. 1 ml Levor IV was added to the degassed solution.

Nitric acid (0.424 N)

26.5 ml concentrated nitric acid was dissolved per litre deionised water.

Phosphate-P standard stock solution (1000 mg l^{-1})

Potassium dihydrogen phosphate was dried at 105 °C for 1 hour and cooled in a desiccator for 30 minutes. 4.394 g of dry potassium dihydrogen phosphate was dissolved per litre deionised water.

Phosphate standard 50 mg l^{-1}

5 ml concentrated sulphuric acid and half a Kjeldtab were added to a digestion tube and heated to dissolve the catalyst tablet. When cool, the solution was carefully diluted and transferred to a 100 ml volumetric flask. 5 ml of 1000 mg l^{-1} stock phosphate standard were added and the solution was made up to 100 ml with deionised water.

Standard 0 mg l^{-1}

5 ml concentrated sulphuric acid and half a Kjeldtab were added to a digestion tube and heated to dissolve the catalyst tablet. When cool, the solution was carefully diluted and transferred to a 100 ml volumetric flask and made up to volume.

Wash chamber solution (5 % H_2SO_4)

50 ml concentrated sulphuric acid is dissolved in 1 litre deionised water.

2.11.5.2 Procedure

No dilution was necessary to measure Kjeldahl-P in digests since the method was linear 0 – 50 mg l^{-1}. The system was run at a rate of 50 samples per hour and phosphate measured at a wavelength of 420 nm.

Nitric acid	1.0 ml min^{-1}
Molybdate-metavanadate	0.32 ml min^{-1}
Sample	0.32 ml min^{-1}

Sample rate	50 per hour
Wavelength	420 nm
Waterbath temperature	37 °C
Calibration range	0 – 50 mg l^{-1}

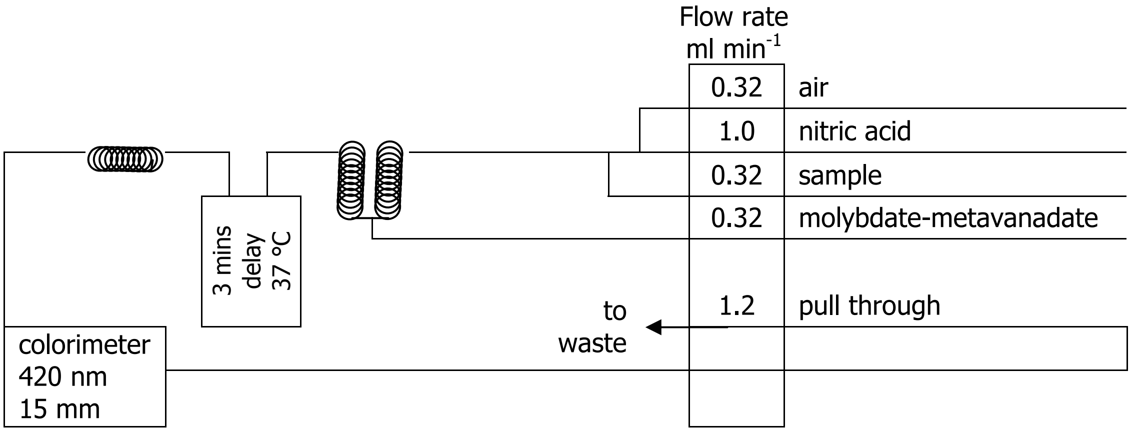


Figure 2-6 Kjeldahl-P phosphovanadate system

2.12 Instrumentation

2.12.1 Atomic absorption spectroscopy

Perkin Elmer atomic absorption spectrometers (models 1100B and Analyst 100) were used for analysis of metals in a variety of samples. The operating conditions are outlined in Table 2-1 below:

Conditions	**Ca**	**Cu**	**Fe**	**Mg**
Wavelength (nm)	422.7	324.8	248.3	285.2
Lamp current (mA)	10	10	30	6
Oxidant	N_2O	Air	Air	N_2O
Fuel	Acetylene	Acetylene	Acetylene	Acetylene
Quantification limit (mg l^{-1})	0.05	0.04	0.05	0.05
Working range (mg l^{-1})	0 - 5.0	0 - 2.5	0 - 5.0	0 - 5.0
Background correction	Off	Off	On	On

Conditions	**Mn**	**Ni**	**Pb**	**Zn**
Wavelength (nm)	279.5	232.0	283.3	213.9
Lamp current (mA)	20	30	15	10
Oxidant	Air	Air	Air	Air
Fuel	Acetylene	Acetylene	Acetylene	Acetylene
Quantification limit (mg l^{-1})	0.03	0.07	0.2	0.02
Working range (mg l^{-1})	0 - 2.0	0 - 1.0	0 - 5.0	0 - 1.0
Background correction	Off	On	Off	On

Table 2-1 Instrument settings and flame conditions for analysis of metals by AAS

Working range standards were prepared from stock solutions of each metal (1000 mg l^{-1}) by dilution in the appropriate extracting solutions. When analysing calcium and magnesium there were ionization interferences, 0.1% K (as KCl) was added to samples and standards alike to control this effect. In iron and manganese samples, the signal could be depressed by the presence of silicon; this was controlled by addition of 0.2% $CaCl_2$.

2.12.2 Flame photometry

A Corning flame photometer 410 was used for sodium and potassium analysis of a variety of samples. The operating ranges are detailed below:

	Sodium	Potassium
Linear working range (mg l^{-1})	0 - 5	0 - 10
Curved working range (mg l^{-1})	0 - 50	0 - 25

Table 2-2 Working standard ranges for sodium and potassium analysis

2.12.2.1 Stock solution preparation

1000 mg l^{-1} sodium stock solution

Sodium nitrate was dried in the oven at 105 °C for 1 hour then 3.6957g was accurately weighed out and dissolved in 1 litre of deionised water. This stock solution was stored in the cold room at 4 °C.

1000 mg l^{-1} potassium stock solution

Potassium nitrate was dried in the oven at 105 °C for 1 hour then 2.5857g was accurately weighed out and dissolved in 1 litre of deionised water. This stock solution was stored in the cold room at 4 °C.

Working range standards were prepared from stock solutions of each metal (1000 mg l^{-1}) and by dilution with the appropriate extracting solutions. Although most measurements were performed on a linear calibration, some samples were measured within the curved calibration range indicated in Table 2-2.

2.12.3 Inductively coupled plasma optical emission spectroscopy

Harvested grass material and soil EDTA extracts were analysed for a suite of metals using ICP-OES at Nobel Enterprises, Ardeer, Scotland. An IRIS Intrepid II XDL (Thermo Electron Corporation) was used. The instrument settings are summarized in Table 2-3.

Operating conditions	
RF power	1150 W
Auxiliary gas flow	0.50 l min^{-1}
Nebulizer gas flow	0.63 l min^{-1}
Flush pump rate	2.22 ml min^{-1}
Analysis pump rate	2.22 ml min^{-1}
Sample flush time	30 seconds
Replicates	3

Table 2-3 Instrument settings for IRIS Intrepid II XDL

Table 2-4 –Table 2-7 show elements analysed, quantification limits, selected wavelengths and calibration standards for each sample type. Working range standards were prepared by dilution of Aristar (BDH, Poole, Dorset) ICP standard stock solutions (1000 or 10000 ppm) in the appropriate extracting solution.

Nitric acid digestion - plant material					
Element	Quantification limit = ½ count/sec		Wavelength (order)	Interferences	Standards (mg l^{-1})
	mg l^{-1}	mg kg^{-1}			
Ba	0.006	3.00	230.424 (146)		5, 10, 20
	0.004	2.00	233.527 (144)		5, 10, 20
	0.0004	0.20	455.403 (74)		5, 10, 20
Ca	0.15	75.0	184.006 (182)		5, 10, 20
Cu	0.01	5.00	324.754 (103)	Fe	5, 10, 20
	0.02	10.00	327.396 (102)	Ni	5, 10, 20
Fe	0.05	25.00	238.204 (140)		5, 10, 20
	0.013	6.50	259.837 (129)		5, 10, 20
	0.011	5.50	259.940 (129)		5, 10, 20
K	0.058	29.00	766.491 (44)	many	5, 10, 20
Li	0.001	0.50	670.784 (50)	Ca	5, 10, 20
Mg	0.0001	0.05	279.553 (120)		5, 10
Mn	0.002	1.00	257.610 (130)		5, 10, 20
Zn	0.005	2.50	202.548 (166)	Cu, Fe	5, 10, 20
	0.006	3.00	206.200 (163)	Cr	5, 10, 20

Table 2-4 Standard nitric acid digests - field trial harvested grass

EDTA extraction – soil samples					
Element	Quantification limit = ½ count/sec		Wavelength (order)	Interferences	Standards (mg l^{-1})
	mg l^{-1}	mg kg^{-1}			
Al	0.055	0.55	308.215 (109)		25, 50
Ba	0.006	0.06	230.424 (146)		1, 5
	0.004	0.04	233.527 (144)		1, 5
	0.0004	0.004	455.403 (74)		1, 5
Ca	0.4	4	183.801 (182)		25, 50, 150
	0.15	1.5	184.006 (182)		25, 50, 150
Co	0.008	0.08	228.616 (147)		1, 5
Cr	0.013	0.13	205.552 (163)		1, 5
Cu	0.01	0.1	324.754 (103)	Fe	1, 5
	0.02	0.2	327.396 (102)	Ni	1, 5
Fe	0.05	0.5	238.204 (140)		10, 25
	0.013	0.13	259.837 (129)		10, 25
	0.011	0.11	259.940 (129)		10, 25
K	0.058	0.58	766.491 (44)	many	5, 10
Li	0.001	0.01	670.784 (50)	Ca	1, 5
Mg	0.0001	0.001	279.553 (120)		10, 25
	0.0004	0.004	280.271 (120)		10, 25
Mn	0.002	0.02	257.610 (130)		1, 5
Mo	0.08	0.8	202.030 (166)	Fe, Al	1, 5
Ni	0.015	0.15	221.647 (152)		1, 5
	0.011	0.11	231.604 (145)	Fe	1, 5
Pb	0.109	1.09	220.353 (152)	Fe, Al	1, 5
Zn	0.005	0.05	202.548 (166)	Cu, Fe	1, 5
	0.006	0.06	206.200 (163)	Cr	1, 5

Table 2-5 EDTA extraction – soil cores Jan 2007

Dilute nitric acid extraction - rockdust					
Element	Quantification limit = ½ count/sec		Wavelength (order)	Interferences	Standards (mg l^{-1})
	mg l^{-1}	mg kg^{-1}			
Al	0.055	0.55	308.215 (109)		5, 10, 20
Ba	0.006	0.06	230.424 (146)		5, 10, 20
	0.004	0.04	233.527 (144)		5, 10, 20
	0.0004	0.004	455.403 (74)		5, 10, 20
Cd	0.004	0.04	228.802 (147)		5, 10, 20
Co	0.008	0.08	228.616 (147)		5, 10, 20
Cr	0.013	0.13	205.552 (163)		5, 10, 20
Cu	0.01	0.1	324.754 (103)	Fe	5, 10, 20
	0.02	0.2	327.396 (102)	Ni	5, 10, 20
Fe	0.05	0.5	238.204 (140)		5, 10, 20
	0.013	0.13	259.837 (129)		5, 10, 20
	0.011	0.11	259.940 (129)		5, 10, 20
Li	0.001	0.01	670.784 (50)	Ca	5, 10, 20
Mn	0.002	0.02	257.610 (130)		5, 10, 20
Mo	0.08	0.8	202.030 (166)	Fe, Al	5, 10, 20
Ni	0.015	0.15	221.647 (152)		5, 10, 20
	0.011	0.11	231.604 (145)	Fe	5, 10, 20
Pb	0.109	1.09	220.353 (152)	Fe, Al	5, 10, 20
Zn	0.005	0.05	202.548 (166)	Cu, Fe	5, 10, 20
	0.006	0.06	206.200 (163)	Cr	5, 10, 20

Table 2-6 Dilute nitric acid extraction - rockdust samples

Nitric acid trace metal digestion – harvest 5					
Element	Quantification limit = ½ count/sec		Wavelength (order)	Interferences	Standards (mg l^{-1})
	mg l^{-1}	mg kg^{-1}			
Al	0.055	0.55	308.215 (109)		1, 5, 10
Ba	0.006	0.06	230.424 (146)		1, 5, 10
	0.004	0.04	233.527 (144)		1, 5, 10
	0.0004	0.004	455.403 (74)		1, 5, 10
Ca	0.4	4.0	183.801 (182)		200, 400, 600
Cd	0.004	0.04	228.802 (147)		1, 5, 10
Co	0.008	0.08	228.616 (147)		1, 5, 10
Cr	0.013	0.13	205.552 (163)		1, 5, 10
Cu	0.01	0.1	324.754 (103)	Fe	1, 5, 10
	0.02	0.2	327.396 (102)	Ni	1, 5, 10
Fe	0.05	0.5	238.204 (140)		1, 5, 10
	0.011	0.11	259.837 (129)		1, 5, 10
	0.013	0.13	259.940 (129)		1, 5, 10
K	0.058	0.58	766.491 (44)	many	250, 750, 1000
Li	0.001	0.01	670.784 (50)	Ca	1, 5, 10
Mg	0.005	0.05	285.213 (117)		50, 100, 200
	0.005	0.05	285.213 (118)		50, 100, 200
Mn	0.002	0.02	257.610 (130)		1, 5, 10
Mo	0.08	0.8	202.030 (166)	Fe, Al	1, 5, 10
Ni	0.015	0.15	221.647 (152)		1, 5, 10
	0.011	0.11	231.604 (145)	Fe	1, 5, 10
Pb	0.109	1.09	220.353 (152)	Fe, Al	1, 5, 10
Zn	0.005	0.05	202.548 (166)	Cu, Fe	1, 5, 10
	0.006	0.06	206.200 (163)	Cr	1, 5, 10

Table 2-7 Nitric acid trace metal digestion – harvest 5 grass samples July 2006

2.12.4 Ion chromatography

Tabatabai and Dick (1983) showed that simultaneous determination of nitrate, chloride, sulphate and phosphate by ion chromatography gave results that closely agreed with traditional steam distillation and colorimetric methods. This technique also gives good precision and requires smaller sample volumes while allowing fast analysis of several analytes. Ion chromatography was therefore used to determine anions in water extracts of rockdust. The configuration of the chromatography system is shown in Table 2-8 below:

Dionex DX500 chromatography system	
Column	Ionpac AS11-HC
Guard column	Ionpac AG11-HC
Eluent	Deionised water/sodium hydroxide gradient
Eluent flow rate	1.5 ml min^{-1}
Low pressure limit	350 psi
High pressure limit	3000 psi
Suppressor	ASRS Ultra II
SRS current	100 mA
Detector type	ED40 electrochemical
Detector operating mode	Conductivity (µS)
Injection loop	25 µl
Data collection time	15 min
Calibration range	0 - 1 mg l^{-1}
Calibration	Linear
Peak area reject	1000 (area counts)

Table 2-8 Dionex ion chromatography method parameters

A gradient separation was used as detailed in Table 2-9 below:

Time (min)	Water (%)	200mM NaOH (%)
0	90	10
0.10	90	10
10.00	90	10
10.10	80	20
14.00	90	10
15.00	90	10

Table 2-9 Eluent gradient conditions

Although retention times for the analyte anions varied from day to day, they remained close to the times detailed in Table 2-10.

Anion	Retention time (min)	Standard concentration (mg l^{-1})	Quantification limit (mg l^{-1})
Chloride	3.25	1.0	0.009
Nitrite-N	3.72	1.0	0.004
Sulphate-S	5.31	1.0	0.004
Nitrate-N	5.86	1.0	0.004
Phosphate-P	8.63	1.0	0.01

Table 2-10 Retention times, standard concentrations and quantification limits for anion chromatography

2.12.4.1 Stock solution preparation

1000 mg l^{-1} chloride stock solution

Potassium chloride was dried in the oven at 105 °C for 1 hour then 2.1014g was accurately weighed out and dissolved in 1 litre of deionised water. This stock solution was stored in the cold room at 4 °C.

1000 mg l^{-1} nitrite-N stock solution

Sodium nitrite was dried in the oven at 105 °C for 1 hour then 4.9357g was accurately weighed out and dissolved in 1 litre of deionised water. This stock solution was stored in the cold room at 4 °C.

1000 mg l^{-1} sulphate-S stock solution

Potassium sulphate was dried in the oven at 105 °C for 1 hour then 5.4299g was accurately weighed out and dissolved in 1 litre of deionised water. This stock solution was stored in the cold room at 4 °C.

1000 mg l^{-1} nitrate-N stock solution

Potassium nitrate was dried in the oven at 105 °C for 1 hour then 7.2214g was accurately weighed out and dissolved in 1 litre of deionised water. This stock solution was stored in the cold room at 4 °C.

1000 mg l^{-1} phosphate-P stock solution

Potassium dihydrogen ortho-phosphate was dried in the oven at 105 °C for 1 hour then 4.3903g was accurately weighed out and dissolved in 1 litre of deionised water. This stock solution was stored in the cold room at 4 °C.

2.12.4.2 Mixed working standard preparation

A 1 mg l^{-1} mixed anion standard was prepared by dilution of standard stock solutions of anions. This one standard contained all the analytes for ion chromatographic analysis and was made up in deionised water.

Chapter 3: Method Development Section

3.1 Rockdust extraction

Although the elemental content of rockdust could be measured by x-ray fluorescence, these total values do not give any information on the nutrient and trace element availability from rockdust. In order that plant available nutrients from rockdust could be measured, some extractions were carried out. The first extraction attempted used deionised water and was designed to show the immediately available nutrients from rockdust. However, the nutrients extracted were in very low concentrations and hence a method had to be developed where blanks could be shown to be consistently low in analyte elements.

3.1.1 Blank contamination

3.1.1.1 Method

Glassware and plasticware used in these experiments were washed thoroughly in Decon 90 solution and rinsed with deionised water before use.

This method is designed to find the source of any contamination from equipment or procedures used in the rock dust extraction. The test samples were prepared as follows:

- Glass Jar –100 ml of deionised water was added to clean 100 ml glass jars by dispenser and shaken for 1 hour on an end-over-end shaker. The samples were stored in the glass jars for analysis. They were not filtered prior to analysis.

- Storage Vial – Approximately 40 ml deionised water was added from a wash bottle to clean, dry auto-sampler vials. They were not filtered prior to analysis.

- Glass Fibre Filters – Deionised water vacuum filtered through Whatman GF/C glass microfibre filters then PALL Life Sciences Supor-200 0.2 µm membrane filters and collected in clean auto-sampler vials.

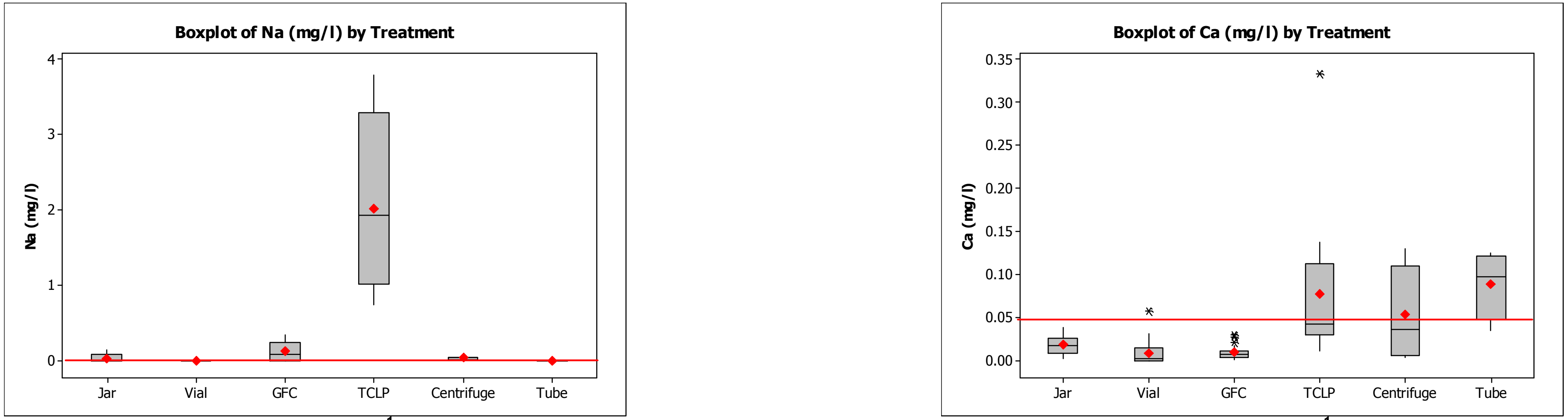
- TCLP Filters – Deionised water vacuum filtered through Whatman TCLP glass microfibre acid treated low metal filters then PALL Life Sciences Supor-200 0.2 µm membrane filters and collected in clean auto-sampler vials.

- Centrifuge – Deionised water centrifuged at 4500 rpm in clean centrifuge tubes for 10 minutes then vacuum filtered through PALL Life Sciences Supor-200 0.2 µm membrane filters into clean auto-sampler vials.

- Centrifuge Tube – Deionised water centrifuged at 4500 rpm in clean centrifuge tubes for 10 minutes then transferred to clean auto-sampler vials. They were not filtered prior to analysis.

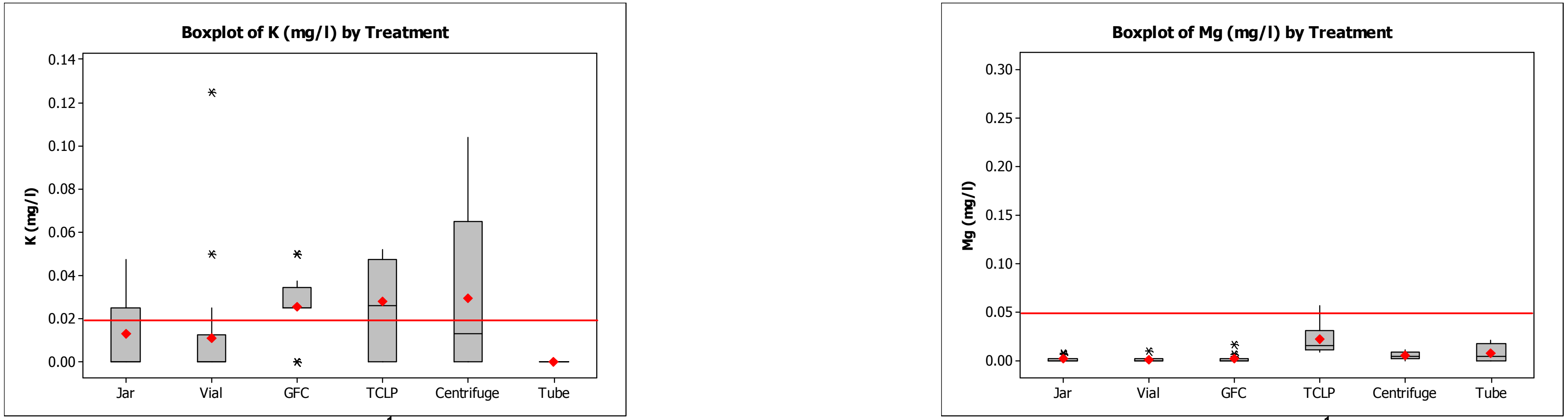
The samples were analysed for metals by Flame Photometer and Atomic Absorption Spectroscopy (Section 2.12).

3.1.1.2 Results



Limit of quantification = 0.05 mg l^{-1} indicated by red line

Limit of quantification = 0.05 mg l^{-1} indicated by red line



Limit of quantification = 0.02 mg l^{-1} indicated by red line

Limit of quantification = 0.05 mg l^{-1} indicated by red line

Figure 3-1 Blank Contamination

3.1.1.3 Discussion

Figure 3-1 shows results of the blank test. It can be seen that TCLP filters were variably high in sodium while the other steps were below the quantification limit. There was a slight problem with potassium in vials with 2 samples giving high readings. The centrifuged samples that had been filtered also showed variable, high values for K while the rest of the samples were at or below the quantification limit. It was thought that the problem with K levels was mainly due to random contamination in the storage vials as opposed to the membrane filters. Calcium was at the quantification limit for all samples although the TCLP filters produced one high, outlying result. Magnesium was below the quantification limit in all samples.

Glass fibre filters gave low, reproducible results for all 4 cations tested compared to TCLP filters that could be quite variable (especially for sodium).

The centrifuge treatment produced similar low concentrations as the glass fibre filters although there was a slight problem with potassium in centrifuged samples. Preliminary experimentation showed that extra rinsing of the washed centrifuge tubes with deionised water reduced this problem (Figure 3-2).

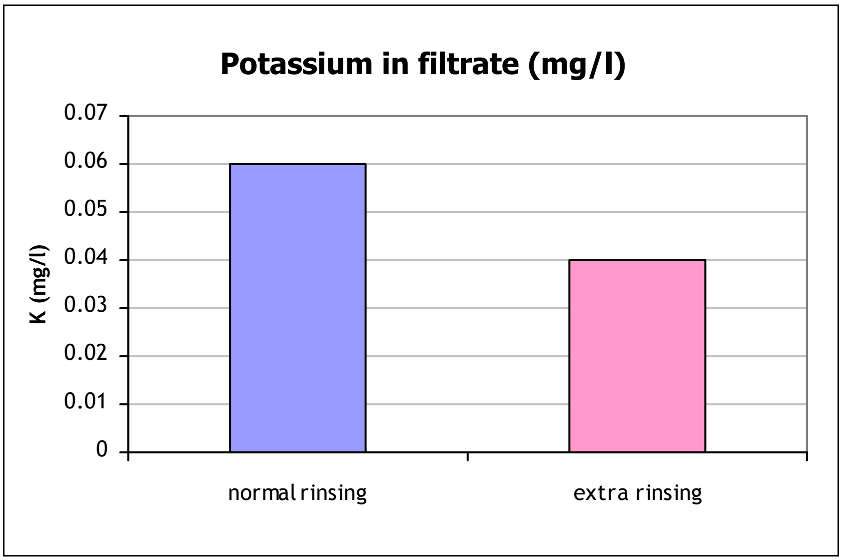


Figure 3-2 Preliminary experiment showing the effect of extra rinsing of washed centrifuge tubes on potassium contamination in blanks

3.1.2 Rockdust extraction filter test

3.1.2.1 Method

Approximately 10 g rockdust was accurately weighed to two decimal places in a 100 ml glass jar and 100 ml of deionised water added by dispenser. The glass jars were shaken on an end-over-end shaker for 1 hour. In order to select an appropriate filtration method for future rockdust extractions, three possible methods were tested. These were:

- The samples were filtered under vacuum through Whatman GF/C glass microfibre filters, then through PALL Life Sciences Supor-200 0.2 µm membrane filters in order to obtain a clear filtrate.
- The samples were filtered under vacuum through Whatman TCLP glass microfibre acid treated low metal filters, then through PALL Life Sciences Supor-200 0.2 µm membrane filters in order to obtain a clear filtrate.
- The samples were placed on the centrifuge at 4500 rpm for 10 min, and then filtered through PALL Life Sciences Supor-200 0.2 µm membrane filters only.

Approximately 30 ml of each sample was collected in clean auto-sampler vials for analysis by Atomic Absorption Spectroscopy (Section 2.12.1) and Flame Photometry (Section 2.12.2). There were 10 replicates of each treatment and 4 blanks per treatment.

3.1.2.2 Results and discussion

Blank concentrations were subtracted from concentrations in the extracts and the solution concentration converted to milligrams of the element per kilogram rockdust. Results of extractions of SEER rockdust and Duntilland quarry rockdust are shown in Table 3-1 and Table 3-2 along with results of statistical analysis using the one-way analysis of variance command in Minitab.

	Na (mg kg^{-1})	K (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})
Glass Fibre Filters	433.81 ab	5.49 b	2.76 ab	< 0.50 a
TCLP Filters	451.78 b	2.88 a	3.01 b	1.96 b
Centrifuge	423.72 a	5.12 b	2.52 a	< 0.50 a

Table 3-1 Effect of filtration techniques on cations in water extracts of SEER rockdust samples (concentrations in the same column with the same letter are not significantly different at p = 0.05 according to Tukey's LSD)

Table 3-1 shows that extracts filtered through TCLP Filters gave higher concentrations of sodium, calcium and magnesium compared with centrifuged samples. TCLP filters gave similar concentrations as glass fibre filters for sodium and calcium in rockdust extracts but gave higher results for magnesium. Potassium levels in sample extracts passed through TCLP filters were statistically lower than those found in samples that had been through glass fibre filters or centrifuged. This was not due to contamination since K levels in blank solutions for all extraction procedures were below quantification limits. It seems that some of the water extractable K from the SEER rockdust samples was held by the TCLP filters leading to lower levels in the filtrate. Detection of magnesium in extracts passed through TCLP filters was not due to contamination since blank levels were all below quantification limits. Extracts passed through glass fibre filters gave statistically the same results as centrifuged samples.

Since glass fibre filters and centrifuge treatments gave statistically the same concentrations of all elements measured (Table 3-1), either could be used as the final extraction method. The main advantage to centrifuging samples was that they were much faster to filter than when glass fibre filters were used. Therefore more samples could be extracted per day using this method.

A rockdust sample from Duntilland quarry was used to further test the hypothesis that TCLP filters and centrifuging gave different concentrations of elements in the filtrate. Since the Duntilland quarry fine rockdust material had higher levels of calcium and magnesium than SEER rockdust; the effect of treatment on concentrations of these elements in the filtrate can be seen more effectively in Table 3-2. The results back up the information in Table 3-1 since TCLP filters produced higher levels of sodium and magnesium in the extracts than the centrifuged samples but lower levels of potassium. Calcium levels were not significantly different in both treatments.

	Na (mg kg^{-1})	K (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})
TCLP Filters	114.62 b	12.57 a	49.61 a	11.08 b
Centrifuge	89.98 a	16.56 b	51.11 a	10.36 a

Table 3-2 Effect of filtration techniques on cations in water extracts of Duntilland quarry fine rockdust samples (concentrations in the same column with the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD)

Centrifuging and filtering through a 0.2 µm membrane filter was chosen for incorporation in the final rockdust extraction procedure since the blanks were low as long as an adequate washing procedure was followed. The TCLP filters were not chosen due to high sodium in blanks, uptake of potassium by the filters and higher concentrations of sodium and magnesium in samples compared to samples filtered through glass fibre filters and centrifuged samples.

3.1.3 Final method for rockdust extractions

Approximately 10 g of rockdust was accurately weighed to two decimal places into a 100 ml glass jar and 100 ml of deionised water added by dispenser. The glass jars were shaken on an end-over-end shaker for 1 hour. The samples were placed on the centrifuge at 4500 rpm for 10 min, and the supernatant filtered through 0.2 µm membrane filters under vacuum. Approximately 30 ml of each clear filtrate was collected in clean auto-sampler vials and stored at 4 °C until analysis.

3.2 Ammonium system

The original ammonium system used in the department was found to be non-linear in the range 0 - 5 mg l^{-1} during routine operations. It was found to be linear 0 - 2.5 mg l^{-1} only. This could be caused by two problems with the system:

1. The system contained potassium sodium tartrate in the complexing reagent. As ammonium-free potassium sodium tartrate could not be provided by the manufacturer, the effect on ammonium analysis when potassium sodium tartrate was removed from the system was investigated.

2. There colorimeters used in the automated system were sub-optimal for analysis at the wavelength used to analyse ammonium. Therefore, the colorimeter system also required optimisation to determine suitable operating conditions for the analysis of ammonium in the range 0 - 5 mg l^{-1}.

3.2.1 Original system

3.2.1.1 Reagents

Complexing reagent
- Sodium citrate 50 g l^{-1}
- Potassium sodium tartrate 50 g l^{-1}
- Sodium nitroprusside 0.5 g l^{-1}

Alkaline phenol
- Phenol 45 g l^{-1}
- Sodium hydroxide 25 g l^{-1}

Hypochlorite solution
- Hypochlorite (6-14 % available chlorine) 50 ml l^{-1}

3.2.1.2 Reagent flow rates

- 0.6 ml min^{-1} complexing reagent
- 0.6 ml min^{-1} alkaline phenol
- 0.16 ml min^{-1} hypochlorite solution
- 0.32 ml min^{-1} sample

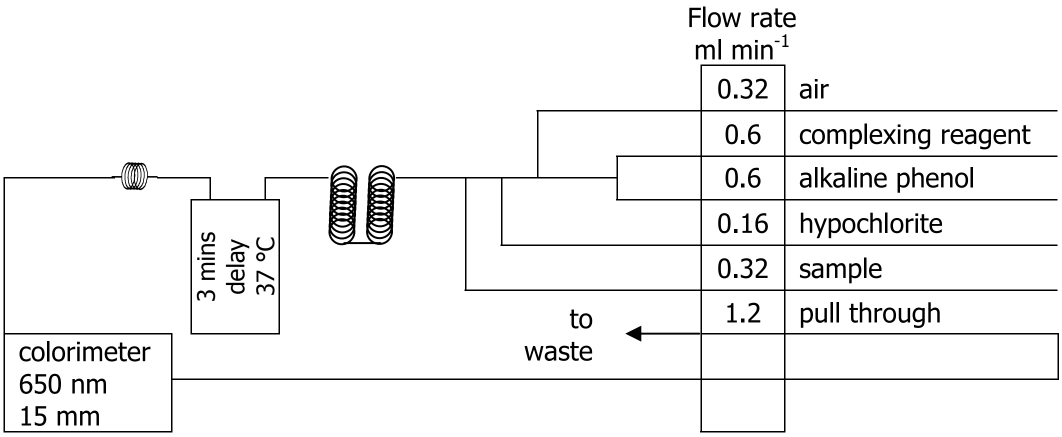


Figure 3-3 Original ammonium-N system

3.2.1.3 Colorimeter settings

- Wavelength 650 nm
- Cetron CE63V phototubes (600-900 nm range)
- Colorimeter 1 (older) in use

3.2.2 Removal of potassium sodium tartrate from complexing reagent

Potassium sodium tartrate and sodium citrate are present in the ammonium-N colorimetric system for two reasons:

1. pH buffering – pH must be maintained between 11.4 and 12.4 (Searle, 1984)

2. To complex interfering metals (Searle, 1975)

However, it was not possible to obtain nitrogen free potassium sodium tartrate (Fisher Scientific certified value = 10 ppm total N). The certified value was shown to be accurate by running a 50 g l^{-1} potassium sodium tartrate solution as a sample on the original ammonium system (Section 3.2.1) with a tartrate-free complexing reagent. The calculated value was 9.93 mg kg^{-1} N in the potassium sodium tartrate. This means that there was 0.497 mg l^{-1} N in the complexing reagent and 0.177 mg l^{-1} N in the system when no samples were running. Nitrogen could be removed from the complexing reagent by raising the pH of the solution and boiling off N as ammonia. Instead of this lengthy step, the effect of complete removal of potassium sodium tartrate from the system was investigated.

3.2.2.1 Method: optimising complexing reagent

To investigate the effect of removal of potassium sodium tartrate from the complexing reagent, three solutions were prepared:

a) Complexing reagent (original concentrations)
  - Potassium sodium tartrate 50 g l^{-1}
  - Sodium citrate 50 g l^{-1}
  - Sodium nitroprusside 0.5 g l^{-1}

b) Complexing reagent
  - No potassium sodium tartrate
  - Sodium citrate 100 g l^{-1}
  - Sodium nitroprusside 0.5 g l^{-1}

c) Complexing reagent
  - No potassium sodium tartrate
  - Sodium citrate 50 g l^{-1}
  - Sodium nitroprusside 0.5 g l^{-1}

The three complexing reagents were run with the other ammonium system reagents and a 5 mg l^{-1} ammonium-N standard. The product was collected in a universal jar and peak absorbance and pH of the product was measured:

Complexing reagent composition	Peak absorbance (nm)	Final pH
a) Original reagent	638.0	13.0
b) No tartrate, double citrate	645.5	12.7
c) No tartrate, original citrate	642.4	12.7

Table 3-3 Effect of complexing reagent composition on peak absorbance and final reagent stream pH

3.2.2.2 Conclusion: optimising complexing reagent

Table 3-3 shows that potassium sodium tartrate could be removed from the complexing reagent without adversely affecting the peak absorbance of the product. There was no need to double the sodium citrate concentration to compensate for tartrate removal as this did not affect the final pH and had little effect on the product peak absorbance. However, the final pH of the system was found to be too high (in the original system as well as in the potassium sodium tartrate-free system) as it should be between 11.4 and 12.4 (Searle, 1984).

3.2.2.3 Method: optimising alkaline phenol reagent

The buffering capacity of the system was reduced when potassium sodium tartrate was removed from the complexing reagent. Hence, the effect of modifying the concentration of sodium hydroxide in the phenol reagent was investigated. Four alkaline phenol reagents were prepared as below:

a) Alkaline phenol
  - Phenol 45 g l^{-1}
  - Sodium hydroxide 15 g l^{-1}

b) Alkaline phenol
  - Phenol 45 g l^{-1}
  - Sodium hydroxide 20 g l^{-1}

c) Alkaline phenol
  - Phenol 45 g l^{-1}
  - Sodium hydroxide 22.5 g l^{-1}

d) Alkaline phenol
- Phenol 45 g l^{-1}
- Sodium hydroxide 25 g l^{-1}

The solutions were run with the original ammonium system reagents (using the new complexing reagent with no potassium sodium tartrate) and a 5 mg l^{-1} ammonium-N standard. The product was collected in a universal jar and peak absorbance and pH of the product was measured. 1 mg l^{-1} standards were run in the ammonium system with each alkaline phenol solution at a fixed standard calibration of 1.0. Recorded peak height was used as an indication of sensitivity of the method. Results are shown in Table 3-4:

Sodium hydroxide concentration in alkaline phenol reagent (g l^{-1})	Peak absorbance (nm)	Final pH	Colorimeter peak height of 1 mg l^{-1} standard
a) 15	618.5	10.70	11.1
b) 20	636.5	12.15	29.7
c) 22.5	643.5	12.69	28.6
d) 25	640.5	12.70	29.5

Table 3-4 Effect of alkaline phenol reagent composition on peak absorbance, final reagent stream pH and peak height of 1 mg l^{-1} standard

The effect of alkaline phenol reagent composition on the absorption spectrum of the final product is shown in Figure 3-4:

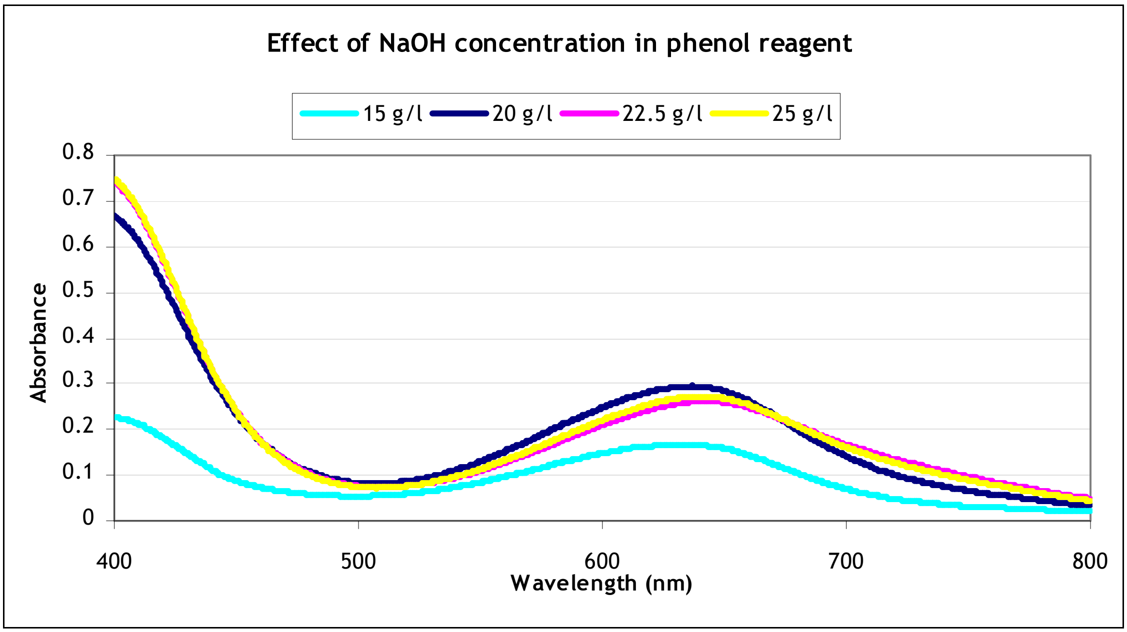


Figure 3-4 Effect of NaOH concentration in phenol reagent on absorption spectrum of final products

3.2.2.4 Conclusion: optimising alkaline phenol reagent

Reducing the sodium hydroxide concentration in the alkaline phenol reagent to 20 g l^{-1} gave an acceptable final pH of 12.15 and a peak of absorbance at 636.5 nm (Table 3-4 and Figure 3-4). Peak height of a 1 mg l^{-1} standard when the colorimeter was fixed to a standard calibration value of 1.0 gave an indication of changes in sensitivity. The greatest sensitivity was recorded in the phenol reagent with 20 g l^{-1} sodium hydroxide. In the nitroprusside catalysed reaction, the colour is stable at final reagent stream pHs between 11.4 and 12.4 according to Searle (1984) and is less susceptible to minor changes in pH around these values.

The phenol concentration was optimized by Metwaly (1999) who recommended a phenol concentration of 45 g l^{-1}, corresponding to 16.07 g l^{-1} in the final solution. The work of Searle (1984) confirmed that the concentration of phenol was unimportant once a threshold concentration had been reached.

3.2.2.5 Method: removal of interfering metals

A metal chelating agent is necessary into this manifold since it is to be used with soil digests which can have high metal concentrations from catalysts used to speed up digestion or due to metals solubilised in the digestion (Searle, 1984).

A Kjeldahl digestion tablets consist of:
- 100 parts K_2SO_4
- 6 parts $CuSO_4.5H_2O$
- 1 part Se

Therefore a 2.5 g tablet dissolved in 100 ml gives:
- 10.5 g K l^{-1}
- 0.4 g Cu l^{-1}
- 0.2 g Se l^{-1}

Kjeldahl digests are diluted 20 x by the system manifold, so the final concentration in measured samples is:
- 0.525 g K l^{-1}
- 0.02 g Cu l^{-1}
- 0.01 g Se l^{-1}

To test the ability of the new complexing reagent (containing 50 g l^{-1} sodium citrate, no potassium sodium tartrate and 0.5 g l^{-1} sodium nitroprusside) to complex out some major cation constituents of soil digests, a set of 5 mg l^{-1} NH_4-N standards were prepared as follows:

- 5 mg l^{-1} NH_4-N in water
- 5 mg l^{-1} NH_4-N plus 500 mg l^{-1} Na
- 5 mg l^{-1} NH_4-N plus 500 mg l^{-1} K
- 5 mg l^{-1} NH_4-N plus 500 mg l^{-1} Ca
- 5 mg l^{-1} NH_4-N plus 500 mg l^{-1} Mg
- 5 mg l^{-1} NH_4-N plus 500 mg l^{-1} Cu

The effect of each cation on NH_4-N peak height was then assessed by comparing the peak height of an ammonium standard in water with that of the ammonium standards prepared with cations. The peak height was expressed as a percentage of the original ammonium standard peak height.

5 mg l^{-1} NH_4-N Standard with:	Peak Height (as % of 5 mg l^{-1} NH_4-N in water)
500 mg l^{-1} Na	98.7
500 mg l^{-1} K	99.5
500 mg l^{-1} Ca	99.9
500 mg l^{-1} Mg	100.0
500 mg l^{-1} Cu	101.3

Table 3-5 Effect of different metals on peak height of 5 mg NH_4-N l^{-1} standard

3.2.2.6 Conclusion: removal of interfering metals

Since each cation only had a negligible effect on peak height of a 5 mg l^{-1} standard (Table 3-5), the complexing reagent was shown to be working effectively in the absence of potassium sodium tartrate. The Kjeldahl digestion catalyst will not interfere with the ammonium system since 500 mg l^{-1} K did not have an effect on the peak height.

3.2.3 New system

With potassium sodium tartrate removal from the ammonium system, the reagent concentrations were slightly adjusted.

3.2.3.1 Reagents

Complexing reagent
- Sodium citrate 50 g l^{-1}
- Sodium nitroprusside 0.5 g l^{-1}

Alkaline phenol
- Phenol 45 g l^{-1}
- Sodium hydroxide 20 g l^{-1}

Hypochlorite solution
- Hypochlorite (6-14 % available chlorine) 50 ml l^{-1}

3.2.3.2 Reagent flow rates

- 0.6 ml min^{-1} complexing reagent
- 0.6 ml min^{-1} alkaline phenol
- 0.16 ml min^{-1} hypochlorite solution
- 0.32 ml min^{-1} sample

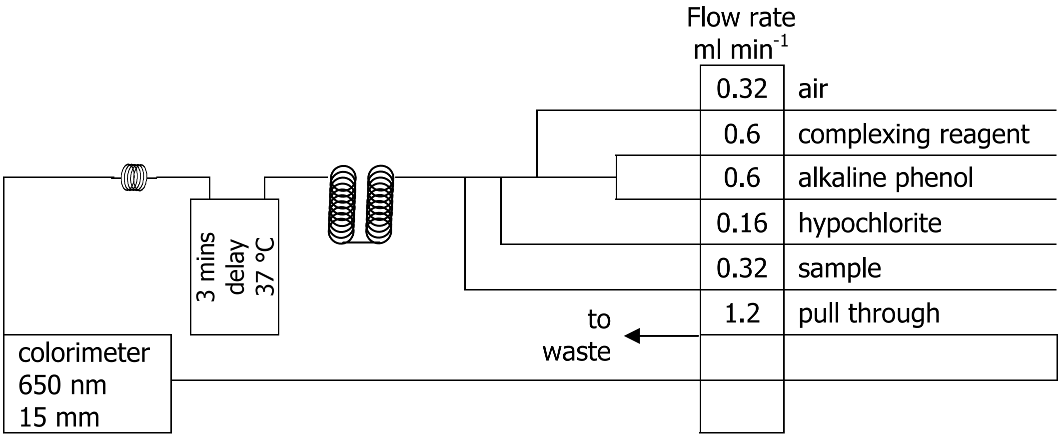


Figure 3-5 New ammonium-N system (no potassium sodium tartrate)

3.2.3.3 Colorimeter settings

- Wavelength 650 nm
- Cetron CE63V phototubes (600-900 nm range)
- Colorimeter 1 (older) in use

3.2.3.4 Comparing the two ammonium systems

The calibration graph obtained using original ammonium system (Section 3.2.1) was compared to that of new ammonium system (Section 3.2.3) by standardising the readings to read as a percentage of the 5 mg l^{-1} reading (Figure 3-6).

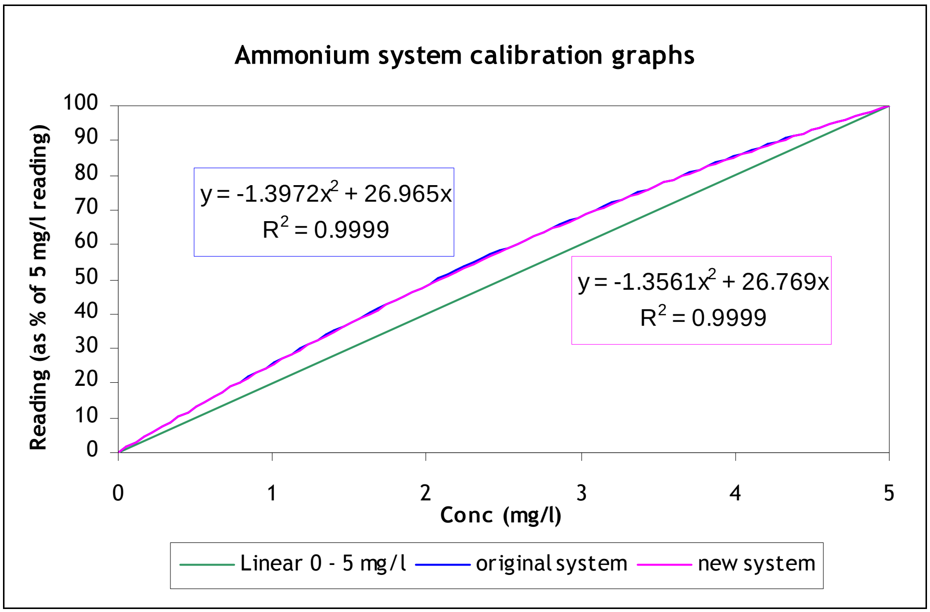


Figure 3-6 Calibration graphs of original system (with potassium sodium tartrate) and new system (without potassium sodium tartrate)

There was little change in the sensitivity from the original system to the new system as shown by the similarity in readings within the linear range. At 1 mg l^{-1} the corresponding peak heights were 26.1 in the original system and 26.0 in the new system.

3.2.3.5 Conclusion

Figure 3-6 shows that removal of potassium sodium tartrate and optimising the pH of the system still produced the same curved calibration as the original system. Both systems produced a curved calibration in the range 0-5 mg NH_4-N l^{-1}. The reasons for the curvature of the graph could be:

- Chemical problem – contaminated reagents, old reagents, reagent concentrations sub-optimal

- Colorimeter problem – old or incorrect phototubes, old source bulb, inherent colorimeter linearity problem

3.2.4 Testing reagents

3.2.4.1 Hypochlorite solution

New hypochlorite stock solution was used in all future work since Weatherburn (1967) showed that when the intensity of colour development from the same reagents decreases abruptly, fresh hypochlorite can correct the problem. However, there was no effect on graph linearity with the new solution. The effect of increasing hypochlorite solution concentration was not investigated since Metwaly (1999) showed that 50 ml l^{-1} was the optimum concentration of hypochlorite in the original ammonium system. This is in agreement with Searle (1984) who showed that the hypochlorite concentration in the nitroprusside catalysed reaction was not critical once the optimum had been reached. Weatherburn (1967) stated that hypochlorite concentration could be increased to as much as 100 ml (5 % hypochlorite) per litre to extend the useful life of the reagent without negatively affecting absorbance of the product.

3.2.4.2 Complexing reagent

Since sodium citrate and potassium sodium tartrate optimisation had already been carried out with no effect on the linearity of the calibration graph (Figure 3-6), no further work was carried out on these. Sodium nitroprusside was included in the system as a catalyst. Although optimisation of sodium nitroprusside for this system had already been carried out by Metwaly (1999), this was carried out as a check that the catalyst was still functioning at its optimum. All other reagent concentrations were maintained as in Section 3.2.3.1.

a) Complexing reagent
  - Sodium citrate 50 g l^{-1}
  - Sodium nitroprusside 0.5 g l^{-1}

b) Complexing Reagent
  - Sodium citrate 50 g l^{-1}
  - Sodium nitroprusside 1.0 g l^{-1}

c) Complexing Reagent
  - Sodium citrate 50 g l^{-1}
  - Sodium nitroprusside 1.5 g l^{-1}

d) Complexing Reagent
- Sodium citrate 50 g l^{-1}
- Sodium nitroprusside 2.0 g l^{-1}

Sodium nitroprusside concentration in complexing reagent (g l^{-1})	0-5 mg l^{-1} Linear or Curved	Equation of calibration graph
a) 0.5	Curved	$y = -0.7957x^2 + 14.391x$
b) 1.0	Curved	$y = -0.777x^2 + 14.117x$
c) 1.5	Curved	$y = -0.822x^2 + 14.288x$
d) 2.0	Curved	$y = -0.7835x^2 + 13.98x$

Table 3-6 Effect of sodium nitroprusside concentration on linearity of ammonium calibration

3.2.4.3 Conclusion

There was no improvement on graph linearity when increasing sodium nitroprusside concentration in the complexing reagent (Table 3-6). The original concentration of 0.5 g l^{-1} was still appropriate.

3.2.4.4 Optimised reagents

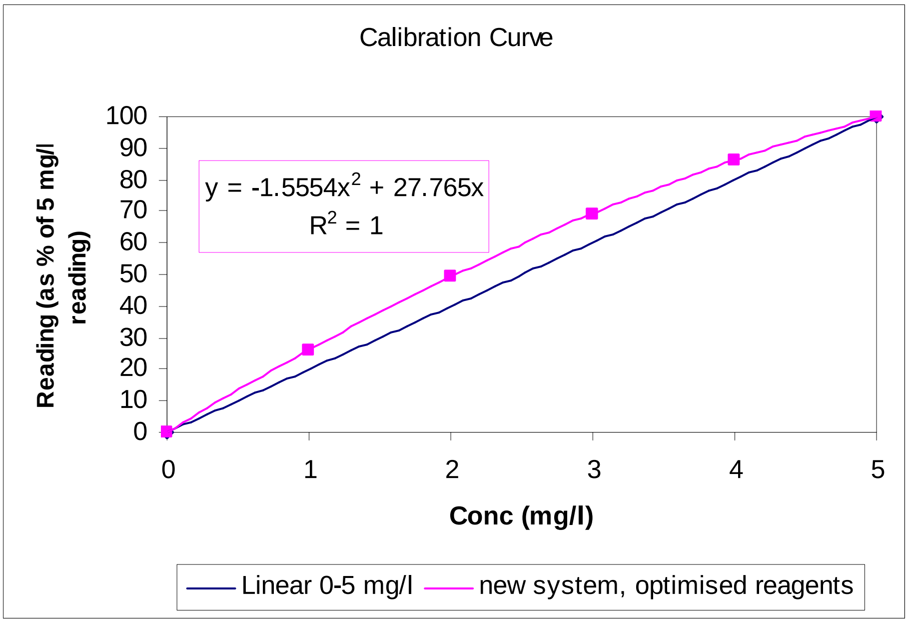


Figure 3-7 Calibration graph with new ammonium system and optimised reagents

3.2.4.5 Conclusion

Figure 3-7 shows that the calibration was curved despite using new, uncontaminated reagents and optimising the reagent concentrations. This shows that the problem with the non-linear calibration was not a chemical one but a colorimeter problem instead.

3.2.5 Testing colorimeters

Since the problem had been pin-pointed to that of a colorimeter problem instead of a chemical one, the colorimeters were tested. Colorimeter 1 was the older of the two Technicon Autoanalyser II colorimeters available in the department.

A stable indophenol-blue product was prepared by mixing (in appropriate ratios) complexing reagent, alkaline phenol, hypochlorite solution (as detailed in Section 3.2.3) and 5 mg l^{-1} ammonium-N standard. The reagents were mixed well and left for 30 mins for full, stable colour development.

The developed indophenol-blue colour was then diluted 1/5, 2/5, 3/5, 4/5 and 5/5 and absorbance at 650 nm was measured on a Hitachi U-1100 spectrophotometer.

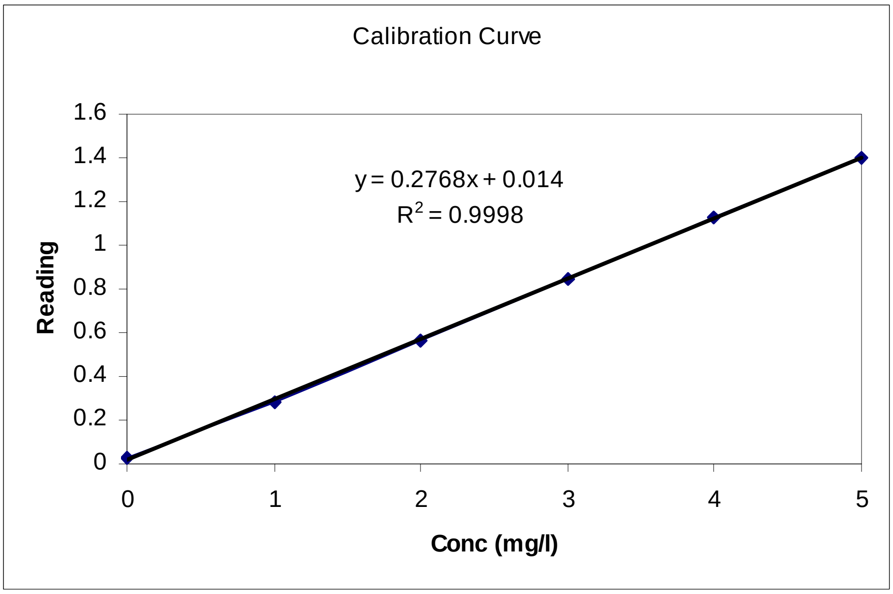


Figure 3-8 Spectrophotometer at 650 nm

It can be seen that the calibration graph obtained using the spectrophotometer was linear 0-5 mg l^{-1} (Figure 3-8). The non-linearity in the calibration graphs obtained with the Technicon colorimeter was definitely due to a colorimeter problem and not a chemical problem.

The solutions were pumped straight through colorimeter 1 and absorbance at 650 nm measured. The CE63V phototubes and 650 nm filters from colorimeter 1 were transferred over to colorimeter 2 (slightly newer colorimeter) and the same stable colour corresponding to 1, 2, 3, 4 and 5 mg l^{-1} pumped straight through.

3.2.5.1 Colorimeter 1

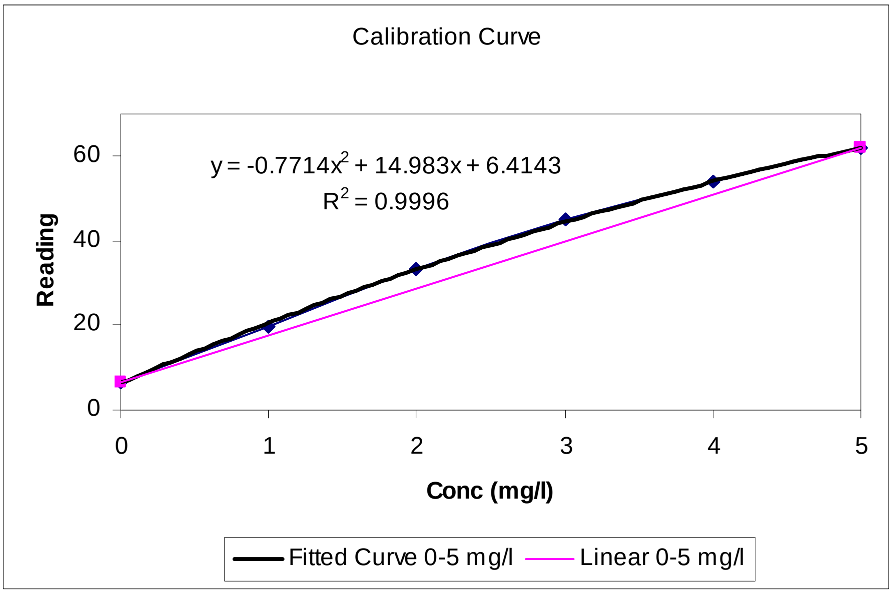


Figure 3-9 Colorimeter 1 CE63V phototubes with 650 nm filters, standard calibration - 0.2

3.2.5.2 Colorimeter 2

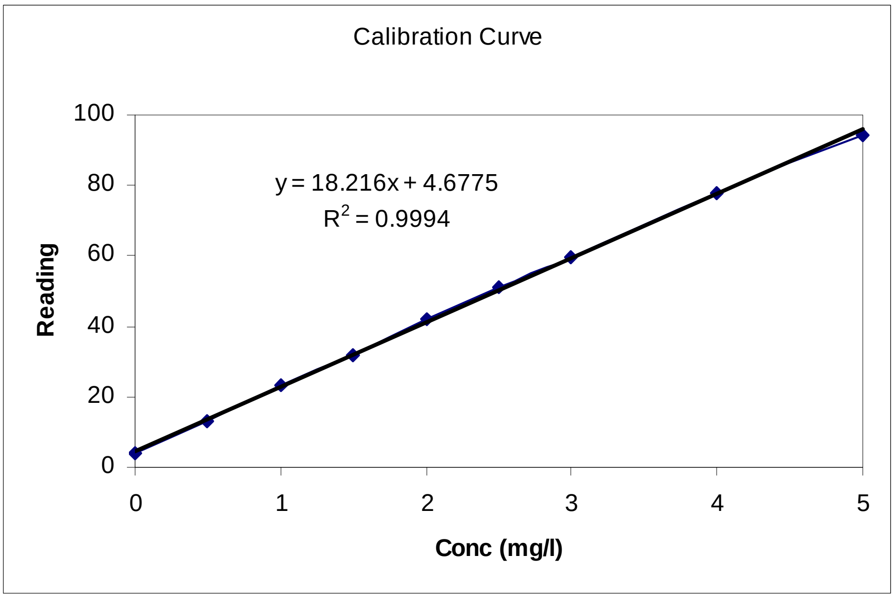


Figure 3-10 Colorimeter 2 CE63V phototubes with 650 nm filters, standard calibration - 0.1

3.2.5.3 Conclusion

Colorimeter 2 was linear (Figure 3-10) although the graph started to slightly curve between 4 and 5 mg l^{-1} while colorimeter 1 was curved (Figure 3-9) beyond about 2.5 mg l^{-1}. The new ammonium system (Section 3.2.3) must be run on colorimeter 2 to obtain a linear calibration 0-5 mg l^{-1} (it is only linear 0-2.5 mg l^{-1} on colorimeter 1).

3.2.6 High range ammonium system

Since colorimeter 1 could not be used beyond 2.5 mg NH_4-N l^{-1} and colorimeter 2 was slightly off-linear beyond 4 mg NH_4-N l^{-1}, a new high range system was developed to be linear 0 - 5 mg NH_4-N l^{-1} on either colorimeter.

To obtain the high range system the sample flow rate was halved. To compensate for the reduced sample flow, the hypochlorite reagent flow rate was doubled (and consequently, the concentration halved).

3.2.6.1 High range reagents

Complexing reagent
- Sodium citrate 50 g l^{-1}
- Sodium nitroprusside 0.5 g l^{-1}

Alkaline phenol
- Phenol 45 g l^{-1}
- Sodium hydroxide 20 g l^{-1}

Hypochlorite solution
- Hypochlorite (6-14 % available chlorine) 25 ml l^{-1}

3.2.6.2 Reagent flow rates

- 0.6 ml min^{-1} complexing reagent
- 0.6 ml min^{-1} alkaline phenol
- 0.32 ml min^{-1} hypochlorite solution
- 0.16 ml min^{-1} sample

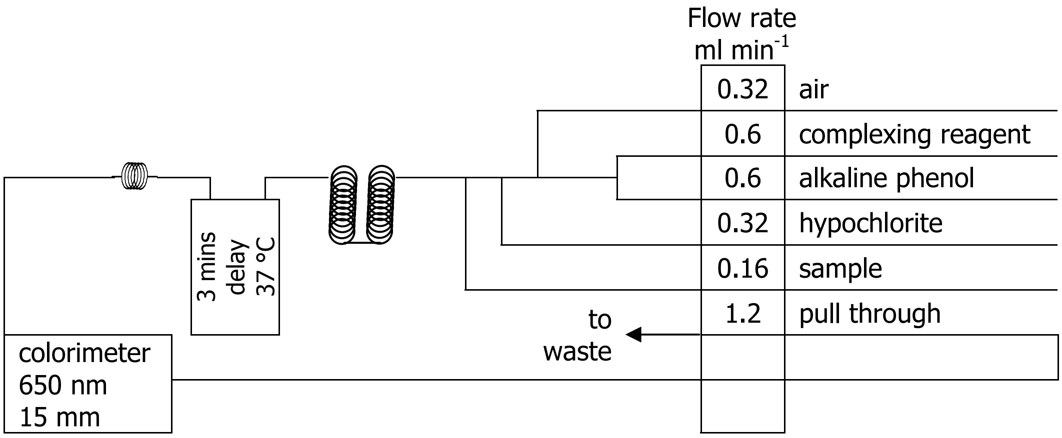


Figure 3-11 New ammonium-N system with changes to reagent flow rates

3.2.6.3 Colorimeter settings

- Wavelength 650 nm
- Cetron CE63V phototubes (600-900 nm range)
- Colorimeter 1 or 2 can be used
- Linear range 0-5 mg l^{-1}

3.2.7 Testing high range system

The new high range system was checked for linearity on both colorimeters using the same set of phototubes and bulb.

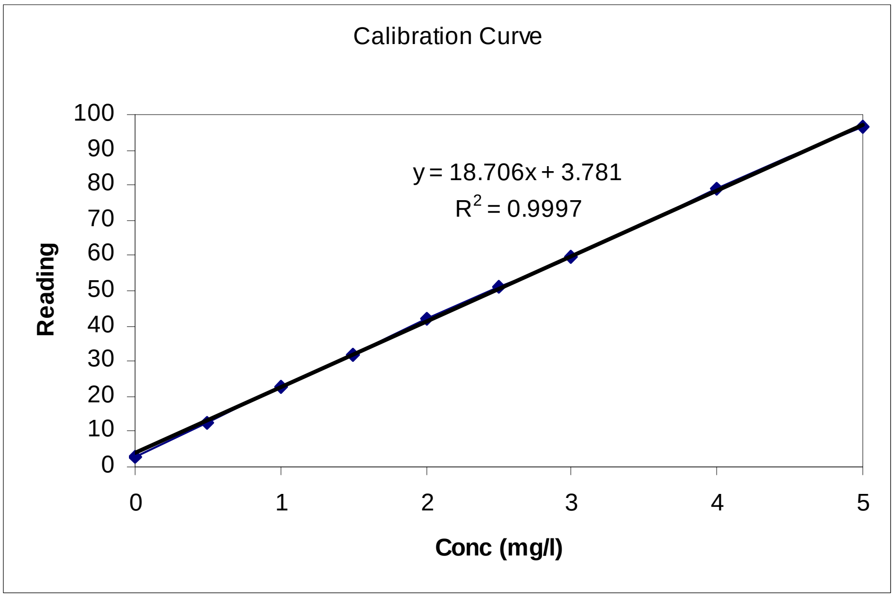


Figure 3-12 Colorimeter 1 CE63V phototubes, high range reagents, standard calibration - 1.3

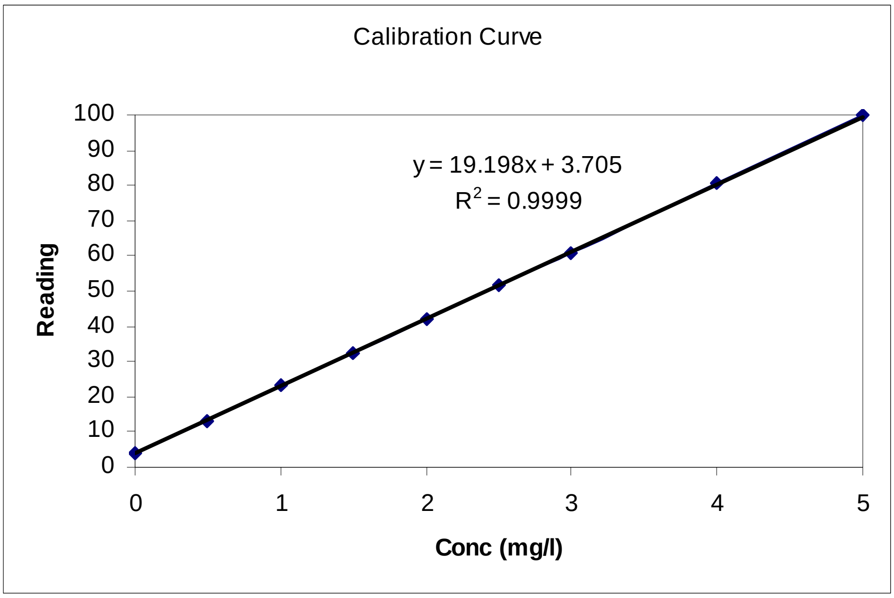


Figure 3-13 Colorimeter 2 CE63V phototubes high range reagents, standard calibration - 1.2

3.2.7.1 Conclusion

By reducing the sample flow rate, it was possible to obtain a linear calibration (to at least 5 mg l^{-1}) on both colorimeters (Figure 3-12, Figure 3-13).

3.2.8 Kjeldahl–N digestion

The high range system (Section 3.2.6) was suitable for Kjeldahl-N analysis since the dilution in the system brings 100 mg l^{-1} standards down to the 5 mg l^{-1} range. Either colorimeter with CE63V phototubes would be suitable as they were both shown to be linear in Section 3.2.7 in this range. However, Hamamatsu R491 phototubes have a better working range for colorimetric determinations (200-650 nm) compared with the Cetron CE63V phototubes (600-900 nm). The R491 phototubes were tested for suitability in both colorimeters.

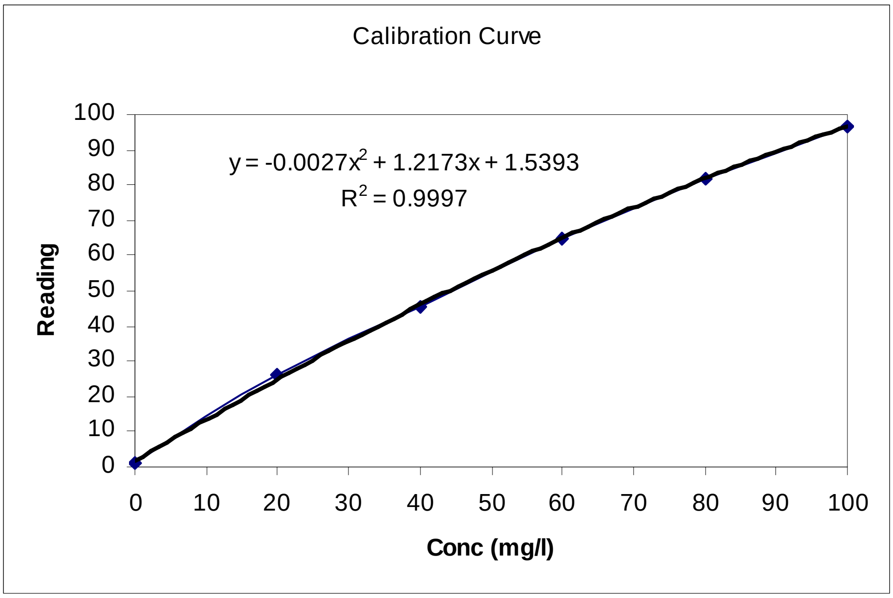


Figure 3-14 Colorimeter 1 R491 phototubes, high range reagents, standard calibration - 2.4

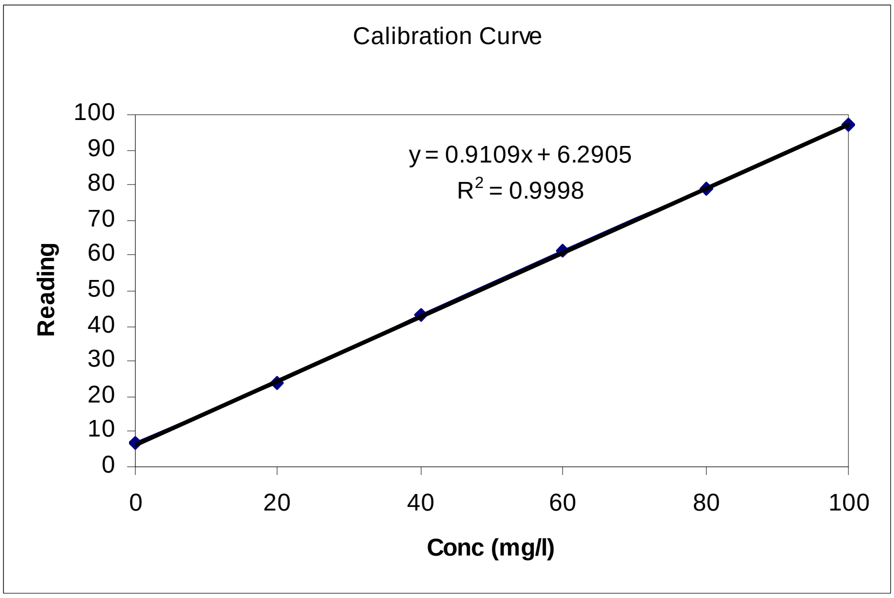


Figure 3-15 Colorimeter 2 R491 phototubes, high range reagents, standard calibration - 1.74

3.2.8.1 Conclusion

R491 phototubes produced a linear graph in colorimeter 2 (Figure 3-15) but the calibration was non-linear with the phototubes in colorimeter 1 (Figure 3-14). Therefore, only colorimeter 2 was suitable to be used with the R491 phototubes to produce a linear calibration for Kjeldahl-N determinations. If Colorimeter 1 was to be used, CE63V phototubes must be used to obtain a linear calibration (Figure 3-16).

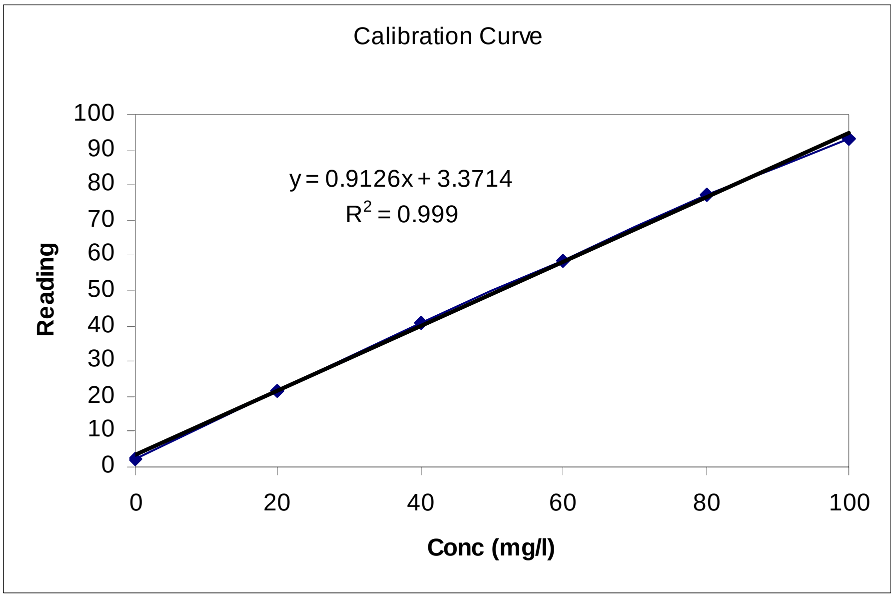


Figure 3-16 Colorimeter 1 CE63V phototubes high range reagents, standard calibration - 1.05

3.2.9 Final high range ammonium system

3.2.9.1 High range reagents

Complexing reagent
- Sodium citrate 50 g l^{-1}
- Sodium nitroprusside 0.5 g l^{-1}

Alkaline phenol
- Phenol 45 g l^{-1}
- Sodium hydroxide 20 g l^{-1}

Hypochlorite solution
- Hypochlorite (6-14 % available chlorine) 25 ml l^{-1}

3.2.9.2 Reagent flow rates

- 0.6 ml min^{-1} complexing reagent
- 0.6 ml min^{-1} alkaline phenol
- 0.32 ml min^{-1} hypochlorite solution
- 0.16 ml min^{-1} sample

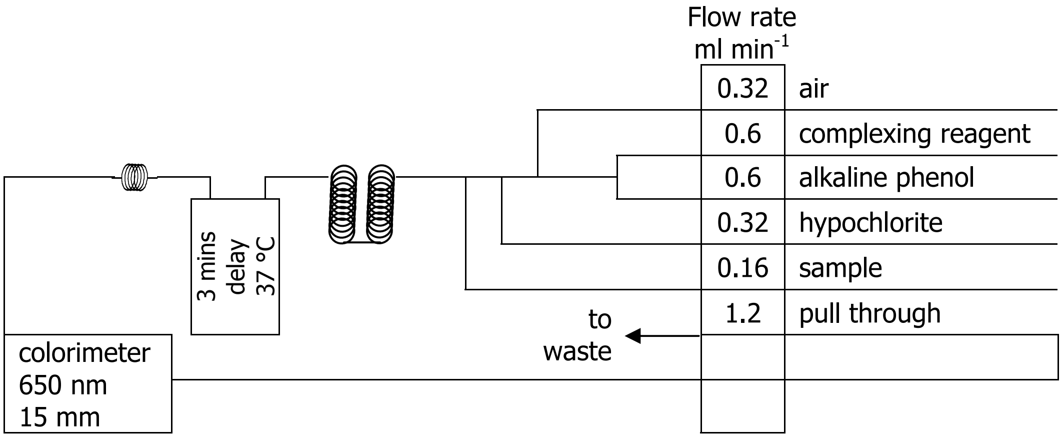


Figure 3-17 New ammonium-N system

3.2.9.3 Colorimeter options

Linear range 0 - 5 mg l^{-1}
- Colorimeter 2 with R491 phototubes to produce a linear calibration
- Colorimeter 1 with CE63V phototubes to produce a linear calibration

Linear range 0 – 100 mg l^{-1} (i.e. Kjeldahl digests)
- Dilution 0.1/2.1
- Colorimeter 2 with R491 phototubes to produce a linear calibration
- Colorimeter 1 with CE63V phototubes to produce a linear calibration

3.3 Nitric acid trace metal digestion

3.3.1 Introduction

In order to investigate the effect of rockdust addition on trace metals in plant material, a different digestion technique was required. This was because the dilution in the standard nitric acid digestion (Section 2.10.1) was suitable for nutrient metals but too high for trace metals. Two techniques were investigated: a hotplate digestion; and a dry ashing method.

For complete dissolution of plant material, a digestion procedure involving the use of hydrofluoric acid would be required. This is because the siliceous residue left as a result of incomplete digestion with other acids (i.e. nitric acid digestion or nitric-perchloric acids digestion) may contain micronutrients (Wikoff and Moraghan, 1986). These workers also found that ternary digestion techniques may only be required for plant digestions as a result of soil contamination of the plant material.

Due to safety concerns, HF digestions were not employed. The nitric-perchloric method was not used since it is also potentially hazardous and it has been shown that nitric acid alone gives similar recoveries (Hseu, 2004). Anderson and Henderson (1988) found that nitric-perchloric digestion gave low K and Mn recoveries but other elements were within standard values. They found that dry ashing gave consistent, acceptable values for most elements.

Dry ashing was also recommended by Haynes (1980) when N content was not required since it gave similar results to nitric-perchloric for Ca, Mg, P and K (except when analysing woody tissue). Dry ashing was recommended by Adrian (1973) as an acceptable method except when dealing with volatile metals.

3.3.2 Methods

3.3.2.1 Nitric acid digestion – hotplate method

Approximately 2.5 g of oven dry plant material was accurately weighed to 2 decimal places into a 100 ml conical flask. 30 ml concentrated HNO_3 was added by dispenser mixed thoroughly. The flasks were covered with small watch glasses and pre-digested overnight. A further 20 ml concentrated HNO_3 was added by dispenser then the flasks were placed on a cool hotplate. The temperature was gradually increased (to control frothing) up to 130 °C. They were covered with small watch glasses (leaving a gap for venting gas) for 1 hour. The samples were evaporated down to a final volume of approximately 5 ml, removed from the hotplate and allowed to cool. They were transferred quantitatively through hardened filter papers into 25 ml volumetric flasks and made up to volume. The final acid concentration was therefore approximately 20 % HNO_3.

3.3.2.2 Dry ashing – nitric acid method

Approximately 5.0 g of oven dry plant material was accurately weighed to 2 decimal places into a new small porcelain basin. The samples were pre-ashed by heating gently with a Bunsen burner until they charred and did not give off any more smoke. Heating was controlled to avoid igniting the sample and loss of material (Gorsuch, 1970). They were then transferred to a muffle furnace and ashed at 500 °C for 8 hours. If a white/grey ash was not obtained at the first attempt, water was added dropwise to the samples to wet the ash then evaporated in the oven at 110 °C (MAFF/ADAS, 1986). They were then placed back in the furnace at 500 °C for another 8 hours to ensure complete destruction of the organic matter. Once ashed, 10 ml concentrated HNO_3 was added carefully to the samples then the basins were transferred to a water bath and evaporated to dryness. The residue was moistened with 5 ml concentrated HNO_3, covered and boiled for 2 min followed by addition of 10 ml water and further boiling. The residue was transferred quantitatively through hardened filter papers to 25 ml volumetric flasks and made up to volume. The final acid concentration was therefore approximately 20 % HNO_3.

3.3.2.3 Trace metal recovery in certified reference materials

Recovery of metals using the nitric acid digestion – hotplate method (Section 3.3.2.1) and dry ashing – nitric acid method (Section 3.3.2.2) were tested using certified reference materials.

Materials tested:

- Pine needles (SRM 1575)
- Tomato leaves (SRM 1573a)
- Bush branches & leaves (NCS DC 73348)
- Hay powder (IAEA-V-10)

To check recoveries, only 1 replicate of tomato leaves and bush branches & leaves and 2 replicates of pine needles were tested using the two digestion techniques. This was due to the large sample weight required in both methods and the high cost of obtaining certified reference materials. Trace elements were measured in the digests using AAS (Section 2.12.1).

Hay powder was intended as the actual reference material to be included in the final method as it was close to the sample matrix expected. This material was digested using the hotplate digestion method (Section 3.3.2.1) with a longer, more intense boiling period. ICP-OES (Section 2.12.3) was used for trace metal and nutrient analysis.

3.3.3 Results

3.3.3.1 Trace metal recovery in pine needles, tomato leaves and bush branches and leaves

Results from initial experiments to show trace metal recoveries from three certified reference materials using the two digestion methods are shown in Table 3-7 – Table 3-9.

Element	Pine needles (SRM 1575)		
	Hotplate digestion	Dry ashing	Certified values
Copper (mg kg^{-1})	3.24	3.04	2.7 – 3.3
Iron (mg kg^{-1})	152.34	95.89	190 - 210
Lead (mg kg^{-1})	9.86	7.84	10.3 – 11.3
Manganese (mg kg^{-1})	532.12	91.18	660 - 690
Nickel (mg kg^{-1})	2.44	2.21	not certified
Zinc (mg kg^{-1})	60.63	57.00	not certified

Table 3-7 Trace metal recovery from pine needles CRM using 2 methods

Element	Tomato leaves (SRM 1573a)		
	Hotplate digestion	Dry ashing	Certified values
Copper (mg kg^{-1})	5.68	5.77	4.56 – 4.84
Iron (mg kg^{-1})	238.42	272.70	361 - 375
Lead (mg kg^{-1})	13.55	10.45	not certified
Manganese (mg kg^{-1})	208.43	188.57	238 - 275
Nickel (mg kg^{-1})	2.99	4.9	1.52 – 1.66
Zinc (mg kg^{-1})	30.78	27.97	30.2 – 31.6

Table 3-8 Trace metal recovery from tomato leaves CRM using 2 methods

Element	Bush branches & leaves (NCS DC 73348)		
	Hotplate digestion	Dry ashing	Certified values
Copper (mg kg^{-1})	5.28	4.90	4.7 - 5.7
Iron (mg kg^{-1})	755.88	821.59	953 - 1087
Lead (mg kg^{-1})	11.16	10.29	6 – 8.2
Manganese (mg kg^{-1})	48.64	41.70	52 - 64
Nickel (mg kg^{-1})	3.29	1.80	1.3 – 2.1
Zinc (mg kg^{-1})	20.27	19.57	18 – 22.4

Table 3-9 Trace metal recovery from bush branches & leaves CRM using 2 methods

3.3.3.2 Trace metal recovery in hay powder

Results from the trace metal recovery experiment using hay powder certified reference material and the nitric digestion method are shown in Table 3-10:

Element	Hay powder certified reference material analysis		
	Measured mean value (mg kg^{-1})	Certified value 95 % confidence interval (mg kg^{-1})	Statistical t-test result
Aluminium	23.13	30 - 87‡	***
Barium	4.26	4 - 7	NS
Calcium	19964	21000 - 22200	NS
Cadmium	0.049	0.02 - 0.05	NS
Cobalt	0.080	0.11 - 0.14	***
Chromium	5.09	5.6 - 7.1	**
Copper	7.92	8.8 - 9.7	***
Iron	105.9	177 - 190	***
Potassium	17130	19600 - 22500‡	***
Magnesium	1142.1	1330 - 1450	***
Manganese	36.48	44 - 51‡	***
Molybdenum	1.953	0.6 - 1.1	***
Nickel	6.71	3.8 - 4.9	**
Lead	3.13	0.8 - 1.9	***
Zinc	13.38	23 - 25	***

‡ information value

Table 3-10 Measured and certified values from hotplate digestion method with results from statistical t-test at 95 % confidence level (NS = not significant; ** = significant effect at $p \leq 0.05$ level; * = highly significant effect at $p \leq 0.01$ level)**

3.3.4 Discussion

3.3.4.1 Trace metal recovery in pine needles, tomato leaves and bush branches and leaves

Although the initial analyses were performed on only 1 or 2 samples, they were a good indication of the ability of the methods employed in recovering trace metal content of plant samples.

The hotplate digestion method was shown to be satisfactory in recovering zinc and copper but gave low recoveries of manganese and iron Table 3-7 – 3-9. Nickel detection was near the method quantification limits hence the higher than 100 % recoveries. Lead levels varied between too high and too low recoveries.

The dry ashing method also gave low recoveries of manganese and iron. Copper and zinc were sometimes satisfactory and sometimes lower than expected. Nickel was satisfactory once and higher than 100 % once. Lead was higher than expected once and lower than expected once (Table 3-7 – 3-9).

The hotplate digestion method was chosen for further testing with the hay powder certified reference material. Although the dry ashing method gave similar results to the hotplate digestion, in some instances there was a large discrepancy between the two (e.g. Table 3-7 manganese and iron). It was also thought that the hotplate digestion method could be improved by boiling for a longer period.

3.3.4.2 Trace metal recovery in hay powder

It can be seen from Table 3-10 that a longer boiling period was insufficient for complete recovery of almost all elements from the certified reference material. Either more nitric acid was necessary to complete the digestion; or use of another acid i.e. perchloric acid once the organic matter was fully oxidised. The trace metal digestion used to analyse Harvest 5 could therefore be regarded more as an extraction rather than a complete digestion.

Chapter 4: Characterisation of rockdusts

4.1 Introduction

Rockdust is produced during quarrying operations that extract and screen rock for the aggregate industry. Screened material < 6 mm is not generally used in asphalt production, generating large stock piles of fine grade 'rockdust' for which there are few uses. This by-product has also been termed rock powder, rock fines, mineral fines and quarry tailings.

Rockdust application to soils could have an effect on soil physical, chemical and biological characteristics. While the effects on soil were investigated in the field trial, rockdust chemical and physical characterisation was carried out on various samples. Appleton (1990) described some of the chemical benefits of different rock additions to soils including phosphate rock, agricultural lime and rocks with high feldspar contents (as K fertilizers).

The SEER Centre advocates the use of basaltic rockdust from Collace quarry in their experimental bed system. However, various researchers have tested other rock types e.g. granite (Coroneos *et al*., 1996; Hinsinger *et al*., 1996; Bolland and Baker, 2000); gneiss (Wang *et al*., 2000); diorite (Hinsinger *et al*., 1996); although many have focused on the use of basalt (Gillman, 1980; Kahnt *et al*., 1986; Hildebrand and Schack-Kirchner, 2000; Gillman *et al*., 2002; Hinsinger *et al*., 2001; Sikora, 2004). Rock type would be expected to have an impact on the amount of nutrients released by weathering of rockdust since the mineralogy of these rocks dictates which nutrient elements are released, and the ease of their release from constituent minerals of the rock. Also, pH effects would be expected to be more pronounced when adding basic rock types (basalt) compared with acid rock types (granite) to soil. In geologic terms, basic and acidic rock types refer to the silica content rather than pH of the rock (Hall, 1996).

Van Straaten (2006) explained that an advantage of using rocks and minerals in agriculture could be the multi-element release although the low solubility of the materials means that nutrient release would be slow. In this chapter, characterisation of nutrient release from rockdust will be investigated using samples from Collace quarry and samples from various quarries in Scotland. Use of different extractants could give information on the ease of release of nutrients from rockdust samples.

Samples of rockdust will also be analysed for total major oxides and trace metal contents. The total analysis of rockdust could also give some information on the plant availability of nutrients. This will involve CIPW normative mineralogy calculations to work out a probable mineralogy of rock samples based on the chemical analysis. Knowledge of weathering rates of these minerals could help predict the ease of nutrient release from rockdust samples.

Another important factor affecting nutrient release from rockdust could be the grain size distribution in samples. It would be expected that decreasing grain size would lead to an increase in rock weathering due to a larger surface area. Therefore, the particle size distributions in samples obtained from these quarries will also be determined.

These analyses will give information on the ease of nutrient release from various rockdust samples, allowing comparisons to be drawn between rockdust derived from different rock types.

4.2 Methods

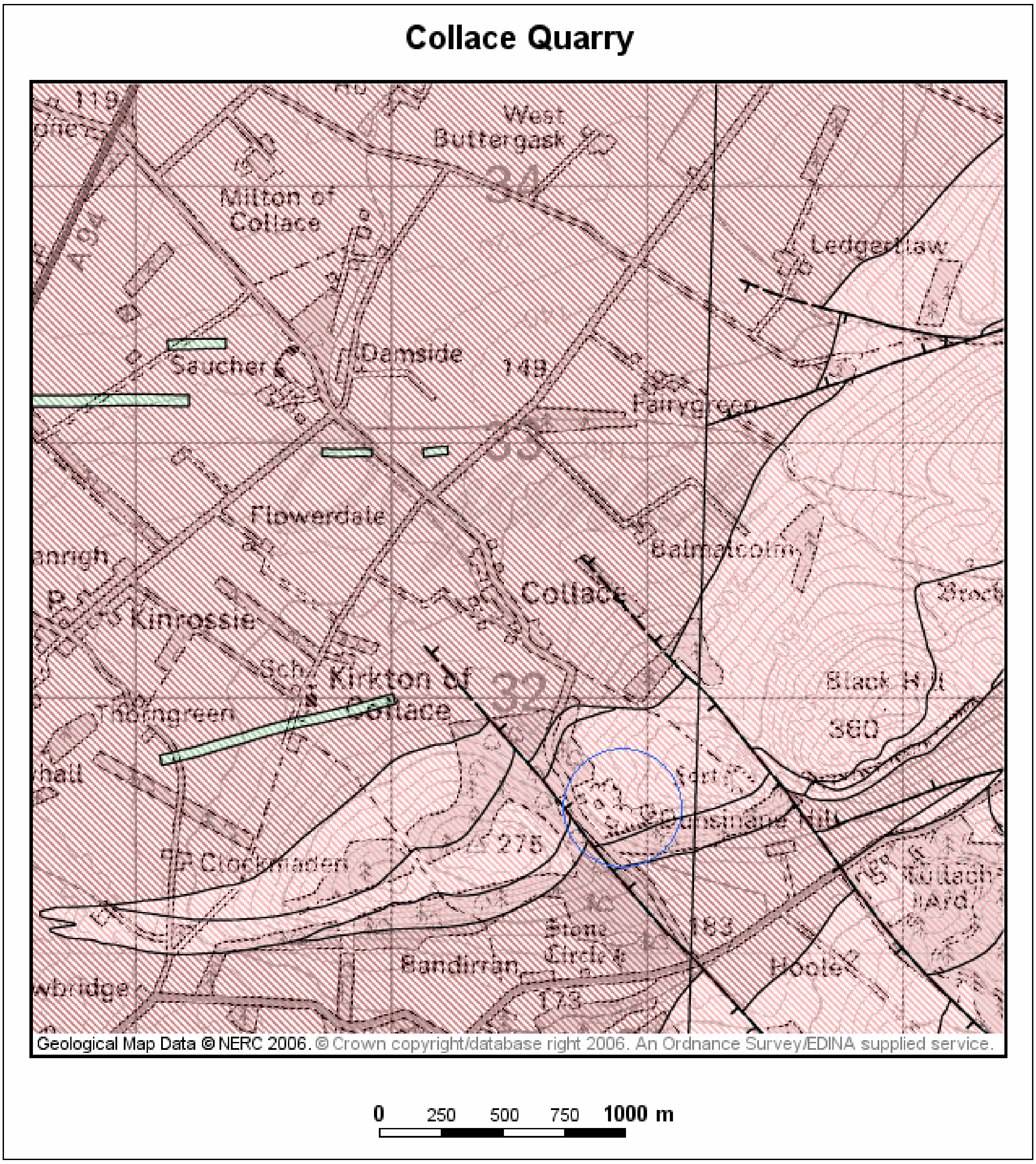
4.2.1 Rockdust samples

Rockdust samples from 5 quarries in Scotland were collected for analysis. Information on these quarries is listed in Table 4-1.

Quarry name	Quarry operator	Quarry location (OS Grid Ref)	Rock type	Rockdust particle size
Collace	Tayside Contracts	Kinrossie, Perthshire (NO209315)	Basaltic/andesitic	fines < 6mm
Clatchard	Ennstone Thistle	Newburgh, Fife (NO246175)	Basaltic/andesitic	fines < 6mm
Orrock	Ennstone Thistle	Kirkaldy, Fife (NT218886)	Basaltic	fines < 6mm
Furnace	Ennstone Thistle	Furnace, Argyll (NN026004)	Granitic	fines < 6mm
Duntilland	Bardon Aggregates	Salsburgh, Lanarkshire (NS843636)	Quartz dolerite	fines < 6mm
Duntilland	Bardon Aggregates	Salsburgh, Lanarkshire (NS843636)	Quartz dolerite	filler < 75 µm

Table 4-1 Rockdust quarry information

Collace quarry was the source for the SEER rockdust that was used in the field trial and that was sold in 20 kg bags. Clatchard quarry rockdust was chosen as it is a similar rock type to Collace rockdust, the underlying geology is the same for these 2 quarries (see Figure 4-1 and 4-2). Orrock quarry rockdust was more basaltic than Collace rockdust while Furnace quarry rockdust was a granitic rock type. Duntilland quarry provided 2 samples of quartz dolerite rockdust: one with particles less than 6 mm in size; one very fine material less than 75 µm. Figure 4-1 – 4-5 show geological maps and lithological information for the quarries where rockdust was sampled.



Geological Map Data © NERC 2006. © Crown copyright/database right 2006. An Ordnance Survey/EDINA supplied service.

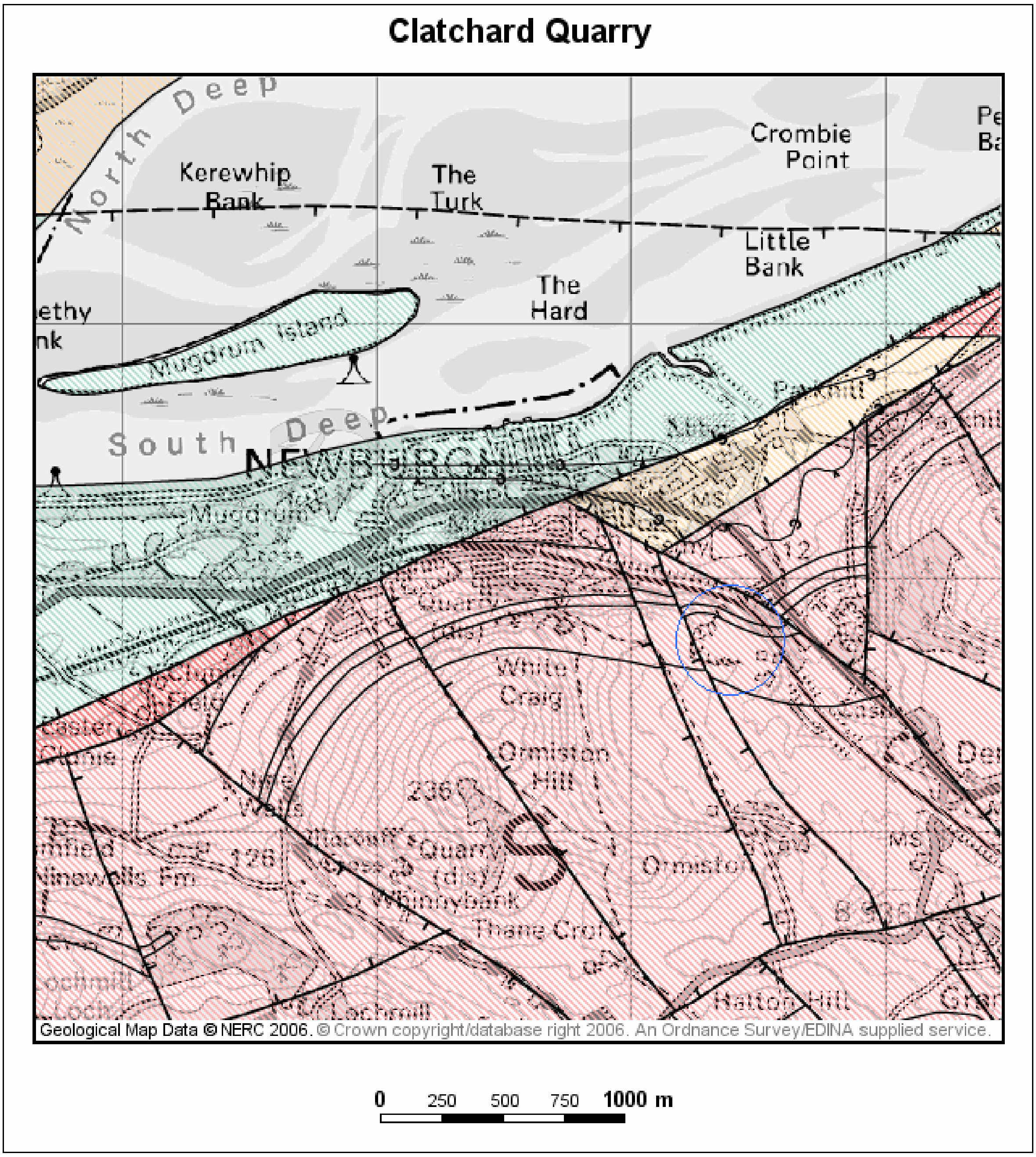
🟩 Central Scotland late Carboniferous tholeiitic dyke swarm

🟥 Ochil volcanic formation

▨ Scone sandstone formation

Formation	Lithological description
Ochil volcanic formation	Pyroxene andesite and olivine basalt lavas. Rhyodacite trachyandesite hornblende andesite and volcaniclastic rocks.

Figure 4-1 Collace quarry underlying geology - Ochil volcanic formation (quarry location indicated by blue circle on map)



▨ Ballagan formation

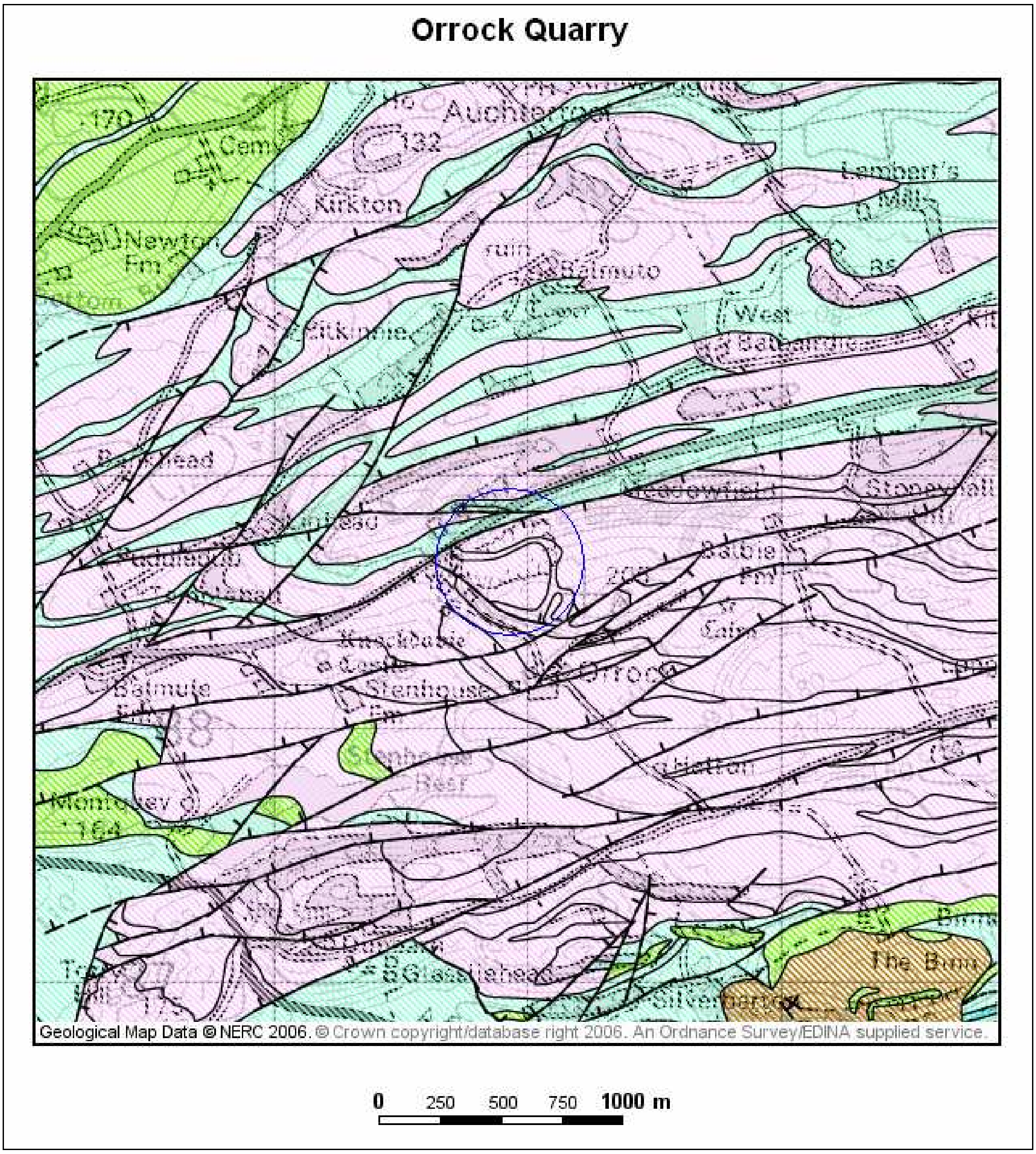
▨ Glenvale sandstone formation

▨ Kinnesswood formation

▨ Ochil volcanic formation

Formation	Lithological description
Ochil volcanic formation	Pyroxene andesite and olivine basalt lavas. Rhyodacite trachyandesite hornblende andesite and volcaniclastic rocks.

Figure 4-2 Clatchard quarry underlying geology - Ochil volcanic formation (quarry location indicated by blue circle on map)



▨ Kinghorn volcanic formation

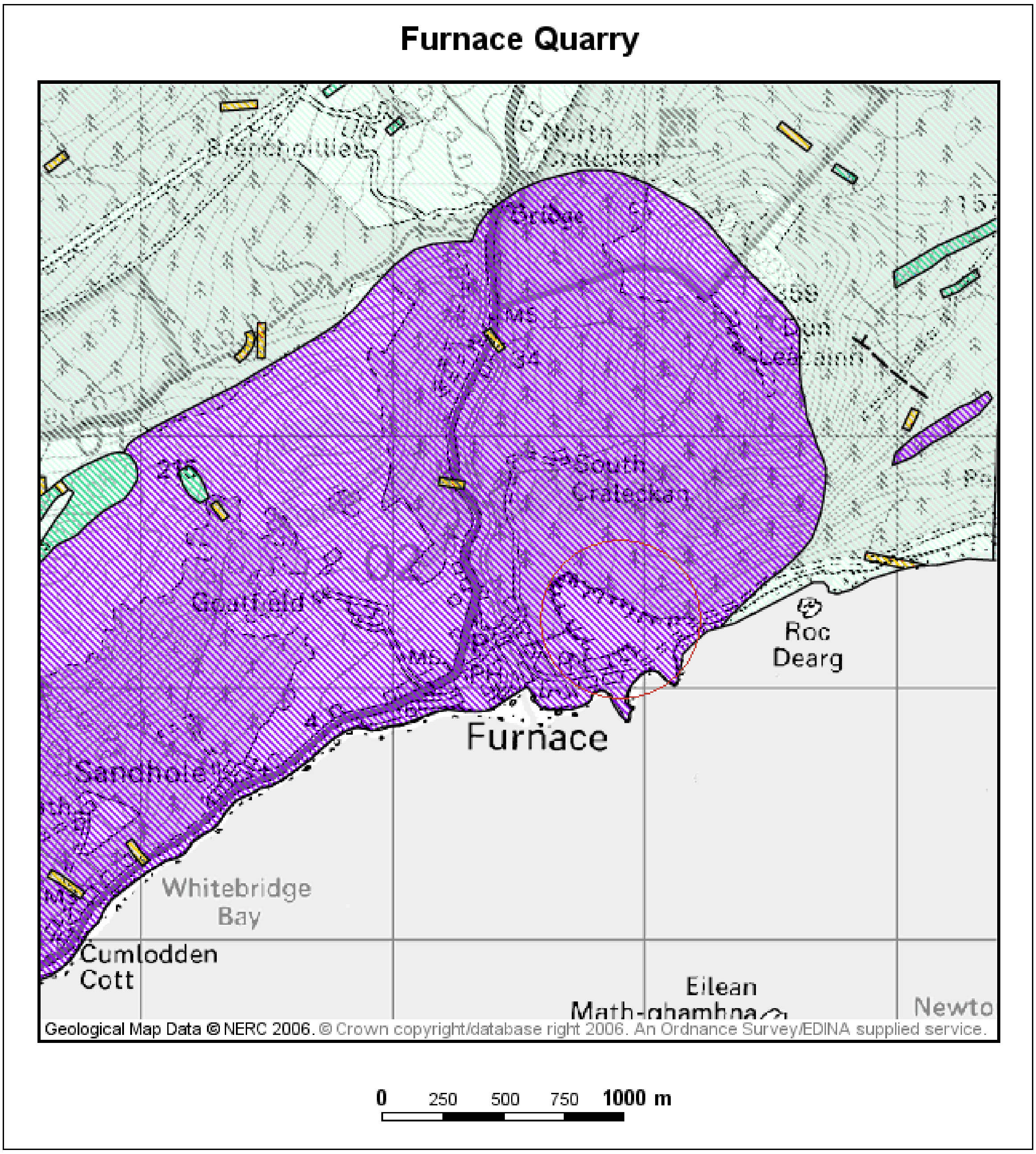
▨ Midland valley sill-complex

▨ Sandy Craig formation

▨ Scottish late Carboniferous to early Permian plugs And vents suite

Formation	Lithological description
Kinghorn volcanic formation	Basaltic lava flows, mostly subaerial but some subaqueous with associated hyaloclastite and pillows, interbedded with tuffs, sandstones, mudstones and limestones.

Figure 4-3 Orrock quarry underlying geology - Kinghorn volcanic formation (quarry location indicated by blue circle on map)



▨ Argyll group

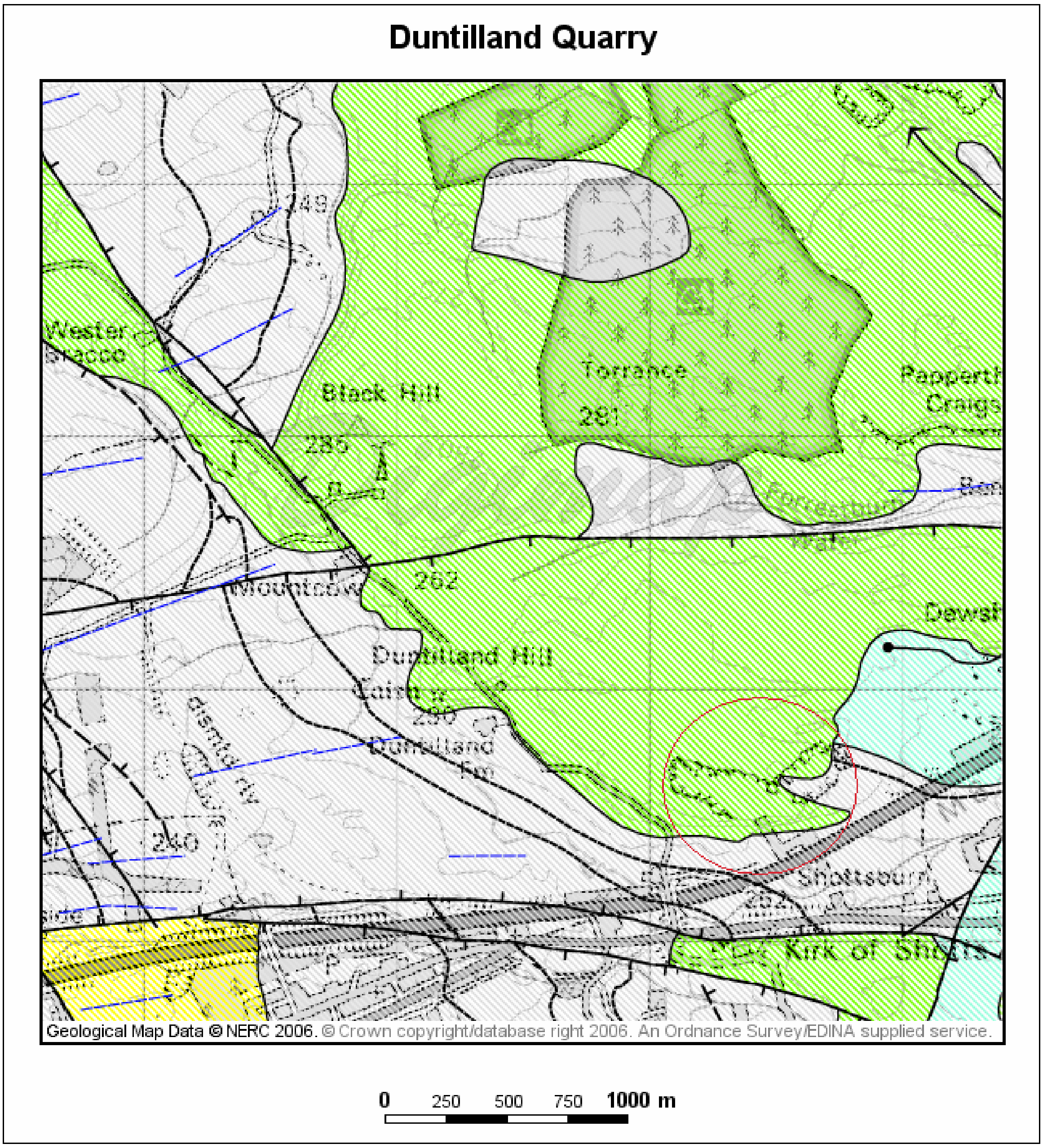
▨ Dalradian supergroup

▨ Mull dyke-swarm

▨ Scottish Highland Siluro-Devonian calc-alkaline minor intrusion suite

Formation	Lithological description
Scottish Highland Siluro-Devonian calc-alkaline minor intrusion suite	compositions derived by crystallisation of magmas forming plugs, dykes, sheets and small intrusions. Composition varies from medium-coarse grained rocks containing hornblende, sodic plagioclase, K-feldspar and quartz

Figure 4-4 Furnace quarry underlying geology - Scottish Highland Siluro-Devonian calc-alkaline minor intrusion suite (quarry location indicated by red circle on map)



⬜ Lower coal measures (Scotland)

🟦 Middle coal measures (Scotland)

🟩 Midland valley sill-complex

🟨 Passage formation

Formation	Lithological description
Midland valley sill complex	Late carboniferous quartz dolerite

Figure 4-5 Duntilland quarry underlying geology - Midland valley sill complex (quarry location indicated by red circle on map)

4.2.2 Rockdust sample descriptions

- Collace quarry
    a) SEER field trial certified quarry – sample as used in the field trial taken from Collace quarry in October 2003
    b) SEER field trial bulk delivery – sample as used in the field trial taken from delivery truck at SEER Centre in October 2003
    c) SEER 20 kg bag March 2005 – sample from SEER Rockdust® sold in March 2005
    d) SEER 20 kg bag April 2005 – sample from SEER Rockdust® sold in April 2005
    e) SEER 20 kg bag July 2005 – sample from SEER Rockdust® sold in July 2005
- Clatchard quarry – sampled July 2005
- Orrock quarry – sampled July 2005
- Furnace quarry – sampled July 2005
- Duntilland quarry coarse – sampled December 2004
- Duntilland quarry fines – sampled December 2004

4.2.3 Rockdust pH

The pH of rockdust samples was measured as in Section 2.1.3.

4.2.4 Particle size distribution of rockdust

Particle size distribution of rockdust samples was measured according to the method in Section 2.6.

4.2.5 Rockdust extractions

Rockdust extractions were carried out using the final method in Section 3.1.3. The extractants used were:

- Deionised water
- Modified Morgan's solution (0.5 M ammonium acetate, pH 4.8)
- 0.05 M ammonium EDTA (pH 7)
- 0.1 M nitric acid

The purpose of these rockdust extractions was to investigate the release of nutrients from rockdust and relate this release to increases in weathering. As 'strength' of extractant increases, it was expected that the release of nutrients from the rockdust would increase.

4.2.5.1 Method for rockdust extractions

Approximately 10 g of rockdust was accurately weighed to two decimal places into a 100 ml glass jar and 100 ml of extractant solution added by dispenser. The glass jars were shaken on an end-over-end shaker for 1 hour. The samples were placed on the centrifuge at 4500 rpm for 10 min, and the supernatant filtered through 0.2 µm membrane filters under vacuum. Approximately 30 ml of each clear filtrate was collected in clean auto-sampler vials and stored at 4 °C until analysis.

The following analytes were measured in the extracts:

Rockdust extract	Cations	Anions
Deionised water	Na, K, Ca, Mg, NH_4-N	SO_4-S, NO_3-N, NO_2-N, PO_4-P, Cl
Modified Morgan's solution	Na, K, Ca, Mg	PO_4-P
EDTA	Na, K, Ca, Mg, Cu, Zn, Fe, Pb	none
Dilute nitric acid	Na, K, Ca, Mg, Al, Fe, Mn, Ba, Co, Cu, Li, Pb, Ni, Zn	PO_4-P

Table 4-2 Analyses on rockdust extracts

4.2.6 Rockdust Kjeldahl digestion

Kjeldahl digestions were carried out on the rockdust samples as in Section 2.9.1 and analysed for nitrogen and phosphorus.

4.2.7 Rockdust total analysis

Samples of rockdust were analysed for total elemental composition by x-ray fluorescence at Royal Holloway, University of London. Some samples of Collace rockdust were also analysed for Tayside Contracts by Bureau Veritas Laboratories in 2004 and 2005.

4.3 Results

4.3.1 Rockdust pH

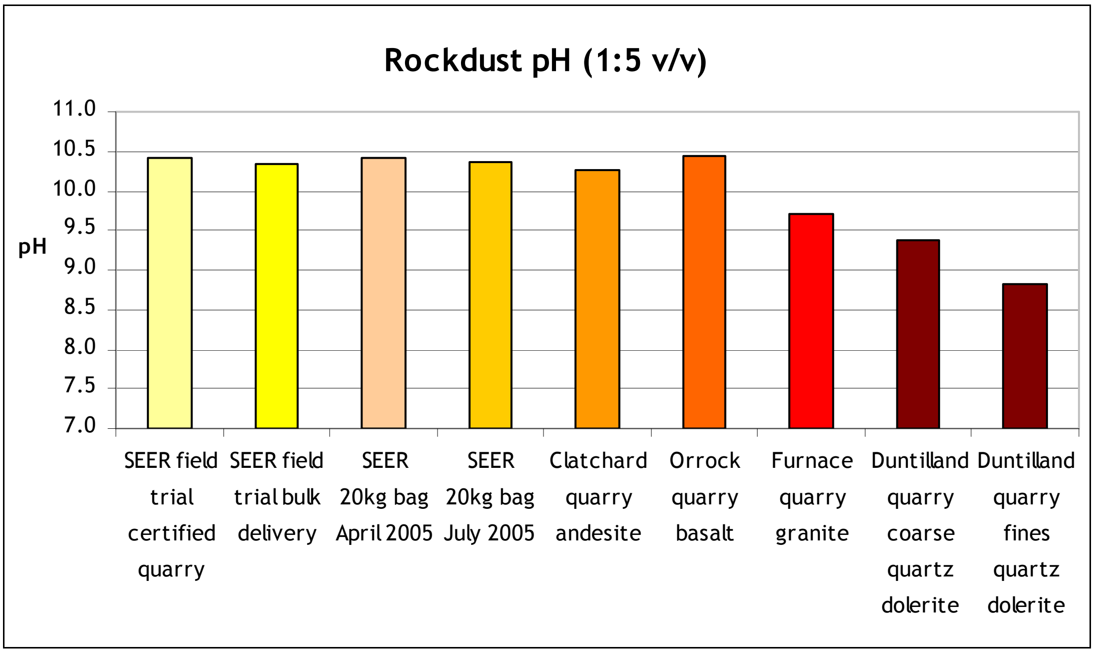


Figure 4-6 pH of rockdust samples

Figure 4-6 shows the differences in pH between rockdust samples. It can be seen that the SEER field trial samples and the SEER bagged samples gave very similar pH values. Clatchard quarry (andesite) and Orrock quarry (basalt) also had similar pHs to Collace (SEER) rockdust samples of about pH 10.4. The granitic rockdust from Furnace quarry gave a lower pH of 9.7 and the quartz dolerite from Duntilland quarry was pH 9.4.

4.3.2 Particle size distribution of rockdust

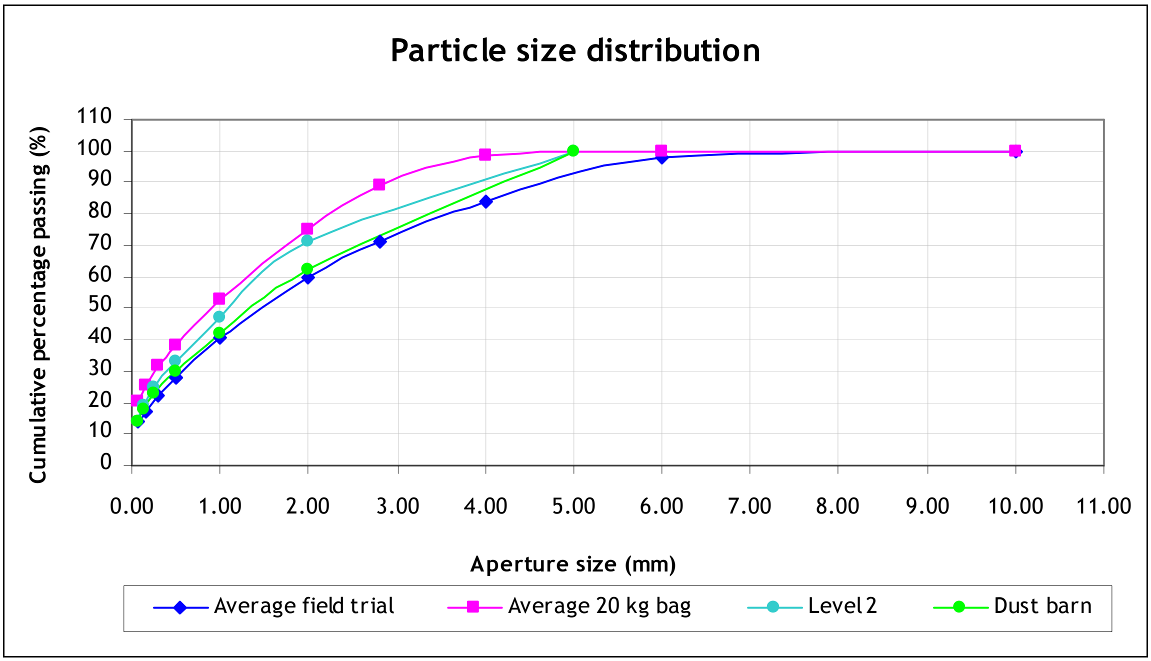


Figure 4-7 Particle size distribution in Collace quarry rockdust samples

Figure 4-7 shows the particle size distributions obtained from different samples from Collace quarry. Samples labelled Level 2 and dust barn were sampled by Collace quarry from two stockpiles in 2005. It can be seen that the field trial samples had a smaller percentage of material less than 1 mm than the 20 kg bag samples. Level 2 and dust barn samples were analysed by Collace quarry. Figure 4-7 effectively shows the variation in particle sizes in samples from Collace quarry. All samples passed a 6mm sieve despite variations in size distribution.

Percentage passing (%)	Average field trial	Average 20 kg bag	Level 2*	Dust barn*
Particles < 1 mm	40.6	53.0	47.0	43.0
Particles < 75 µm	14.3	20.3	nd	nd
Particles < 63 µm	nd	nd	14	14

* Particle size analysis carried out by Collace quarry

Table 4-3 Percentage of Collace rockdust particles passing specified sieve sizes (nd = not determined)

As is shown by Table 4-3 the percentage of particles less than 1 mm varies from 41 % (average field trial) – 53 % (average 20 kg bag). Fine content was lower in the field trial samples compared to the average 20 kg bagged samples. The samples analysed by Collace quarry were intermediate between the field trial and 20 kg bagged samples.

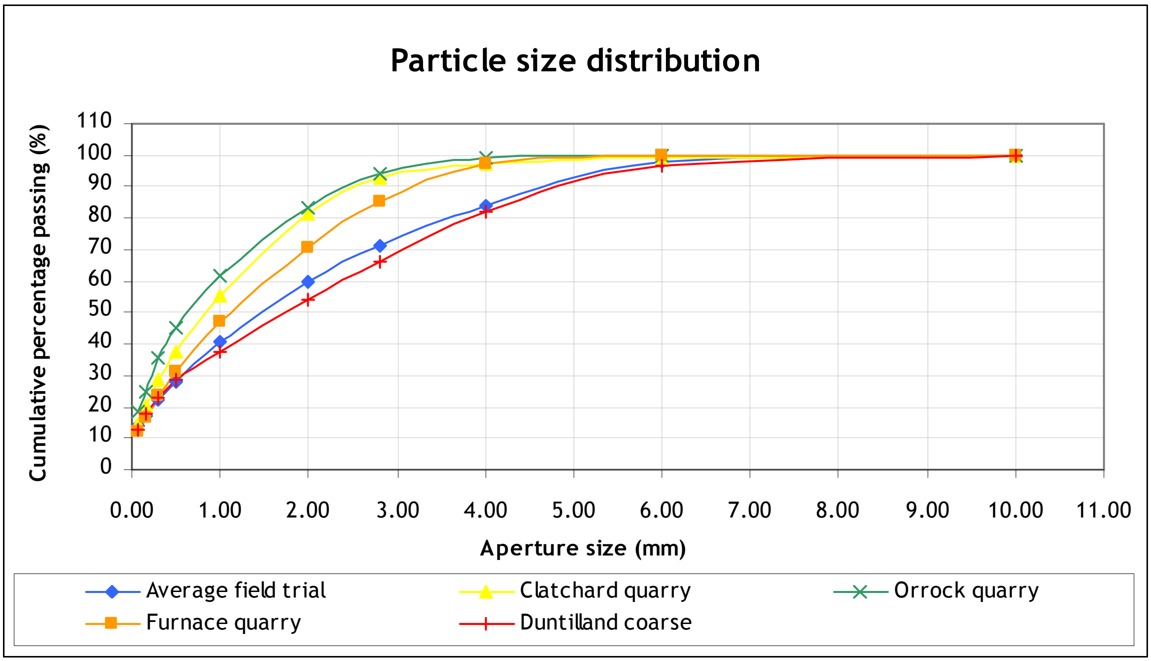


Figure 4-8 Particle size distribution in rockdust samples from various quarries

Figure 4-8 shows that although the samples from each of the quarries were < 6 mm, their individual particle size distributions could be quite variable between samples.

Percentage passing (%)	Average field trial	Clatchard quarry	Orrock quarry	Furnace quarry	Duntilland quarry
Particles < 1 mm	40.6	55.0	61.9	47.3	37.5
Particles < 75 µm	14.3	14.8	18.1	12.2	12.9

Table 4-4 Percentage of rockdust particles passing specified sieve sizes

Table 4-4 shows that the percentages of rockdust passing a 1 mm sieve varied from as high as 62 % (Orrock quarry) or as low as 37.5 % (Duntilland quarry). The SEER field trial samples were one of the coarser rockdust samples compared to Orrock and Clatchard quarries but quite similar in particle size distribution to Duntilland quarry. Very fine particles < 75 µm in size varied from 12.2 % (Furnace quarry) to 18.1 % (Orrock quarry).

4.3.3 Rockdust extractions

4.3.3.1 Deionised water rockdust extraction

Nutrients in rockdust (mg/kg)	Collace quarry					Clatchard quarry (andesite)	Orrock quarry (basalt)	Furnace quarry (granite)	Duntilland quarry coarse (quartz dolerite)	Duntilland quarry fines (quartz dolerite)
	SEER field trial certified quarry	SEER field trial bulk delivery	SEER 20 kg bag March 2005	SEER 20 kg bag April 2005	SEER 20 kg bag July 2005					
Sodium	448.4	428.1	733.8	325.4	353.5	220.3	438.9	20.6	98.1	78.6
Potassium	3.2	5.6	14.1	1.0	2.5	3.9	3.4	8.0	6.4	18.0
Calcium	2.3	2.1	10.2	< 0.5	< 0.5	5.1	2.1	26.0	18.5	35.4
Magnesium	6.9	4.7	1.0	< 0.5	3.1	3.9	13.8	6.4	2.5	8.1
Ammonium-N	< 1.0	< 1.0	53.0	1.8	3.4	< 1.0	< 1.0	< 1.0	< 1.0	3.5
Chloride	6.2	6.4	67.2	8.4	34.5	2.7	10.5	9.1	4.1	9.8
Nitrate-N	1.0	1.7	5.2	2.7	1.6	0.8	3.8	3.5	0.3	0.6
Nitrite-N	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	< 0.04	7.3	2.4	< 0.04	< 0.04
Phosphate-P	< 0.1	< 0.1	2.5	0.4	5.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Sulphate-S	0.7	1.2	458.6	4.4	18.1	0.2	12.0	2.3	24.0	36.3

Table 4-5 Water extractable nutrients from rockdust

4.3.3.2 Deionised water extractable nutrients

It can be seen from Table 4-5 that the only element extracted by water from all rockdust samples to any great extent was sodium with negligible amounts of other nutrient ions. Water extractable nutrients varied considerably between Collace quarry samples. The ionic balance in the water extracts of the rockdust was mostly made up by the bicarbonate anion. This was only qualitatively established since the ion chromatography technique was insensitive to bicarbonate and could not be used to measure this ion quantitatively. This is in agreement with the rockdust pH data (Section 4.3.1) as the presence of the bicarbonate ion can also cause a higher pH (Rowell, 1994).

There appeared to be some contamination in the SEER 20 kg bag samples as elevated levels of ammonium, chloride and sulphate were found here (especially in the March 2005 sample). Since rockdust was not a source of inorganic nitrogen, and ammonium was detectable in the SEER 20 kg bag samples and not the field trial samples, cross-contamination at the bagging plant could be the source of these nutrients. This explanation probably follows for the other ions that showed elevated concentrations in the 20 kg bag samples. Likely contamination was confirmed (personal communication) as the bagging plant also handled a variety of other products including organic and inorganic fertilizers.

Collace samples were similar to Clatchard quarry (andesitic rockdust) and Orrock quarry (basaltic rockdust) in water extractable nutrients (Table 4-5). Again, these two rockdust samples were low in water extractable nutrients except sodium. Since they were also low in ammonium, chloride and sulphate, this further backs up the conclusion that the bagging plant added contamination to the SEER 20 kg bag samples. Furnace quarry rockdust was low in water extractable nutrients showing the differences between basaltic rockdust and granitic rockdust. Furnace quarry (granitic rockdust) was much lower in sodium but slightly higher in potassium and calcium compared to Collace quarry rockdust. Duntilland quarry (quartz dolerite) was an intermediate rock type and this was reflected by the amounts of ions extracted by water. Duntilland fine material was obtained by the quarry operator by washing coarse grade rockdust and allowing the material > 75 µm to settle out. The fine material remaining in suspension was pumped away to a storage lagoon. It was this sludge material that was collected, dried and broken down to obtain the fine Duntilland sample. Washing could either lead to higher levels through contamination of the sample by the wash water, or lower levels due to water soluble nutrients being washed out of the sample. Table 4-5 shows increased levels of water extractable nutrients in the finer material pointing to either contamination or increased availability due to particle size differences between the two Duntilland samples.

Copper, iron, manganese, lead and zinc were found to be below quantifiable levels in all rockdust extracts and hence not shown in Table 4-5.

4.3.3.3 EDTA rockdust extraction

Nutrients in rockdust (mg/kg)	Collace quarry			Clatchard quarry (andesite)	Orrock quarry (basalt)	Furnace quarry (granite)	Duntilland quarry coarse (quartz dolerite)	Duntilland quarry fines (quartz dolerite)
	SEER field trial certified quarry	SEER 20 kg bag April 2005	SEER 20 kg bag July 2005					
Sodium	1788	1499	1567	441.6	1381	49.6	185.1	143.2
Potassium	29.2	22.2	28.3	24.1	94.5	13.9	32.8	81.9
Calcium	4242	3023	3430	3882	6821	2505	3640	9774
Magnesium	81.3	36.4	82.4	95.4	102.4	20.1	98.6	449.4
Copper	< 0.4	< 0.4	0.7	< 0.4	0.9	< 0.4	1.0	2.5
Iron	21.6	29.4	31.0	22.2	48.0	7.0	53.4	175.0
Lead	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	2.9
Zinc	0.2	0.5	0.2	0.2	0.4	< 0.2	4.5	10.3

Table 4-6 EDTA extractable nutrients from rockdust

4.3.3.4 EDTA extractable nutrients

Some trace metals became measurable in EDTA extracts as shown in Table 4-6 although they were available in low concentrations. EDTA extractable nutrients in Collace quarry rockdust were similar between samples (Table 4-6). They were low in extractable metals apart from sodium and calcium. There was variation between samples, reflecting the variable nature of the product. This time, the field trial sample was slightly higher in EDTA extractable nutrients than the 20 kg bag samples showing that the possible contamination highlighted in Table 4-5 was not a major problem.

The highest concentrations of nutrient elements were extracted in the EDTA extraction from Orrock quarry basaltic rockdust and Duntilland quarry rockdust. Table 4-6 shows that Duntilland quarry fines released the highest quantities of calcium, magnesium, copper, zinc, iron and lead. There was a substantial increase in the release of these elements compared with the Duntilland coarse sample.

4.3.3.5 Modified Morgan's solution rockdust extraction

Nutrients in rockdust (mg/kg)	Collace quarry				Clatchard quarry (andesite)	Orrock quarry (basalt)	Furnace quarry (granite)	Duntilland quarry coarse (quartz dolerite)	Duntilland quarry fines (quartz dolerite)
	SEER field trial certified quarry	SEER field trial bulk delivery	SEER 20 kg bag April 2005	SEER 20 kg bag July 2005					
Sodium	1671	1524	1498	1494	429.5	1495	39.9	189.5	152.0
Potassium	36.8	35.6	32.3	43.5	34.0	122.5	22.2	44.5	103.3
Calcium	2942	2395	1900	1832	3380	5507	1911	2971	6610
Magnesium	120.2	99.6	77.2	85.3	107.3	191.5	41.5	151.2	416.0
Phosphate-P	4.8	5.5	1.9	8.0	2.0	7.9	3.2	0.7	0.6

Table 4-7 Modified Morgan's solution extractable nutrients from rockdust

4.3.3.6 Modified Morgan’s solution extractable nutrients

The results shown in Table 4-7 show modified Morgan’s solution extractable nutrients from rockdust. These extractions were chosen to show the major nutrients available in the medium to longer timescale i.e. after some weathering of the rockdust in the soil. An increase in calcium, magnesium, potassium and phosphate was seen in all samples compared to the water extraction (Table 4-5). This extraction again showed the high release of sodium from all rockdust samples (except Furnace quarry).

Again, Collace and Orrock samples gave the highest release of sodium. Duntilland quarry fines and Orrock rockdust gave the highest levels of calcium, although Collace, Clatchard and Duntilland quarry coarse rockdust samples all gave appreciable levels of available calcium. Furnace quarry rockdust had the lowest concentration of extractable elements of all the rockdust sampled.

4.3.3.7 Dilute nitric acid rockdust extraction

Nutrients in rockdust (mg/kg)	Collace quarry				Clatchard quarry (andesite)	Orrock quarry (basalt)	Furnace quarry (granite)	Duntilland quarry coarse (quartz dolerite)	Duntilland quarry fines (quartz dolerite)
	SEER field trial certified quarry	SEER field trial bulk delivery	SEER 20 kg bag April 2005	SEER 20 kg bag July 2005					
Sodium	2009	1569	1605	1561	440.6	3246	73.7	350.2	242.5
Potassium	44.2	38.6	37.7	50.5	37.6	156.9	48.4	67.5	125.7
Calcium	4204	3075	2983	2861	5651	6810	3056	4376	8281
Magnesium	755.7	617.5	877.9	945.8	366.6	900.5	48.1	989.8	1234
Aluminium	755.4	598.8	1005	1064	605.9	2729	393.0	1382	1840
Iron	1247	953.2	2403	2636	901.7	1460	151.2	2419	2223
Manganese	93.1	85.4	81.0	77.2	53.3	84.0	24.3	55.8	126.0
Barium	2.5	1.2	2.6	2.2	9.4	3.7	22.4	9.9	33.9
Cobalt	0.7	0.6	0.9	0.9	0.4	2.1	< 0.1	3.3	4.9
Copper	0.9	0.9	2.0	2.3	1.2	5.1	1.3	7.2	9.9
Lithium	0.8	0.6	0.5	0.5	1.0	0.7	0.6	0.7	1.2
Lead	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.3	1.5	2.2	2.6
Nickel	0.4	0.2	0.3	0.3	< 0.1	9.2	0.2	2.2	2.4
Zinc	2.8	2.6	4.3	4.3	1.4	2.3	0.6	21.32	33.0
Phosphate-P	504.5	418.3	449.0	488.9	844.3	286.4	282.2	463.1	197.6

Table 4-8 0.1 M nitric acid extractable nutrients from rockdust

4.3.3.8 Dilute nitric acid extractable nutrients

Dilute nitric acid extraction samples were analysed by a combination of Colorimetric analysis, Atomic Absorption Spectroscopy, Flame Photometry and Inductively Coupled Plasma Emission Spectroscopy hence trace metals could be analysed at lower detection limits. This extraction (Table 4-8) showed a large calcium release from all rockdust samples. Magnesium, phosphate and potassium were shown to be extractable in higher quantities than in earlier extractions reflecting the need for rock weathering before nutrients could become plant available. Table 4-8 shows that phosphate could be provided by rockdust in the long term since concentrations in earlier extractions were very low until the dilute nitric acid extraction where between 197 and 844 mg kg^{-1} could be released depending on the rockdust type. A similar pattern was seen as in earlier extractions whereby Orrock quarry rockdust and Duntilland quarry fines gave highest nutrient release followed by SEER, Clatchard and Duntilland coarse rockdust. Furnace quarry rockdust mostly released the fewest nutrients although this release was higher than in previous extractions.

Iron extracted from all rockdust samples was shown to increase dramatically compared to the earlier EDTA extraction. There was a large amount of variation between Collace quarry samples in extractable iron with the 20 kg bag samples releasing far higher quantities than the field trial samples. This may again be contamination from the bagging plant. Duntilland quarry rockdust (coarse and fine samples) were also similarly high in extractable iron showing that this is not a particle size effect. Despite lower detection limits in ICP analysis, this extraction was shown to release only low concentrations of trace metals.

4.3.3.9 Rockdust Kjeldahl digestion

Nutrients in rockdust (mg/kg)	Collace quarry					
	SEER field trial quarry sample	SEER field trial delivery sample	SEER 20 kg bag (April 2005)	SEER 20 kg bag (July 2005)	SEER crushed field trial quarry sample B	SEER crushed field trial quarry sample C
Nitrogen	51.2	< 50.0	75.5	143.3	< 50.0	< 50.0
Phosphate	1151	1164	1147	1045	1380	1377

Nutrients in rockdust (mg/kg)	Clatchard quarry (andesite)	Orrock quarry (basalt)	Furnace quarry (granite)	Duntilland quarry coarse (quartz dolerite)	Duntilland quarry fines (quartz dolerite)
Nitrogen	< 50.0	126.9	< 50.0	75.0	214.1
Phosphate	1800	1956	411.2	1157	1880

Table 4-9 Kjeldahl-N and Kjeldahl-P from rockdust digests (bdl = below detection limit)

The results in Table 4-9 show that some rockdust samples contained low levels of nitrogen but (since nitrogen is not found in rock forming minerals) that its presence was probably due to contamination. This theory is somewhat backed up by the fact that the most processed samples (i.e. SEER 20 kg bag and Duntilland quarry fines) had the highest levels. The reason for the high level of nitrogen in Orrock quarry rockdust was unclear.

Table 4-9 also shows that these rockdust samples could provide phosphate over the long-term at approximately 1 – 2 g kg^{-1}; but that substantial weathering is required to release this as only a small fraction of this was plant available (Table 4-7).

4.3.3.10 Nutrient availability in rockdust samples

The increase in nutrient availability with increasing extractant 'strength' (and hence increasing weathering of the rock) for sodium, potassium, calcium, magnesium and phosphate are shown in Figure 4-9 – 4-13. These elements were chosen as they were released in the highest quantities from rockdust samples.

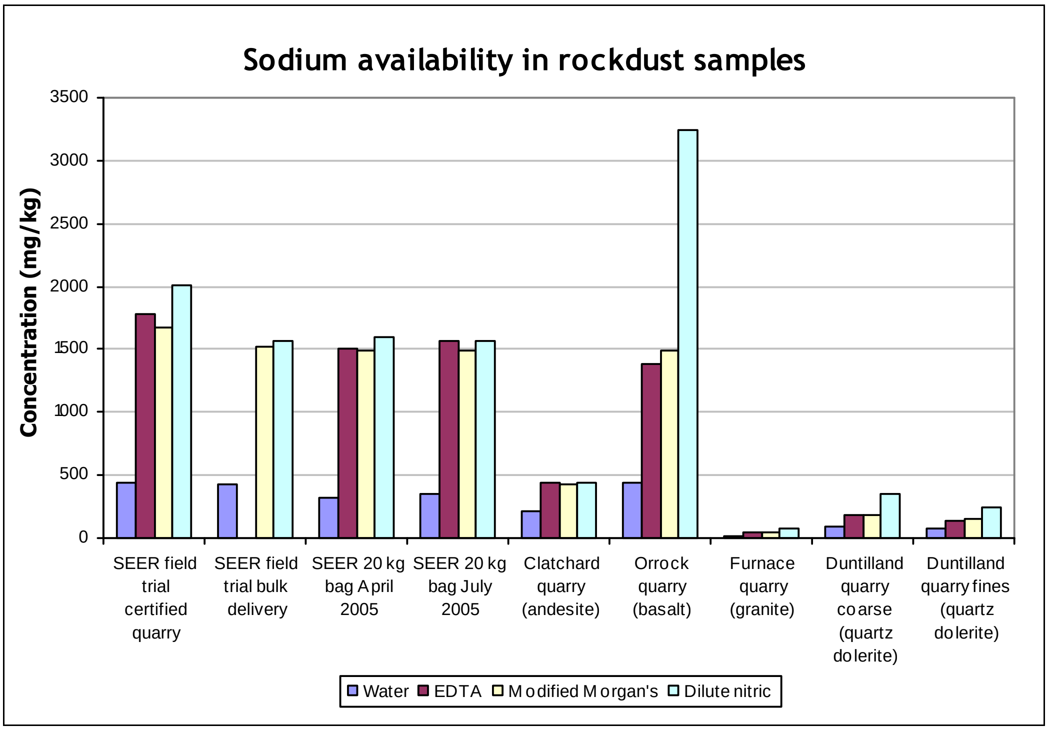


Figure 4-9 Sodium released from rockdust samples with increasing extractant 'strength'

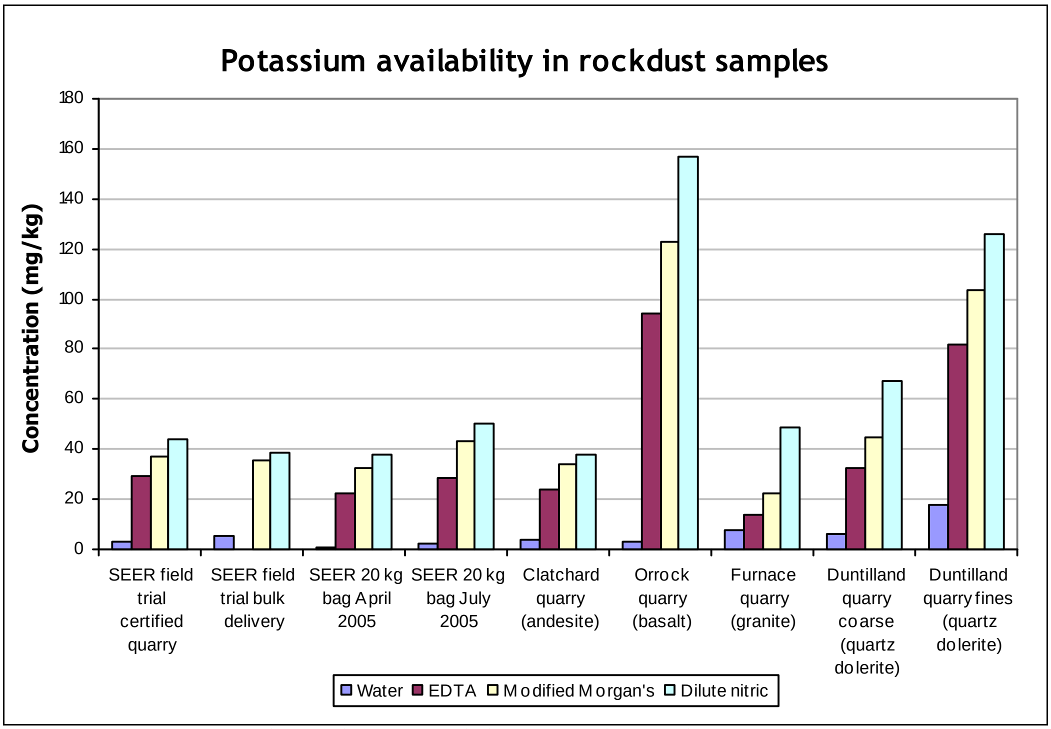


Figure 4-10 Potassium released from rockdust samples with increasing extractant 'strength'

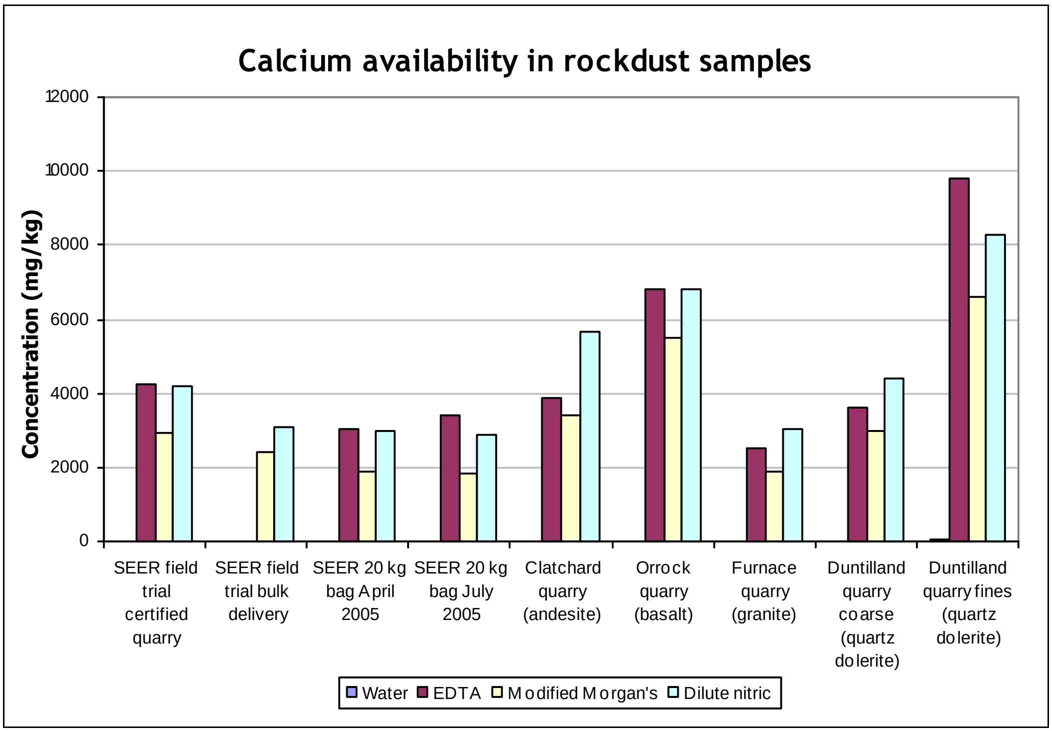


Figure 4-11 Calcium released from rockdust samples with increasing extractant 'strength'

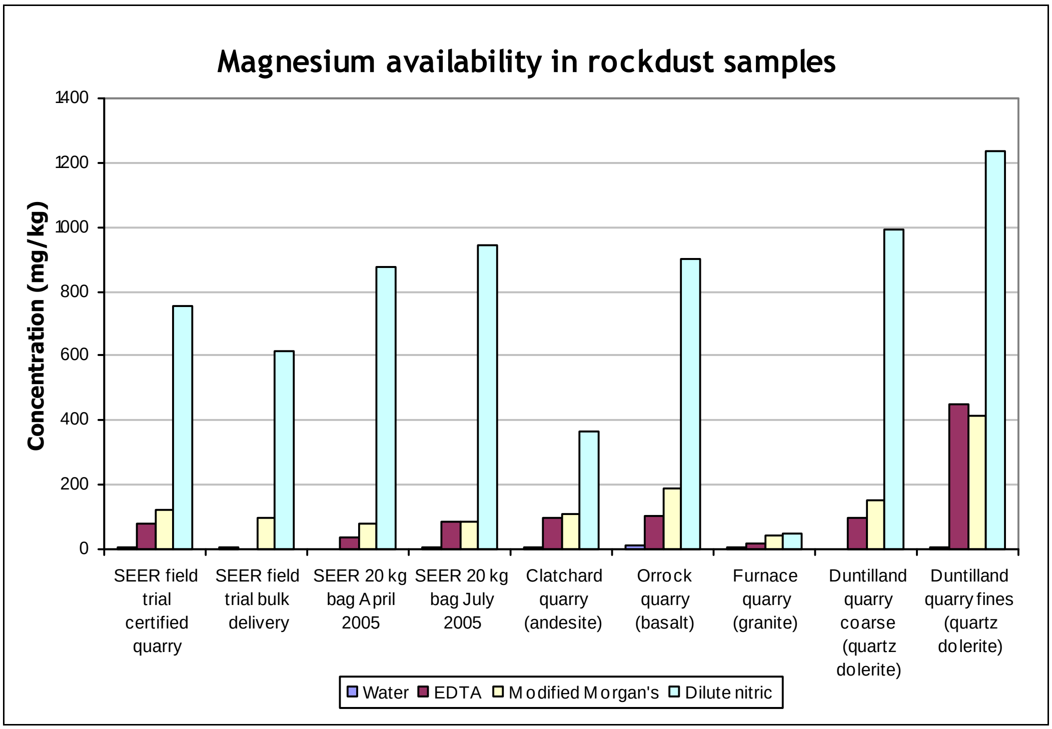


Figure 4-12 Magnesium released from rockdust samples with increasing extractant 'strength'

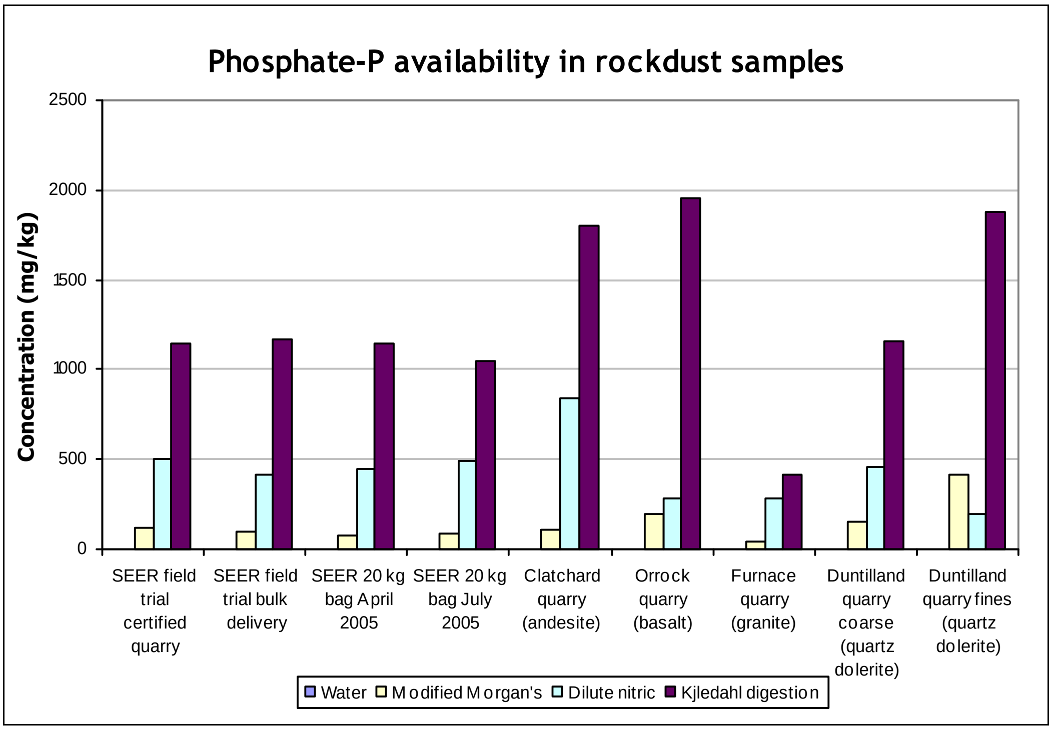


Figure 4-13 Phosphate-P released from rockdust samples with increasing extractant ‘strength’

4.3.4 Rockdust total analysis

4.3.4.1 XRF analysis

Sample date	Weight (%)									
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
2003*	54.94	17.02	7.39	3.42	5.26	4.17	1.72	1.08	0.26	0.08
2004†	54.92	17.44	7.83	3.99	6.39	4.33	1.60	1.47	0.34	0.14
2005†	55.43	17.94	7.89	3.71	6.13	4.19	1.58	1.51	0.29	0.12
2006*	54.22	17.36	8.00	4.11	5.41	4.08	1.77	1.43	0.28	0.11

* analysed at Royal Holloway, University of London

† analysed at Bureau Veritas Laboratories

Table 4-10 XRF analysis of major constituents of Collace rockdust

Based upon the silica content (Table 4-10) of these rockdust samples, all Collace quarry samples would be classed as intermediate rocks (Hughes, 1982).

Quarry	Weight (%)									
	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO
Collace‡	55.86	17.82	8.14	3.78	6.22	4.32	1.69	1.53	0.31	0.13
Clatchard	57.10	18.15	8.01	3.68	4.39	4.93	2.08	1.17	0.44	0.10
Orrock	46.06	13.59	11.99	10.81	10.47	2.84	1.05	2.44	0.60	0.19
Furnace	67.39	16.87	2.57	1.41	2.22	5.71	3.19	0.31	0.14	0.05
Duntilland coarse	50.62	13.63	14.5	5.89	8.11	2.98	1.24	2.56	0.30	0.20
Duntilland fines	49.80	13.80	15.21	6.71	7.96	2.57	0.99	2.34	0.38	0.20

‡ SEER 20 kg bag sampled 2005

Table 4-11 XRF analysis of major constituents of samples used in rockdust extraction experiments

Based on the silica content (Table 4-11) of these rockdust samples, Clatchard and Duntilland quarry samples would also be classed as intermediate rocks. The mineralogy of the SEER 20 kg bag sample was in line with the rest of the Collace quarry samples (Table 4-10). Orrock would be classified as a basic rock type while Furnace quarry would be classed as acid rock type (Hughes, 1982).

Trace elements analysed by XRF are shown in Table 4-12. Some differences in trace element contents were apparent between the various rockdust samples. While Collace quarry and Clatchard quarry rockdust were similar in trace element content, Orrock quarry was highest in most trace elements (most noticably in chromium, copper, nickel and strontium). Furnace quarry rockdust was lowest in most trace elements (with the exception of strontium). The trace element content of Duntilland samples were very similar and typically intermediate between samples with high or those with low trace element contents.

	Trace elements in rockdust samples (mg kg^{-1})																
	Ba	Co	Cr	Cu	Li	Ni	Sc	Sr	V	Zn	Zr	Pb	U	Th	Rb	Nb	Cs
Collace 2003	365	19	20	15	20	14	14	461	99	70	208	18	1.76	5.1	30	14	1.08
Collace 2006	367	23	19	19	7	13	15	464	103	86	216	11	1.74	5.1	39	12	0.85
Clatchard	-	-	4	8	-	5.5	13	479	111	109	261	13	-	6.3	45	13	-
Orrock	-	-	354	53	-	228	23	871	226	82	251	4	-	4.9	23	57	-
Furnace	-	-	12	3.5	-	7.6	4.2	1253	36.4	39	75.6	12	-	0.7	34	3	-
Duntilland coarse	-	-	52	63	-	50.4	28	423	387	126	182	7	-	3.6	34	16	-
Duntilland fines	-	-	60	69	-	62.7	26.8	374	350	146	190	8	-	4.4	28	18	-

	Hf	Ta	Tl	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu	Mo	Sn
Collace 2003	4.76	0.90	0.29	33	22.1	48.7	5.8	28.5	5.9	1.6	5.34	4.97	1.12	2.78	2.21	0.43	nd	nd
Collace 2006	4.73	0.82	0.37	29	22.1	47.4	6.0	28.0	6.1	1.7	4.53	4.63	0.87	2.46	2.73	0.38	0.56	0.99
Clatchard	-	-	-	29	-	63.9	-	32.3	-	-	-	-	-	-	-	-	-	-
Orrock	-	-	-	28	-	82.2	-	37.3	-	-	-	-	-	-	-	-	-	-
Furnace	-	-	-	6.5	-	21.9	-	12.1	-	-	-	-	-	-	-	-	-	-
Duntilland coarse	-	-	-	31	-	51.9	-	29.8	-	-	-	-	-	-	-	-	-	-
Duntilland fines	-	-	-	33	-	58.6	-	31.2	-	-	-	-	-	-	-	-	-	-

Table 4-12 XRF analysis of trace elements in samples used in rockdust extraction experiments

4.3.4.2 CIPW normative mineralogy

The XRF data in Table 4-10 and Table 4-11 were used to calculate the CIPW normative mineralogy according to Hughes (1982) as shown in Table 4-13 and Table 4-14. The CIPW normative mineralogy (norm) allows the chemical analysis of an igneous rock to be converted into a probable mineralogy by assigning appropriate mineral species according to a fixed sequence. Results are expressed as simplified end-members of solid solution series (Hughes, 1982).

4.3.4.3 Weathering of minerals

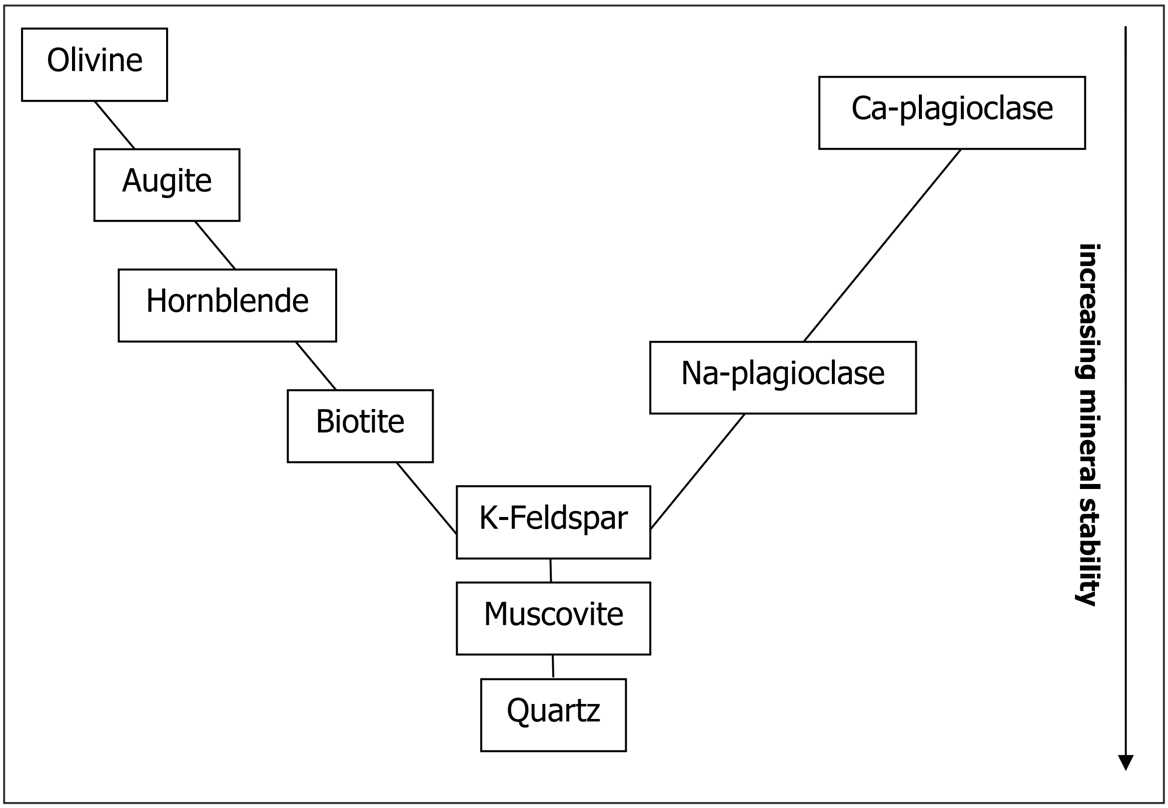


Figure 4-14 Goldich's mineral-stability series in weathering (Goldich, 1938)

Figure 4-14 shows the mineral stability series proposed by Goldich (1938). Quartz is the most stable mineral and olivine is the least stable. This series can be used to estimate ease of weathering of rock samples based on mineralogical analyses.

Sample	CIPW normative minerals (%)																			
									di			hy		ol						
	Q	C	or	ab	an	ne	lc	ac	wo	en	fs	en	fs	fo	fa	mt	hm	il	ap	Total
Collace quarry 2003	6.0	0	10.6	37.2	23.9	0	0	0	1.0	0.6	0.4	8.5	6.8	0	0	2.3	0	2.1	0.6	100.1
Collace quarry 2004	3.3	0	9.5	37.2	24.1	0	0	0	2.8	1.6	1.1	8.6	5.9	0	0	2.3	0	2.9	0.6	99.8
Collace quarry 2005	4.9	0	9.5	36.2	26	0	0	0	1.4	0.8	0.6	8.7	6.2	0	0	2.3	0	2.9	0.6	100.0
Collace quarry 2006	4.0	0	11.1	35.6	24.8	0	0	0	0.6	0.4	0.2	10.3	7.1	0	0	2.3	0	2.9	0.6	99.9
Collace quarry 20 kg bag 2005	3.9	0	10.0	36.7	24.5	0	0	0	2.1	1.1	0.9	8.4	6.4	0	0	2.3	0	2.9	0.6	99.7

Table 4-13 CIPW normative analysis of Collace rockdust

Symbol	Normative Mineral	Formula	Note
Q	Quartz	SiO_2	
C	Corundum	Al_2O_3	
or	Orthoclase (K Feldspar)	$K_2O.Al_2O_3.6SiO_2$	
ab	Albite (Na Plagioclase)	$Na_2O.Al_2O_3.6SiO_2$	
an	Anorthite (Ca Plagioclase)	$CaO.Al_2O_3.2SiO_2$	
ne	Nepheline	$Na_2O.Al_2O_3.2SiO_2$	
lc	Leucite	$K_2O.Al_2O_3.4SiO_2$	
ac	Acmite	$Na_2O.Fe_2O_3.4SiO_2$	
wo	Wollastonite	$CaO.SiO_2$	
di { en	Diopside { Enstatite	$MgO.SiO_2$	Pyroxene
fs	Ferrosilite	$FeO.SiO_2$	
hy { en	Hypersthene { Enstatite	$MgO.SiO_2$	Pyroxene
fs	Ferrosilite	$FeO.SiO_2$	
ol { fo	Olivine { Fosterite	$2MgO.SiO_2$	
fa	Fayalite	$2FeO.SiO_2$	
mt	Magnetite	$FeO.Fe_2O_3$	
hm	Haematite	Fe_2O_3	
il	Ilmenite	$FeO.TiO_2$	
ap	Apatite	$3CaO.P_2O_5$	

Note

Calculated norm not always the precise mineralogy because:

1. Weight % of minerals from weight % of oxides used to calculate norm, whereas actual minerals present (calculated or estimated) on volume % basis
2. Complex hydroxyl bearing mineral species i.e. hornblende and biotite omitted from normative calculations – anhydrous pyroxenes used instead (less of a problem for basic rocks compared to acid rocks)
3. Calculation of the norm using a fixed sequence of mineral species expressed as simplified end-members of solid-solution series. This cannot ever fully match the outcome of natural solid-solution

Sample	CIPW normative minerals (%)																			
									di			hy		ol						
	Q	C	or	ab	an	ne	lc	ac	wo	en	fs	en	fs	fo	fa	mt	hm	il	ap	Total
Clatchard quarry	3.3	0.7	12.2	41.9	19.5	0	0	0	0	0	0	9.2	7.5	0	0	2.3	0	2.3	0.9	99.8
Orrock quarry	0	0	6.1	17.8	21.5	3.4	0	0	11.5	7.7	2.9	0	0	13.7	5.6	3.5	0	4.7	1.2	99.6
Furnace quarry	14.5	0.3	18.9	48.2	10.2	0	0	0	0	0	0	3.5	2.6	0	0	0.7	0	0.6	0.3	99.8
Duntilland quarry	1.1	0	7.2	25.7	20.3	0	0	0	7.8	4.0	3.6	10.8	9.5	0	0	4.2	0	4.9	0.6	99.7
Duntilland quarry fines	1.5	0	6.1	22.0	23.3	0	0	0	5.9	3.1	2.6	13.8	11.6	0	0	4.4	0	4.6	0.9	99.8

Table 4-14 CIPW normative analysis of rockdust from various quarries in Scotland

Symbol		**Normative Mineral**		**Formula**	**Note**
Q		Quartz		SiO_2	
C		Corundum		Al_2O_3	
or		Orthoclase (K Feldspar)		$K_2O.Al_2O_3.6SiO_2$	
ab		Albite (Na Plagioclase)		$Na_2O.Al_2O_3.6SiO_2$	
an		Anorthite (Ca Plagioclase)		$CaO.Al_2O_3.2SiO_2$	
ne		Nepheline		$Na_2O.Al_2O_3.2SiO_2$	
lc		Leucite		$K_2O.Al_2O_3.4SiO_2$	
ac		Acmite		$Na_2O.Fe_2O_3.4SiO_2$	
	wo		Wollastonite	$CaO.SiO_2$	
di {	en	Diopside {	Enstatite	$MgO.SiO_2$	Pyroxene
	fs		Ferrosilite	$FeO.SiO_2$	
hy {	en	Hypersthene {	Enstatite	$MgO.SiO_2$	Pyroxene
	fs		Ferrosilite	$FeO.SiO_2$	
ol {	fo	Olivine {	Fosterite	$2MgO.SiO_2$	
	fa		Fayalite	$2FeO.SiO_2$	
mt		Magnetite		$FeO.Fe_2O_3$	
hm		Haematite		Fe_2O_3	
il		Ilmenite		$FeO.TiO_2$	
ap		Apatite		$3CaO.P_2O_5$	

Note

Calculated norm not always the precise mineralogy because:

1. Weight % of minerals from weight % of oxides used to calculate norm, whereas actual minerals present (calculated or estimated) on volume % basis
2. Complex hydroxyl bearing mineral species i.e. hornblende and biotite omitted from normative calculations – anhydrous pyroxenes used instead (less of a problem for basic rocks compared to acid rocks)
3. Calculation of the norm using a fixed sequence of mineral species expressed as simplified end-members of solid-solution series. This cannot ever fully match the outcome of natural solid-solution

4.3.4.4 Weathering of minerals in Collace quarry rockdust

Using the mineral stability series and the CIPW normative mineralogy (Table 4-13) it was possible to determine a possible weathering series for Collace quarry rockdust and to determine which elements would be released most readily. Table 4-13 shows that the most abundant mineral in the Collace samples was albite (sodium plagioclase) followed by anorthite (calcium plagioclase).

Figure 4-14 shows that calcium plagioclase is weathered more readily than sodium plagioclase but since there was more sodium plagioclase in the rock, sodium and calcium would be expected to be released at similar rates from the Collace rockdust. The next most abundant mineral was orthoclase (potassium feldspar) but this is a more stable mineral (Figure 4-14) hence less potassium than sodium and calcium would be expected to be released from the rockdust.

Hypersthene (pyroxene) was the next most abundant mineral in the rockdust with more enstatite (magnesium-rich) than ferrosilite (iron-rich). Pyroxenes are represented by augite in Figure 4-14 and are more resistant to weathering than olivine (Wilson, 2004) but would be expected to be reasonably easily weathered according to the stability series, releasing magnesium and iron upon weathering. Quartz was present at about 5 % in this rock, although this is the most stable mineral in the weathering series and not expected to readily weather. The remaining minerals in the CIPW normative analysis included magnetite, ilmenite, diopside (pyroxene) and apatite. Nutrients released would include iron, titanium, calcium, magnesium and phosphate although release would be slow since these mainly occur as accessory minerals (except diopside) and would not be easily accessed for weathering.

4.3.4.5 Weathering of minerals from other rockdust samples

The CIPW analysis of Clatchard quarry rockdust (Table 4-14) was similar to that of Collace quarry rockdust (Table 4-13) hence they will have similar mineralogies and weather following a similar pattern. Clatchard had slightly less quartz and anorthite (Ca-plagioclase) than Collace but slightly higher albite (Na-plagioclase), orthoclase (K-feldspar) and hypersthene (pyroxene). Sodium and calcium, as with Collace rockdust, would be released in highest amounts from Clatchard quarry rockdust. This would be followed by the iron and magnesium from the easily weathered pyroxene and potassium from K-feldspar would be released slowly.

Orrock quarry rockdust would be expected to be the most easily weathered rockdust due to higher contents of minerals with low stability to weathering. This rockdust contained olivine (the most easily weathered mineral according to Figure 4-14) that would release magnesium and iron upon weathering. Since there was more fosterite than fayalite (Table 4-14), there would be higher amounts of magnesium released than iron from this rockdust. Orrock rockdust also had appreciable contents of albite, anorthite and diopside and hence there would also be release of sodium, calcium, magnesium and iron from these minerals. The main difference between Orrock rockdust and Collace rockdust would be expected to be a higher weathering of ferro-magnesian minerals and hence higher quantities of Fe and Mg released.

Furnace quarry rockdust was shown to be an acid rock type (Section 4.3.4) and hence had the highest quartz content of all the rockdust tested (Table 4-14). This means that a large portion of this rockdust would be resistant to weathering as quartz is the most stable rock-forming mineral (Figure 4-14). There was a high content of albite (Na-plagioclase) in this sample but less anorthite than the Collace rockdust. Hence, despite the relative stability of albite versus anorthite, it would be expected that more sodium than calcium would be released. There was a higher content of orthoclase than in other samples in the Furnace quarry rockdust. However, since this mineral is quite resistant to weathering, only small amounts of K would be expected to be provided by this rockdust.

Duntilland quarry rockdust (coarse and fine samples) were shown to be similar in total mineralogy and were shown to be between Collace and Orrock rockdusts in terms of total nutrients (Table 4-11). The most abundant minerals were anorthite and albite, hence calcium and sodium would be provided by these samples upon weathering. The pyroxenes diopside and hypersthene were present in relatively high concentrations showing that magnesium and iron could also be released when these weather. There were low contents of orthoclase suggesting that potassium release from these samples would be quite slow. The lower contents of albite and orthoclase in the Duntilland fines compared to the Duntilland coarse sample (Table 4-14) indicated that this sample may have undergone more weathering. This could be attributed to the smaller particle size which would enhance the rate of weathering.

4.4 Discussion

4.4.1 Rockdust pH

The differences in pH could be related to mineralogy of the rock types. The pH of rockdust samples is related to the solubility of metal cations (vanLoon and Duffy, 2000). Cation exchange of the soluble cations with free H^+ will occur until all of the exchangeable cations have been replaced. Basalt and andesite have higher contents of basic minerals, whereas granite and quartz dolerite have higher silica contents and fewer basic minerals (McLean, 1982). The Duntilland fine material had a lower pH than the coarse material (0.5 pH unit lower). This may be because the fine material had undergone more extensive weathering (and consequently more loss of basic minerals). The high pH of rockdust samples tested in this chapter show that rockdust may have potential as a liming material but the effect would be much lower than that of agricultural lime. This was also the conclusion of Hinsinger *et al*. (1996) who used granite rock dust in incubation experiments and found that the maximum pH increase was 0.3 pH units.

4.4.2 Particle size distribution of rockdust

The particle size distribution analysis of Collace quarry rockdust samples showed that there was variation between the field trial and bagged samples whereby the bagged samples seemed to have a slightly higher fine content (material < 75 μm). This variation shows that although these products are all less than 6 mm, there can be differences in the fine content. These products are not ground specifically but rather exist as by-products of the grinding and screening process that separate quarried rocks for use in the aggregate industry. Hence, natural variation in the effectiveness of screening and sampling variation can occur as was shown by differences in the particle size distributions.

There were also some differences between particle size distributions in the other quarry samples tested. Furnace, Clatchard and Orrock quarry rockdusts were similar and had higher fine contents than Collace and Duntilland quarry samples.

All of these rockdust samples were less than 6 mm but showed some variation in the distribution of particle size below this. It is believed that finer rockdust would be more effective as there is a greater surface area for chemical weathering to occur. Möller and Giese (1997) showed that finer grain sized rocks led to higher leached fractions of metals in batch leaching experiments. They stated that intensive grinding may also expose most of the accessory minerals attached to the surface of rock forming minerals. However, in order to achieve a larger fine content, all of these rockdust samples would require extra processing. This could be achieved by further screening, extra grinding or (as in the case of the Duntilland quarry fine sample) sedimentation of coarser material.

The only sample that was fine enough to be classed as a 'dust' was the Duntilland quarry fine sample. As this material was obtained by washing and settling of coarse material, it had a high fine content (99 % passed a 75 µm sieve in tests). This material would require dewatering if it was to be sold as a fertilizer and because of its fine nature could be difficult to apply to soil.

There is a balance between fine content, cost and benefit of further processing and ease of application to soil. As the unprocessed samples are by-products of the quarrying industry, they are very cheap to produce. The cost is in bagging or transportation of the material. It is unlikely that quarries would go to the extra expense of further processing rockdust unless there was a cost benefit (i.e. if customers would pay more for a finer product). Customers may be satisfied with a cheap product that has not been further processed unless a clear benefit to using very fine material i.e. higher nutrient release could be shown. The SEER Centre has always used the unprocessed by-product from Collace quarry. They state that larger particles represent a longer-term nutrient addition due to the increased time required to chemically weather larger particles because of the lower surface area.

A very dusty material would be difficult to incorporate into agricultural soil and if applied dry, a high percentage of the fines could be lost. Hence a damp product might be more easily spread. A good compromise to the problem of further processing could be in the methods used by Duntilland quarry operator Bardon Aggregates. The coarse material recovered in the sedimentation of this rockdust is used in sand and gravel operations at the quarry and the very fine material is in a wet state already and hence could be applied easily to agricultural soil.

4.4.3 Rockdust extractions

The most soluble elements from rockdust were calcium, sodium, magnesium, potassium and phosphorus. This was in agreement with Silva *et al*. (2005) who showed that calcium and magnesium were most soluble from granite powder compared with silicon, aluminium and iron. Gillman (1980) stated that a single large application of crushed basalt might reduce the need to apply Ca and Mg for many years. Gillman *et al*. (2002) showed that finely ground basalt rock could provide substantial amounts of Ca, Mg and K but only a fraction of the total amount in the rocks was released. The extractions shown in this chapter agree with this conclusion and show that a high degree of weathering has to occur before there is release of any other elements.

Gillman *et al*. (2002) also showed that basalt rock could reduce the P requirement in soils as applications raised the extractable P levels. This agrees with the dilute nitric acid extraction and Kjeldahl-P digestion data that showed phosphorus could be provided in the long term from rockdust although earlier extractions (deionised water and modified Morgan's solution) did not extract significant P concentrations.

In these extractions Furnace quarry granite rockdust was shown to be lowest in extractable nutrients reflecting the mineralogical composition of this rock type. Hence, granitic rockdusts have the lowest potential for use as fertilizers. Duntilland quarry fines and Orrock quarry rockdust provided the highest concentration of elements in most extractions showing that these samples have the greatest potential. Orrock quarry rockdust was the only true basalt tested and was shown to have the most easily weathered mineral constituents (Section 4.3.4.5) and Duntilland quarry fines was the finest particle size product tested hence readily subjected to chemical weathering. All Collace quarry, Clatchard quarry and Duntilland quarry (coarse) products were shown to release nutrients similarly. They all released more nutrients than Furnace quarry rockdust but less than Orrock quarry and Duntilland quarry fines.

The water extraction of rockdust samples was only able to extract low concentrations of nutrients from all rockdust samples showing that rockdust addition to soil would not be an immediate nutrient addition.

The EDTA extraction was shown to release only low concentrations of plant-available trace elements from all rockdust samples. The EDTA extractable nutrients from Collace quarry samples agreed closer to Clatchard quarry than Orrock quarry, probably because the rock type in Collace quarry samples was closer to andesite than basalt.

The dilute nitric acid extraction again showed that only minor concentrations of trace elements can be released from rockdust. This explains why trace metals could not be analysed in earlier water extractions. Even in the long term (i.e. using the 'strongest' strength extractant) trace elements added by all rockdusts are still very low and hence are probably not a significant trace element fertilizer. This was again shown in Table 4-12 in the XRF analysis of various rockdust samples by the low trace element.

The results from rockdust extractions described in this chapter (Sections 4.3.3.1, 4.3.3.3, 4.3.3.5 and 4.3.3.7) show increasing nutrient release with increasing extractant 'strength' (especially calcium, phosphate, magnesium, potassium and iron). These analyses could be useful when determining probable effectiveness of a rockdust sample. Fyfe *et al.* (2006) discussed a problem to the use of rock powders in agriculture as the lack of agreement on standard methods of analysis when determining the complex fertility of these materials. Using a system of extractions instead of the total analysis (see Section 4.3.4) could be more valuable for determining the fertilizer potential of rockdust. However, these extractions also show that the trace elements provided rockdust additions would be very low especially in the short term. The most important nutrient additions are likely to be calcium and phosphate with magnesium, iron, potassium and manganese available in the longer term.

Unfortunately, the nutrients released from all rockdust types were low compared to levels added by soluble fertilizers (especially potassium) and hence could not be substituted for inorganic fertilizers. Appleton (1990) stated that rock and mineral fertilizers may only be economic in poor countries with lateritic soil where local mining operations are more economically viable than imported fertilizer. Gilkes and Young (1974) showed that the K provided by slightly oxidised micas was much less available to plants than KCl-K. Unlike other previous research articles, plant potassium uptake from rockdust was not investigated in pot trials (Chapter 8) because of the low extractable levels shown in these experiments.

4.4.4 Rockdust total analysis

4.4.4.1 CIPW norm and nutrient release from Collace quarry rockdust

The results from the CIPW normative mineralogy explains the nutrient release seen in the Collace rockdust extractions. These extractions showed a large initial release of sodium which was overtaken by calcium release with increasing ‘strength’ of extractants. This reflects the fact that the CIPW normative mineralogy showed an abundance of sodium plagioclase followed by calcium plagioclase. Since the calcium plagioclase weathers more readily than sodium plagioclase; the release of these two nutrients would be expected to occur at a similar rate. The use of ‘stronger’ extractants led to more release of Ca from the more easily weathered anorthite than Na from the more stable albite. Hinsinger *et al*. (2001) agreed that Ca and Na were preferentially released from basalt due to plagioclase dissolution. They also showed that anorthite (Ca plagioclase) dissolved faster than albite (Na plagioclase). Möller and Giese (1997) showed that sodium release from basalt exceeded other elements and also related the release to plagioclase dissolution. Meheruna and Akagi (2006) also showed possible preferential dissolution of plagioclase from andesite in hydroponic pot trials with rockdust addition.

Potassium release from Collace rockdust was much lower than sodium and calcium. This is explained by the lower abundance of potassium feldspar in the rockdust. Also potassium feldspar is more resistant to weathering than plagioclase feldspar. This explains why there was less of an increase in potassium release as extractant ‘strength’ was increased. Faster weathering of pyroxene explains the preferential release of magnesium compared with potassium since augite is more susceptible to weathering (and hence release of magnesium and iron) than orthoclase (K-feldspar). There was a higher release of magnesium than iron in EDTA extracts of rockdust because there was more Mg-rich pyroxene than Fe-rich.

4.4.4.2 CIPW norm and nutrient release from other rockdust samples

The differences in CIPW normative mineral analysis can be used to explain the nutrient release from rockdust samples as described in the rockdust extraction experiments.

In the deionised water extraction (Section 4.3.3.1), Collace quarry, Orrock quarry and Clatchard quarry all released high amounts of sodium while Furnace quarry and Duntilland quarry released low amounts. This is partly explained by the albite contents of these rockdusts although Furnace quarry had the highest content of albite but the lowest extractable sodium. This perhaps reflects the stability of albite to weathering and shows that Furnace rockdust was very resistant to weathering compared to the other rock types. It is difficult to make any other comparisons between the water extractable nutrients since concentrations were very low.

Calcium release in the extractions of rockdust samples was shown to be highest in Duntilland quarry fines and Orrock quarry samples. The lowest concentration was released from Furnace quarry rockdust. This release is explained by the particle size of Duntilland fines and by the high anorthite content of Orrock rockdust. As Furnace quarry had the lowest anorthite content, the low release (compared to other rockdust samples) was explained. The pattern of extractable iron and magnesium is also explained by the small particle size (and therefore higher weathering rate) of Duntilland fines and by the mineralogy of the rockdust samples. The amount of ferro-magnesian minerals was shown to be highest in Orrock quarry and Duntilland quarry samples. Hence higher amounts of iron and magnesium were shown to be released in the extractions. This pattern of release of magnesium was repeated in all extractions with the highest release from the basic/intermediate rock types (Orrock, Duntilland and Collace) and the lowest release from the more acidic rock types (Clatchard quarry and Furnace quarry).

Interestingly, the sodium release from Furnace quarry was never comparable to that of other rock types in any extraction despite the highest Na_2O (and consequently albite) concentrations. This suggests that the albite in this rock type was very stable and resistant to weathering. The albite in the other rockdusts may not have existed as pure minerals (since the distinction between calcium and sodium plagioclase exists as a continuum) and hence may have been more susceptible to weathering when more calcium was present as there was in the other samples.

The results from these extractions and mineralogical analysis seem to show that rocks with high stable silicate minerals (i.e granite and andesitic rock types) were the lowest in available nutrients. The Duntilland quarry sample that was very high in fine content released a high concentration of nutrients probably because of the particle size rather than mineralogy. Basalt rockdust with lowest quantity of stable silicates (quartz and feldspar) was shown to release highest quantities of nutrients. In agreement to these findings, Weerasuriya *et al*. (1993) concluded that rocks containing greater percentages of sheet silicates were more promising as multi-nutrient fertilizers than those with high percentages of quartz and feldspars.

4.5 Summary

Rockdust application to acid soil may provide a small liming effect although this would be much less than that of agricultural lime. Basaltic or andesitic rock types would be expected to give the greatest pH effect while granitic rock types or highly weathered samples would give the poorest results.

There can be differences in the particle size distributions between and within rockdust samples due to screening variation and sampling variation (i.e. location of pile that sample is taken from as coarse grains would be expected to fall to the bottom). Further processing of rockdust would be required to produce a very fine product. This would increase the price to the customer who would require a clear concurrent increase in nutrient availability to justify the increased price.

All rockdust samples released negligible quantities of nutrients in short-term weathering equivalent extractions and showed that there could be release of calcium, phosphate, magnesium, iron, manganese and potassium in the longer term. The highest nutrient release was from the most basic rock type (Orrock quarry basalt) and the finest material (Duntilland quarry fines). However, the trace elements provided by all of the samples were very low (below detectable levels in many extractions). Hence, rockdust is an unlikely trace element fertilizer since nutrients added in the short term are low.

The system of increasing extractant ‘strength’ could be used to assess the potential effectiveness of rockdust as fertilizer although knowledge of the rock type may be sufficient to give a rough indication of probable effectiveness. Although total major oxide analysis (by XRF) of rockdust samples doesn’t give information on the ease of nutrient release, the use of CIPW normative mineralogy could give useful information on the minerals present in rock samples. Knowledge of weathering rates can give information that agrees closely with the nutrient extraction experiments.

Chapter 5: Greenwaste compost materials

5.1 Introduction

5.1.1 Greenwaste compost

Greenwaste compost is the end product of composting operations that degrade organic gardening wastes. The starting materials are leafy or woody materials such as grass cuttings, tree clippings, hedge trimmings and other plant material. Source segregated organic garden wastes are collected by local authorities during domestic kerbside collections and at civic amenity sites. In a 2005/06 SEPA local authority waste arisings survey in Scotland, it was estimated that approximately 5 % of household waste was classed as organic garden waste (SEPA, 2007). As 2.89 million tonnes of household waste was collected in this period, this shows that there is potential for significant production of greenwaste compost from garden waste. In 2005/06 286,500 tonnes of materials were composted (SEPA, 2007), the main sources were:

- Kerbside collection – 179,400 tonnes
- Bring sites – 67,100 tonnes
- Local authority parks, gardens or grounds – 33,200 tonnes

Hence, there is a need to find suitable uses for the composted material that make use of this valuable resource.

5.1.2 Specification for Composted Materials

BSI PAS 100 is a non-statutory document that shows compost has met minimum quality standards and is compliant to a number of minimum safety parameters. Specified requirements include the composting process, input materials, analysis of the compost and traceability of composted products.

The composting process must be closely monitored following a hazard analysis and critical control point (HACCP) plan including measurement of temperature and moisture during the process. To eradicate pathogens during the sanitization stage, a temperature greater than 65 °C and a moisture content above 50 % (mass/mass) should be maintained for 7 days. The material should be mixed at least twice in this period. The input materials for composting must be source segregated and separated from non-biodegradables. Composting must go through an actively managed stage to conform to the HACCP plan including the steps of sanitization and stabilization. Table 5-1 shows the parameters and limits that composted material must pass to become BSI PAS 100 certified.

BSI PAS 100: 2005 Minimum compost quality for general use		
Parameter	Unit	Upper Limit
Pathogens		
Salmonella spp	in 25 g of fresh mass	absent
Escherichia coli	CFU g^{-1} fresh mass	1000
Potentially toxic elements		
Cadmium	mg kg^{-1} dry matter	1.5
Chromium	mg kg^{-1} dry matter	100
Copper	mg kg^{-1} dry matter	200
Lead	mg kg^{-1} dry matter	200
Mercury	mg kg^{-1} dry matter	1.0
Nickel	mg kg^{-1} dry matter	50
Zinc	mg kg^{-1} dry matter	400
Stability/maturity		
Microbial respiration rate	mg CO_2/ g organic matter/ day	16
Plant response		
Germination and growth test	Reduction in germination of plants in amended compost as % of germinated plants in peat control	20
	Reduction in plant mass above surface in amended compost as % of plant mass above surface in peat control	20
	Description of any visible abnormalities	no abnormalities
Weed seeds and propagules		
Germinating weed seeds or propagule regrowth	mean number per litre of compost	0
Physical contaminants		
Total glass, metal, plastic and any other non-stone fragments > 2 mm	% (mass/mass) of air-dry sample	0.5 (of which 0.25 is plastic)
Stones > 4 mm in grades other than mulch	% (mass/mass) of air-dry sample	8
Stones > 4 mm in mulch grade	% (mass/mass) of air-dry sample	16

Table 5-1 Parameters measured and upper limits in BSI PAS 100: 2005

The compost product must be sampled and tested when the batch has completed the process, after particle size screening or before blending with other materials. Parameters to be tested are: pathogens, potentially toxic elements, stability/maturity, physical contaminants and stones, plant response and weed seeds and propagules. PAS 100 sets out upper limits for those parameters tested and ensures that compost is fit for its intended purposes. During validation of the HACCP plan sampling is required on 3 consecutive batches in order to become certified. Failure on one parameter in one batch results in an overall failure. If a batch fails on any parameter, the compost must be sampled and tested again until three consecutive batches pass the parameter(s). During on-going activities, it is a requirement of PAS 100 that compost is sampled at least once per 5000 m^3 or once per year (whichever is sooner). At this point, if any test results fail, additional sampling above the minimum will be required. There are also a number of parameters than can be tested in addition that are not required for PAS 100 certification. These include water and extractable nutrients, total nutrients, physico-chemical properties and particle size distribution.

5.1.3 Quality Protocol for compost

The Quality Protocol for compost (Environment Agency and WRAP, 2007) was produced to set out criteria for use in the production of compost that defines the point at which the waste materials become a product. It also aims to encourage trust in the final product by ensuring that compost may be used without risk to the environment or human health. In the Quality Protocol for compost, there are three designated market sectors for composted materials:

- Land restoration and soft landscape operations
- Horticulture (including domestic use)
- Agriculture and soil-grown horticulture

Compost is defined as a product rather than a waste when the producer becomes PAS 100 certified (Environment Agency and WRAP, 2007). If the producer has complied with the protocol, no waste regulatory controls are applicable. Increasing the quality of compost produced from source-segregated waste by complying with the protocol could also encourage greater recycling with increased market confidence.

5.1.4 Composting process

The composting processes used by the two sources of greenwaste compost described in this chapter are very similar. They both use the open windrow method followed by maturation and screening of the material. While Forth Resource Management Limited compost is already PAS 100 certified, Dundee City Council is currently working towards certification.

5.1.4.1 Dundee City Council

The composting process used by Dundee City Council is described on their website (www.dundeecity.gov.uk/wasteman/compost). The council collect domestic garden waste and it is taken to the Riverside Composting Facility where it is mixed with suitable greenwaste from parks, landscaping and commercial operations. The fresh material is shredded, mixed and placed into 'windrows'.

The windrows are continually monitored to ensure high temperatures that eliminate weed seeds and any potential plant and human pathogens. Microbiological activity causes the temperature to rise to about 70 °C which destroys weed seeds and pathogens. The material remains in windrows for approximately two or three months and is mixed intermittently. The material from several windrows is then mixed into a large pile to mature for up to nine months. When the compost has reached the required maturity, the material is screened (10 mm or 20 mm) to remove any oversized objects. The 10 mm screened compost is marketed as 'Discovery compost'.

The final product can be used as a soil conditioner, mulch, or top soil substitute for domestic gardens. The compost can also be used in large quantities by landscape gardeners and for all types of horticultural and agricultural use.

5.1.4.2 Forth Resource Management

The open windrow method of composting is also used by Forth Resource Management Limited and is described on their website (www.frmrecycling.co.uk). Greenwaste materials are processed by shredding and building into a windrow typically 3-4 m wide and 2-3 m high. The windrows are left until microbial action has caused the internal temperature to increase rapidly. Air, moisture and temperature conditions within the windrow are controlled by 'turning' the windrow. This sterilization stage (high temperature and moist conditions) ensures that weed seeds and plant and animal pathogens are destroyed. The cycle of allowing the windrow to break down undisturbed and turning to speed up the process is repeated for a minimum of four turns per batch.

The material is stockpiled to stabilize and mature, during which time microbial activity comes to an end, pH drops, and the compost temperature stabilizes. When the stabilisation has been deemed sufficient the compost is screened to appropriately sized fractions:

- 0–10 mm – a soil improver and general gardening use. This produce is marketed and sold as 'Green Goodness compost'.

- 0–20 mm – a soil improver for horticultural and agricultural purposes.

- 10–20 mm – a landscaping mulch cover or can be re-shredded for re-composting.

After screening and before packaging or selling, samples of each batch of compost are tested for a range of parameters to ensure it meets the standards of BSI PAS 100 specification.

5.2 Methods

5.2.1 Compost analysis

Greenwaste compost for the field trial was supplied by Dundee City Council in 2004 and 2005. Forth Resource Management Limited supplied the greenwaste compost in 2006. The compost samples were analysed annually in spring for the field trial applications and samples from Dundee City Council were also taken in August 2005 and 2006 for use in greenhouse pot experiments.

Routine analysis for the field trial is described in Section 6.2.2.5. These analyses generally consisted of:

- Kjeldahl-N (Section 2.11.4)
- Available NH_4-N (Section 2.11.1)
- Available NO_3-N (Section 2.11.2)
- Available PO_4-P (Section 2.11.3)
- Available K (Section 2.12.2)

Other parameters also tested at various stages included:

- pH (Section 2.1.2)
- Conductivity (Section 2.2.1)
- Moisture content (Section 2.3.1)
- Total nutrients (as part of non-statutory PAS 100 compost analysis)

PAS 100 Certification data was provided by the compost suppliers and had been analysed by private laboratories.

5.3 Results

5.3.1 Available macro-nutrients

Nutrients in compost (mg kg^{-1} dry matter)	Dundee compost April 2004	Dundee compost March 2005	Dundee compost August 2005	Dundee compost August 2006	FRM compost April 2006
NH_4-N	80.3	39.9	21.6	18.4	24.2
NO_3-N	234	323	363	254	301
NH_4-N : NO_3-N	0.34	0.12	0.06	0.07	0.08
PO_4-P	1995	2035	nd	1772	1896
K	8331	5836	nd	5931	5497

Table 5-2 Available nutrients in greenwaste compost samples (nd = not determined)

Table 5-2 shows the available macro-nutrients calculated on a dry mass basis and gives information on the available-N in the material. The analyses show that ammonium levels were highest in Dundee compost from 2004 although a reduction was shown in subsequent years. Nitrate levels were variable from year to year although the general trend was for higher nitrate when ammonium levels were lower. The available-N analyses show that the compost samples all had low NH_4-N: NO_3-N ratios showing that these samples were adequately matured. This ratio also improved with year of sampling as is shown in Table 5-2.

Nutrients in compost (kg $tonne^{-1}$ fresh matter)	Dundee compost April 2004	Dundee compost March 2005	Dundee compost August 2005	Dundee compost August 2006	FRM compost April 2006
NH_4-N	0.05	0.02	0.01	0.01	0.01
NO_3-N	0.14	0.17	0.23	0.18	0.18
PO_4-P	1.21	1.10	nd	1.22	1.14
K	5.06	3.15	nd	4.09	3.30

Table 5-3 Available nutrients in greenwaste compost samples (nd = not determined)

Table 5-3 shows the available macro-nutrients in greenwaste compost samples analysed between 2004 and 2006. The analysis shows that the material is low in available nitrogen but is a good source of available P and especially K. Although the analyses show variation from year to year, the levels of nutrients were similar in all samples tested.

5.3.2 Other parameters tested

	Dundee April 2004	Dundee March 2005	Dundee August 2005	Dundee August 2006	FRM April 2006
Total nitrogen (mg kg^{-1} dry matter)	11668	9576	nd	11484	11981[*]
Total calcium (mg kg^{-1} dry matter)	nd	nd	nd	nd	21299[*]
Total magnesium (mg kg^{-1} dry matter)	nd	nd	nd	nd	3732[*]
Total sulphur (mg kg^{-1} dry matter)	nd	nd	nd	nd	1745[*]
Total boron (mg kg^{-1} dry matter)	nd	nd	nd	nd	94[*]
Total iron (mg kg^{-1} dry matter)	nd	nd	nd	nd	26292[*]
Total manganese (mg kg^{-1} dry matter)	nd	nd	nd	nd	566[*]
Total nitrogen (kg tonne^{-1} fresh matter)	7.22	5.30	nd	8.56	7.20
pH	nd	nd	7.9	8.4	8.0
Conductivity (µS cm^{-1})	nd	nd	1711	951	498[*]
Moisture content (% mass/mass)	39.3	46.1	36.8	31.0	39.9

[*] analysed as part of PAS 100 certification by private laboratory

Table 5-4 Analyses of greenwaste compost samples (nd = not determined)

The analyses shown in Table 5-4 show that the total nitrogen in the composted material was variable from year to year probably reflecting the different input materials. The pH of greenwaste compost was generally slightly alkaline and approximately pH 8. The conductivity could also be quite variable between samples. As this is a measure of the water soluble nutrients from this material, it seems that the Dundee compost was higher in available nutrients than the FRM compost and could be slightly less matured. The moisture content of the compost samples was variable between samples but it was roughly 40 %. The PAS 100 certification analysis of FRM compost shows that it could supply large amounts of nutrients, especially calcium and iron when applied to soil.

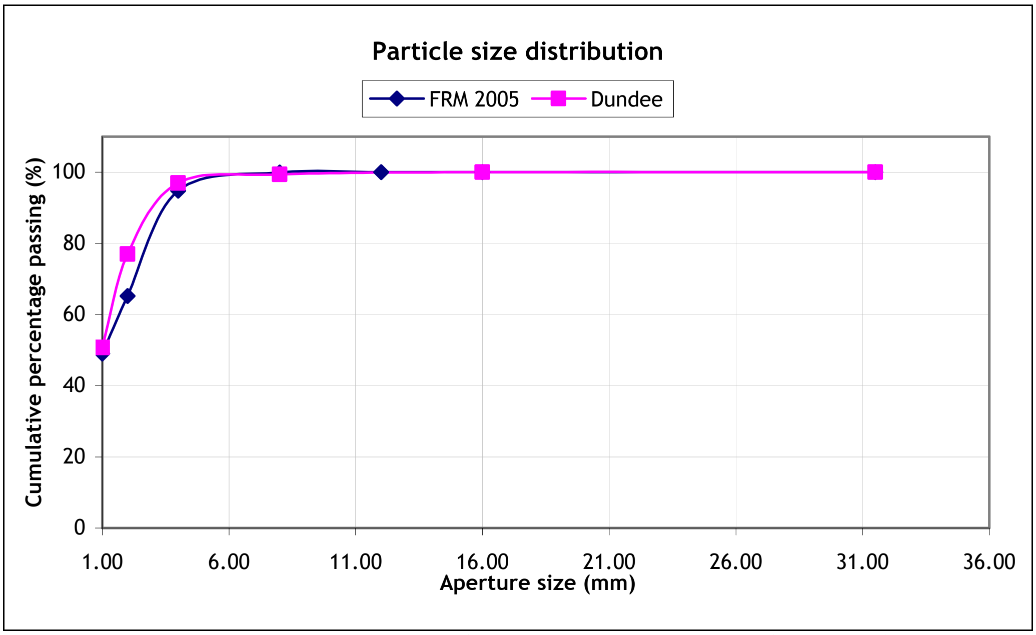


Figure 5-1 Particle size distribution in composted material

Figure 5-1 shows the particle size distributions that were measured as part of PAS 100 certification. This analysis shows that the material produced by Dundee and FRM complies with the < 10 mm stated. Approximately 50 % of the compost is less than 1 mm showing that there is a large portion of fines in these composts.

5.3.3 PAS 100 certification

5.3.3.1 Dundee City Council greenwaste compost

BSI PAS 100: 2005 Minimum compost quality for general use		
Parameter	Unit	Result
Pathogens		
Salmonella spp	25 g fresh mass	Absent
Escherichia coli	CFU g^{-1} fresh mass	< 20
Potentially toxic elements		
Cadmium	mg kg^{-1} dry matter	0.44
Chromium	mg kg^{-1} dry matter	25.80
Copper	mg kg^{-1} dry matter	57.60
Lead	mg kg^{-1} dry matter	99.60
Mercury	mg kg^{-1} dry matter	0.23
Nickel	mg kg^{-1} dry matter	24.30
Zinc	mg kg^{-1} dry matter	169.50
Stability/maturity		
Microbial respiration rate	mg CO_2/ g organic matter/ day	8.39
Plant response		
Germination and growth test	Reduction in germination of plants in amended compost as % of germinated plants in peat control Reduction in plant mass above surface in amended compost as % of plant mass above surface in peat control Description of any visible abnormalities	- - none
Weed seeds and propagules		
Germinating weed seeds or propagule regrowth	mean number per litre of compost	0
Physical contaminants		
Total glass, metal, plastic and any other non-stone fragments > 2 mm	% mass/mass of air-dry sample	0 (of which 0 is plastic)
Stones > 4 mm in grades other than mulch	% mass/mass of air-dry sample	
Stones > 4 mm in mulch grade	% mass/mass of air-dry sample	

Table 5-5 Dundee compost (0 - 10 mm) non-certified values 2007
Analysis of compost for PAS 100 certification

As Dundee City Council is currently working towards certification, a limited amount of data is available for those parameters that have been passed (Table 5-5).

5.3.3.2 FRM greenwaste compost

BSI PAS 100: 2005 Minimum compost quality for general use		
Parameter	Unit	Result
Pathogens		
Salmonella spp	25 g fresh mass	Absent
Escherichia coli	CFU g^{-1} fresh mass	< 10
Potentially toxic elements		
Cadmium	mg kg^{-1} dry matter	0.45
Chromium	mg kg^{-1} dry matter	15.20
Copper	mg kg^{-1} dry matter	44.00
Lead	mg kg^{-1} dry matter	79.60
Mercury	mg kg^{-1} dry matter	0.20
Nickel	mg kg^{-1} dry matter	18.30
Zinc	mg kg^{-1} dry matter	183.00
Stability/maturity		
Microbial respiration rate	mg CO_2/ g organic matter/ day	4.23
Plant response		
Germination and growth test	Reduction in germination of plants in amended compost as % of germinated plants in peat control	3.6
	Reduction in plant mass above surface in amended compost as % of plant mass above surface in peat control	0
	Description of any visible abnormalities	none
Weed seeds and propagules		
Germinating weed seeds or propagule regrowth	mean number per litre of compost	0
Physical contaminants		
Total glass, metal, plastic and any other non-stone fragments > 2 mm	% mass/mass of air-dry sample	0.07 (of which 0 is plastic)
Stones > 4 mm in grades other than mulch	% mass/mass of air-dry sample	6.72
Stones > 4 mm in mulch grade	% mass/mass of air-dry sample	6.72

Table 5-6 FRM compost (0 – 10 mm) certified values 2005 – 2006
Analysis of compost for PAS 100 certification

The analysis (Table 5-6) shows that the FRM compost passed all parameters required for PAS 100 certification by The Composting Association.

5.4 Discussion

5.4.1 Nutrients in greenwaste compost

The compost samples analysed in this chapter were adequately matured as was shown by low NH_4-N: NO_3-N ratios. The decreasing ratio in Dundee samples shows the increasing quality of the compost produced there. Although the available nutrients from compost were variable between samples the analysis in this chapter can be used to calculate typical nutrients from greenwaste compost (Table 5-7).

Nutrient in compost	(mg kg^{-1} dry matter)	(kg $tonne^{-1}$ fresh matter)
Available NH_4-N	36.9	0.02
Available NO_3-N	295	0.18
Available PO_4-P	1925	1.17
Available K	6399	4.04
Total N	11177 (1.12 %)	7.07

Table 5-7 Average available nutrients from greenwaste compost

Table 5-7 shows the typically low available nitrogen in greenwaste compost although there is substantially more nitrogen in organic forms (total-N less available-N) that could become available through mineralization. P and K are available in larger quantities from greenwaste compost and could reduce the need for phosphate and potash inorganic fertilizers. Garcia (1991) calculated that the agronomic value in NPK of compost is approximately 16 – 18 % of mineral fertilizer.

However, the nutrient analysis carried out in addition to the PAS 100 analysis showed that FRM compost could also have substantial levels of calcium and iron (Table 5-4). Hence, the value of greenwaste compost is not limited to NPK as is the case with traditional inorganic fertilization, other essential plant macro and micro nutrients can also be provided.

5.4.2 PAS 100 compost analysis

5.4.2.1 Potentially toxic elements in compost

The PAS 100 certification shows that levels of potentially toxic elements were within permitted limits. In the Quality Protocol for Compost (Environment Agency and WRAP, 2007), it is recommended that soil analysis for PTEs is carried out prior to the first compost application and again when the predicted concentrations approach 75 % of the limit values in The Code of Practice for the Agricultural Use of Sewage Sludge (Department for the Environment, 1989). These values are summarized in Table 5-8 below:

PTE	Maximum permissible concentration of PTE in soil (mg kg^{-1} dry solids)				Maximum permissible average annual rate of PTE addition over 10 year period (kg ha^{-1})
	pH 5.0<5.5	pH 5.5<6.0	pH 6.0<7.0	pH >7.0	
Zinc	200	200	200	300	15
Copper	80	100	135	200	7.5
Nickel	50	60	75	110	3
	for pH 5.0 and above				
Cadmium	3				0.15
Lead	300				15
Mercury	1				0.1
Chromium	400				15
Molybdenum	4				0.2
Selenium	3				0.15
Arsenic	50				0.7
Fluoride	500				20

Table 5-8 The Code of Practice for the Agricultural Use of Sewage Sludge (1989) Maximum permissible concentrations of potentially toxic elements in soil after application of sewage sludge and maximum annual rates of addition

Assuming an average application rate of 20 – 30 t ha^{-1} as was applied in the SEER field trial (Chapter 6) and the analysis of PTEs provided in the PAS 100 certification (Table 5-5 and Table 5-6), the maximum average annual rate of PTE addition specified in Table 5-8 would not be exceeded.

5.4.2.2 Other analyses of compost

The PAS 100 analysis shows that the FRM greenwaste compost passed all parameters measured. The analysis showed that the compost was suitably stable as shown by a low microbial respiration rate. Human and animal pathogens were sufficiently low in the compost and there were no germinating weed seeds. This means that the compost had suitably completed the thermophilic stage that ensures pathogens and weeds are killed. Although there was a slight reduction in plant germination compared with a peat based control, this was well within permissible levels. There was no reduction in plant growth nor were there any visible abnormalities. Physical contaminants including plastic were below maximum permissible levels showing that the compost input materials were suitably segregated from non-biodegradable materials.

As Dundee City Council are currently working towards PAS 100 certification, some data on plant growth tests were missing. However, as all other parameters were within the upper limits, PAS 100 certification should be achieved once these final data are received.

It is required that compost is analysed at least once per year in accordance with PAS 100 regulations. This ensures that the end-user of the compost can be assured they are receiving a good quality product.

5.4.3 Compost and the soil strategy

The Environment Agency stated in its soil strategy report (Environment Agency, 2007) that it was a priority to continue regulating and advising on the land-spreading of sewage sludge and industrial, municipal and agricultural wastes as organic matter recycling to land is important to protecting the soil as a resource. Greenwaste compost could be seen as a more acceptable addition than sewage sludge since it can be regarded as a product rather than a waste when processed according to PAS 100 standards.

5.4.4 Suitability of greenwaste compost as growth media

The pH of greenwaste compost samples analysed in this chapter was generally around pH 8. This is in contrast to the low pH of peat based growth media that are typically around pH 5. This compost may therefore not be suitable for use as a container growth medium for some plants. However, greenwaste compost could be mixed with peat to produce a growth medium. Mathur and Voisin (1996) found that food and wood waste compost could ‘substantially replace peat in container growth media' due to (amongst other reasons) the increased plant growth and increased water-supplying capacity of mixtures of peat with this compost.

Hoitink and Poole (1980) discussed that packaged compost would need a moisture content of less than 40 %. The analysis of compost samples in this chapter shows that the greenwaste compost tested are within this limit (except Dundee compost in March 2005). FRM Ltd compost is currently being sold in 20 kg bags by Angus Horticulture Ltd and the analysis shows that the moisture content of the product is appropriate for a packaged product.

Fines are needed in the compost if it was to be used a container media to raise the CEC and moisture capacity (Hoitink and Poole; 1980). It was shown that 50 % of the compost samples passed a 1 mm sieve showing that these materials had adequate fine content for use in container media.

5.5 Summary

Greenwaste compost has been shown to be a valuable resource for application to agricultural soil or a container media. The PAS 100 minimum specifications of compost for general use provide a useful benchmark for compost quality. Certification ensures that this material can be considered as a product rather than a waste which makes compost much more acceptable to the user. There are a number of measurements that are not statutory for PAS 100 certification but are routinely carried out in addition that could also encourage the use of greenwaste compost. These include nutrient analysis and physico-chemical analysis.

Analysis of greenwaste compost samples over a 3 year period allowed calculation of 'typical' nutrient contents. This information would be important when compost is used in agriculture for determining likely nutrient addition in an application. Regular soil nutrient and PTE content analysis is recommended when applying compost to agricultural soil. This ensures that compost applications match crop nutrient requirements while minimising the risk of high soil metal contents.

Greenwaste compost could also be used as container media to be used as an 'environmentally friendly' peat substitute. The fine content and available nutrients are very important in this application since growing periods are likely to be too short for mineralization of organically bound nutrients. Hence, it is possible that inorganic-N addition might be required in some instances.

Chapter 6: SEER Centre Field Trial

6.1 Introduction

6.1.1 Background to the field trial

The SEER Centre Trust was established in 1997 to demonstrate the results when using rockdust and municipal compost to regenerate native soil. Increased plant yields shown were unquantifiable in the demonstration gardens set-up by the charity. There was therefore a need for a scientifically designed and managed field trial of rockdust to demonstrate and measure the effects on a number of parameters. The field trial could also be important as an extension to the use of rockdust in the agricultural sector.

Despite various incubation and pot trial experiments carried out on rockdust and crushed minerals (see Chapter 1), there are few field-scale trials of these materials in peer-reviewed scientific literature, and even fewer investigating the use of rockdust in an agricultural context. Bakken *et al*. (2000) carried out grassland trials of crushed rocks and mine tailings as K fertilizers over 3 years. They measured dry yields of herbage, plant nutrient uptake and K content of soil. The field trial described by Supanjani *et al*. (2006) used phosphate and potassium rocks (along with solubilising bacteria) during the cultivation of hot pepper. They measured P and K availability, plant nutrient uptake, photosynthesis, leaf area, biomass harvest and fruit yield compared with a control. Sanz Scovino and Rowell (1988) looked at the effects on plant yield, nutrients in plant tissue and nutrients in the soil after application of finely ground feldspar. The field trial lasted for 14 months in this case. Powdered granite was applied at 2 and 20 t ha^{-1} by Bolland and Baker (2000) to investigate effects on wheat grain yield in a nutrient poor soil. Leonardos *et al*. (1987) carried out a field trial with *Eucalyptus pellita* using coarse-grained (grain size up to 1 mm) basalt and measured height and standard diameter of the trees as a function of age. The only field trial to use compost and rockdust together was described by Mitchell *et al*. (2004) who reported on large-scale trials of compost and quarry fines in raised bed plot experiments assessing grass and tree growth.

Field-scale trials have also included the use of rockdust materials on acid forest soils. von Mersi *et al*. (1992) investigated the effects of basic rock powders on microbial activity and pH in forest soils at 3 different sites. von Wilpert and Lukes (2003) investigated the ecochemical effects of finely crushed phonolite (volcanic silicate rock type) on an acidified glacial loam. Hartmann *et al*. (1999) looked at the effects of adding N-enriched rock powder to mine spoil on soil chemistry, development of field layer vegetation, the nutritional status of pine seedlings and decomposition of lignin.

A field trial of basalt rockdust in combination with various organic and inorganic amendment materials over a period of at least 3 years would therefore provide information on the usefulness of these materials in an agricultural setting.

The SEER Centre field trial was hence carried out using controlled, scientific methodology to test the following hypothesis:

> "Applications of rockdust, with organic composts, to Scottish soils will have significant implications for soil improvement, crop yield, carbon sequestration and nutritive cycling."

As the majority of the positive growth effects shown in published scientific literature occurred when adding rockdust to nutrient poor soil types (see Chapter 1); it was hypothesised that a positive plant yield effect could be achieved by addition of rockdust to a low nutrient content Scottish soil.

The field trial was set up within a field on a flat area measuring approximately 2500 m^2 using native soil and the existing pasture grass as the test crop. The initial planned duration of the trial was 3 years but could be continued beyond this.

The initial research in the field trial involved analysis of the soil chemistry, crop yield and crop nutrient content. This chapter will describe the field trial in detail including background analysis of the site and methods used in routine harvesting, and crop and soil sampling. Results from the first 3 years of the field trial will be presented.

6.1.2 Location of the field trial

The SEER Centre field trial was located at the SEER Centre, Straloch, near Pitlochry, Scotland (NO024639) 270 m above sea level and is shown in Figure 6-1.

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Figure 6-1 Location of SEER Centre: Straloch, Perthshire (indicated by red circle)

The field was previously used for sheep grazing and hay production with permanent grass. Figure 6-2 below shows the approximate location of the trial within a larger field. Wooden posts marked the corners of individual plots. The field trial area was separated from the rest of the field by electric fencing with at least 5 m of buffer zone to reduce inputs from the surrounding field area.

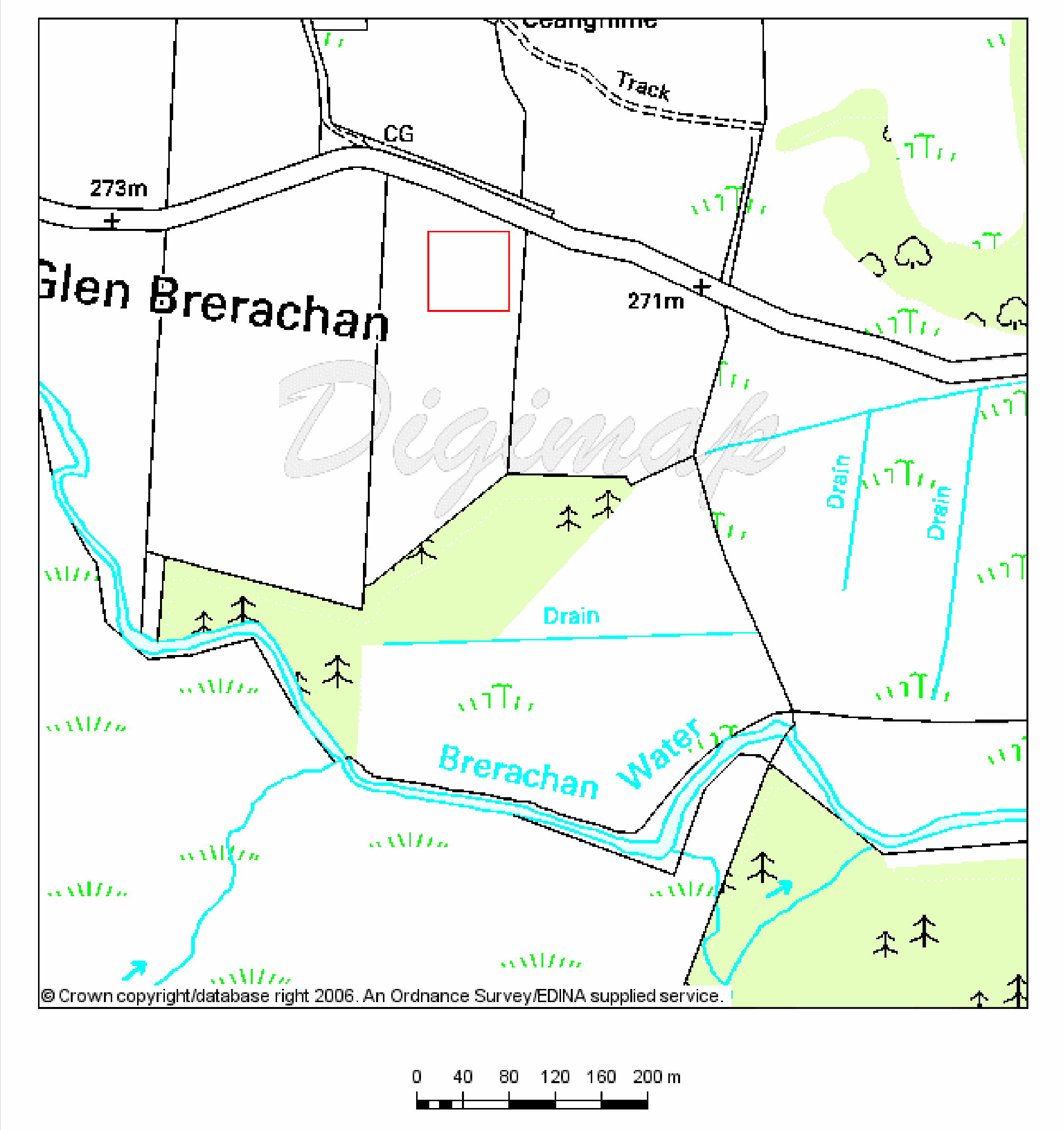


Figure 6-2 Location of SEER Centre field trial (fenced area indicated by red box)

The field was most recently seeded in 2001. In 2003, prior to establishment of the field trial, the field was fertilized with 20:10:10 NPK fertilizer at a rate of 432 kg ha^{-1}.

6.1.3 Treatments in the field trial

The 64 plot field trial was set up in October 2003 based on 8 treatments, each replicated 8 times in a Latin square design. The treatments are shown in Table 6-1:

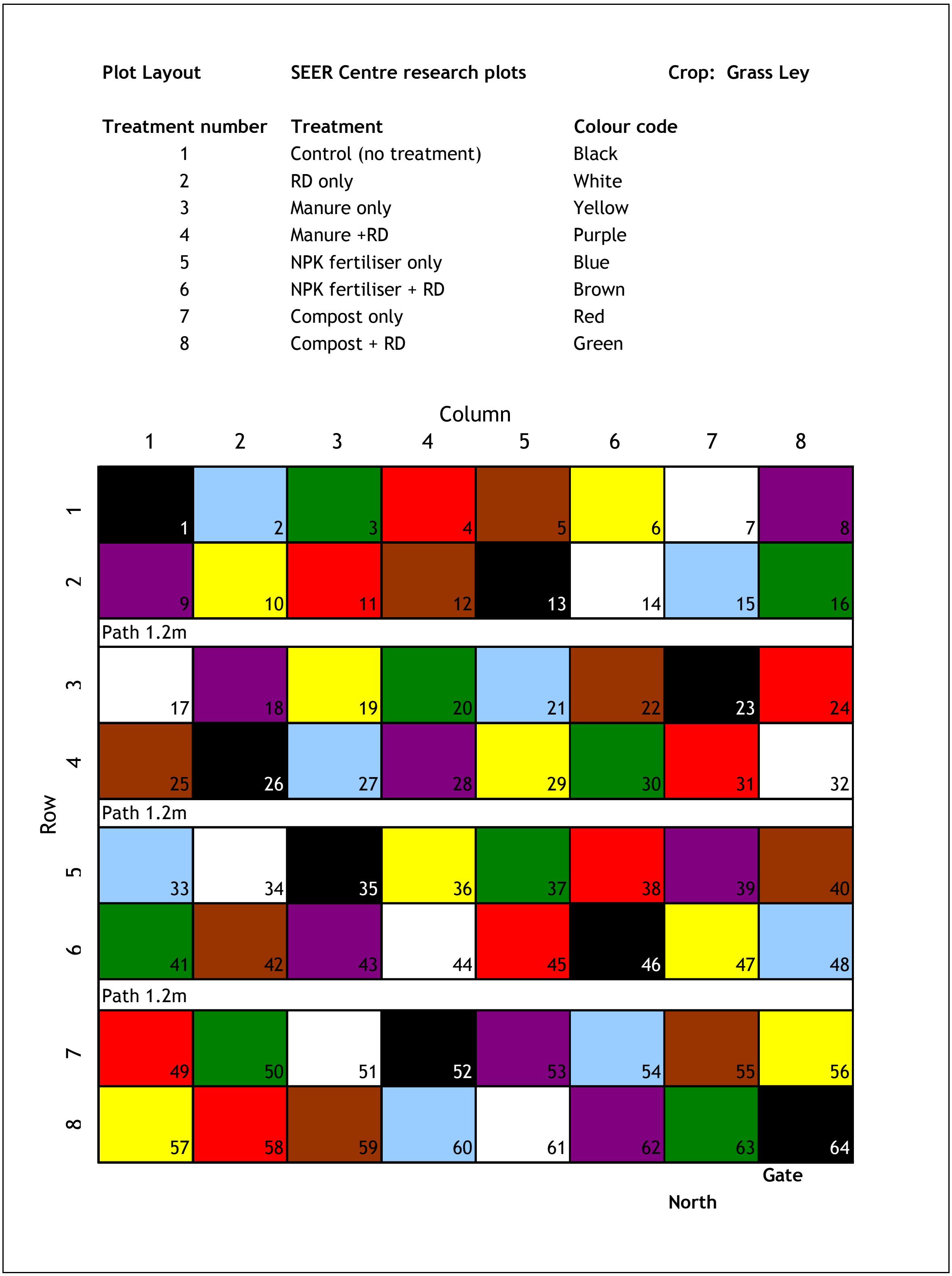
Treatment	Amendment	Rockdust
1	Control	No rockdust
2	Control	Rockdust
3	Farmyard manure	No rockdust
4	Farmyard manure	Rockdust
5	NPK fertilizer	No rockdust
6	NPK fertilizer	Rockdust
7	Greenwaste compost	No rockdust
8	Greenwaste compost	Rockdust

Table 6-1 Amendment/rockdust combinations in SEER field trial

Hence, rockdust was applied to half of the plots (with and without organic/inorganic amendments). This layout allowed investigation into the effects of rockdust overall, in addition to when applied in combination with other amendments. The field trial also allowed the effect of amendment type to be investigated, allowing comparisons between the organic/inorganic amendments without rockdust application.

6.1.4 Layout of field trial

The 25 m^2 plots were placed in an 8 x 8 Latin Square design to reduce the spatial variability (Figure 6-3). There were 3 paths to allow access to individual plots.



Plot Layout **SEER Centre research plots** **Crop: Grass Ley**

Treatment number	Treatment	Colour code
1	Control (no treatment)	Black
2	RD only	White
3	Manure only	Yellow
4	Manure +RD	Purple
5	NPK fertiliser only	Blue
6	NPK fertiliser + RD	Brown
7	Compost only	Red
8	Compost + RD	Green

Column

Row	1	2	3	4	5	6	7	8
1	⬛ 1	🟦 2	🟩 3	🟥 4	🟫 5	🟨 6	⬜ 7	🟪 8
2	🟪 9	🟨 10	🟥 11	🟫 12	⬛ 13	⬜ 14	🟦 15	🟩 16
	Path 1.2m							
3	⬜ 17	🟪 18	🟨 19	🟩 20	🟦 21	🟫 22	⬛ 23	🟥 24
4	🟫 25	⬛ 26	🟦 27	🟪 28	🟨 29	🟩 30	🟥 31	⬜ 32
	Path 1.2m							
5	🟦 33	⬜ 34	⬛ 35	🟨 36	🟩 37	🟥 38	🟪 39	🟫 40
6	🟩 41	🟫 42	🟪 43	⬜ 44	🟥 45	⬛ 46	🟨 47	🟦 48
	Path 1.2m							
7	🟥 49	🟩 50	⬜ 51	⬛ 52	🟪 53	🟦 54	🟫 55	🟨 56
8	🟨 57	🟥 58	🟫 59	🟦 60	⬜ 61	🟪 62	🟩 63	⬛ 64

Gate

North

Figure 6-3 Plot layout of field trial

6.1.5 Background data on field trial site

The soil textural classification was sandy loam (see Section 6.3.1.4) with an organic matter content of approximately 8% (see Section 6.3.1.2). The initial soil pH was 6.2 (see Section 6.3.1.2). The monthly total rainfall data shown in Figure 6-4 was measured at the Kindrogan Field Centre (a Met Office meteorological recording station), 3.2 km from the SEER Centre (see Figure 6-1). Temperature data was also measured at the station but sunshine hours was not recorded here.

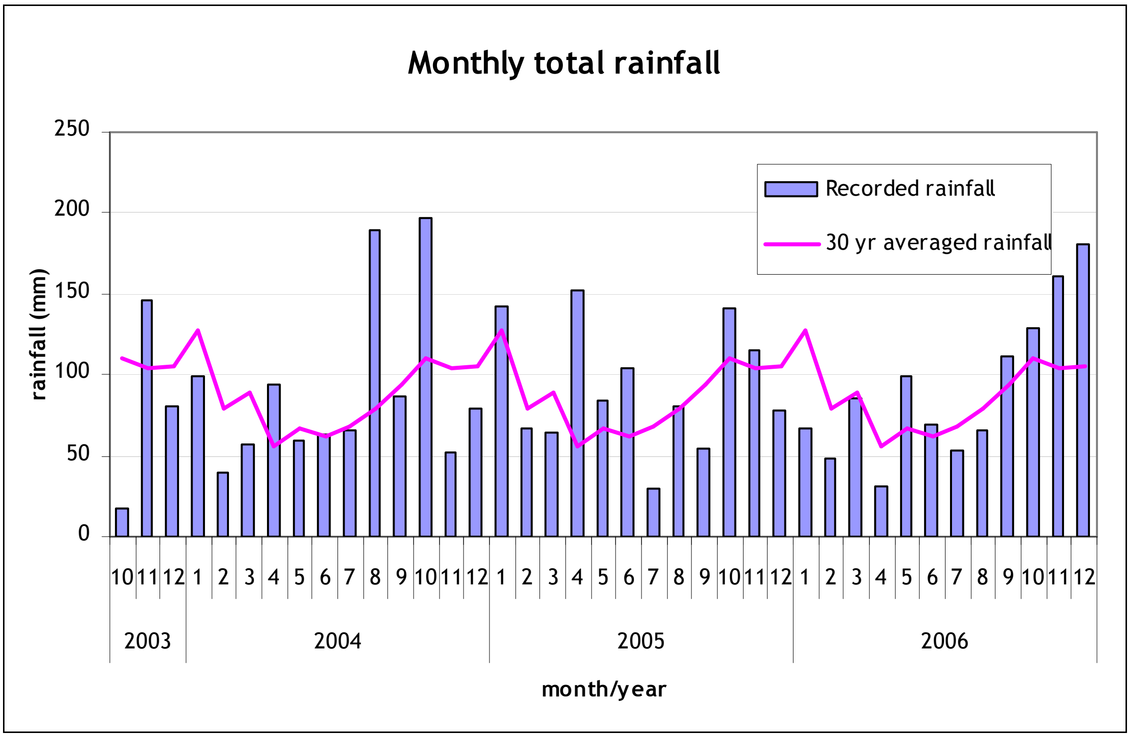


Figure 6-4 Monthly total rainfall data for duration of SEER Centre field trial plus monthly long-term (1971-2000) averaged data (Met Office data: Kindrogan Field Centre)

Year	Annual Rainfall (mm): Kindrogan
2003	773
2004	1080
2005	1111
2006	1096
Average 1971 - 2000	**1040**

Table 6-2 Annual rainfall during field trial (Met Office data: Kindrogan Field Centre)

The annual rainfall data in Figure 6-4 and Table 6-2 shows that 2005 was the wettest year. The plots were established in October 2003 at the end of a dry year. Annual rainfall totals in 2004, 2005 and 2006 were very similar and close to the 30 year average rainfall (Table 6-2) although deviations from the long-term monthly averages were evident (Figure 6-4).

Rainfall recorded at the Kindrogan Field Centre during the growing season (May – October) in 2004 – 2006 is shown in Table 6-3 below:

Month	Rainfall (mm)		
	2004	2005	2006
May	59.1	84.2	98.9
June	62.9	103.5	68.7
July	65.8	29.3	53
August	189	80	65.7
September	86.3	54.5	110.9
October	196.6	140.9	128.1
Total (6 months)	**659.7**	**492.4**	**525.3**
% of total annual	**61.08**	**44.32**	**47.93**

Table 6-3 Growing season rainfall 2004 - 2006 (Met Office data: Kindrogan Field Centre)

The data in Table 6-3 shows that the first growing season of the field trial was the wettest even though this year had the lowest annual rainfall (Table 6-2). In contrast, 2005 was the driest summer with the wettest winter months. These differences in rainfall could have an impact on the plant yields at harvest.

Temperature data for the duration of the field trial is shown in Figure 6-5. The three years were very similar with monthly average maximum temperatures peaking at about 20 °C in July/August. Minimum monthly average temperatures occurred in January/February each year and were approximately -2 °C. These temperatures were similar to the long-term averages (Figure 6-5).

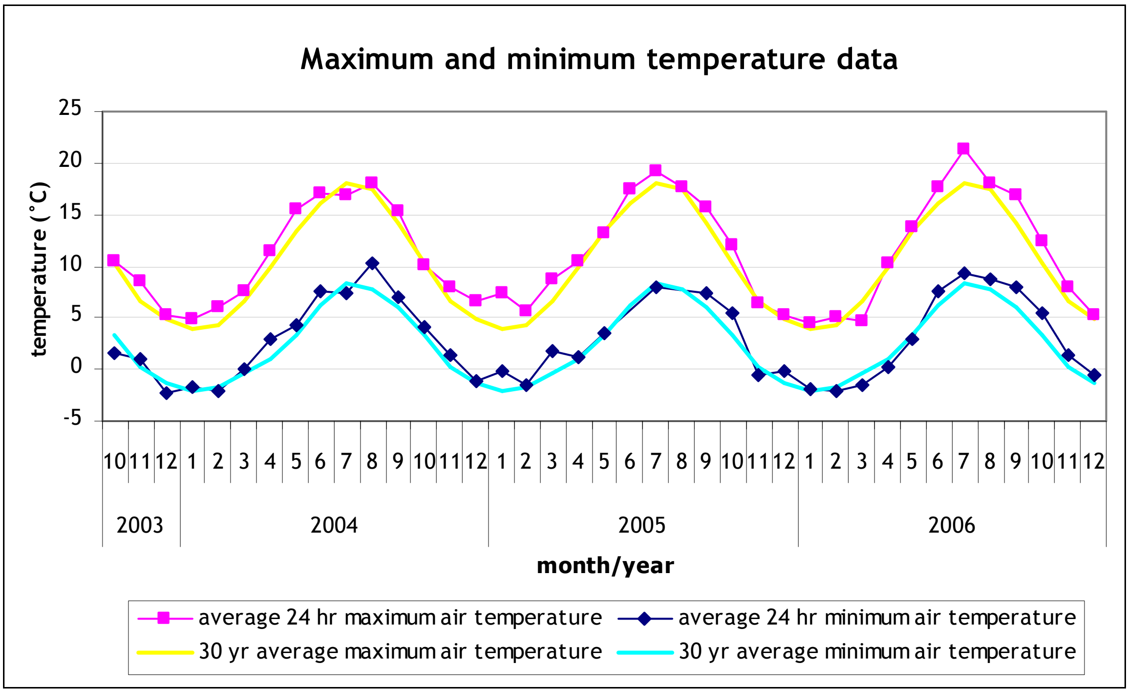


Figure 6-5 Monthly average 24 hr maximum and minimum temperature data for duration of SEER Centre field trial (Met Office data: Kindrogan Field Centre)

6.2 Methods

6.2.1 Baseline soil analysis

6.2.1.1 Soil core sampling

Soil cores were taken from the field trial three times during the project. Initially, 32 plots were sampled for baseline data prior to any additions in October 2003.

A stainless steel corer with an internal diameter of approximately 7 cm capable of holding a 50 cm length removable plastic core sleeve was used for all core sampling. The cores were usually 20 – 25 cm in depth. The cores were transported intact back to the laboratory for analysis.

The sleeve was opened and total core length measured. Any clear subsoil was identified and separated from the topsoil. Topsoil < 25 cm was identified and the actual depth of topsoil recorded. Any interface material different in character to topsoil, or topsoil > 25 cm was separated from topsoil and stored.

6.2.1.2 Air dry soil preparation

Plant tissue was removed from the top of the core and the soil was air dried for several days then sieved to 2 mm in a stainless steel sieve. Stones > 2 mm were weighed and discarded. Fine earth < 2 mm was weighed and kept for analysis.

6.2.1.3 Soil analyses

Analyses carried out on the air dry soil < 2 mm were:

- Moisture content (%)

The moisture content on all 32 samples was determined as in Section 2.3.2.

- pH

The pH was measured on all 32 samples as in Section 2.1.2.

- Organic matter content (%)

The soil organic matter content was determined on all 32 samples as in Section 2.4.

- Extractable P and K

Extractable P and K were determined in modified Morgan's solution extracts of all 32 samples as described in Section 2.7.2.

- EDTA extractable metals

Extractable metals were determined in 0.05 M ammonium EDTA solution extracts of all 32 samples as described in Section 2.7.3.

- Soil textural classification (8 samples)

8 samples were selected for particle size fractionation analysis to give information on soil textural class. These samples were: 1, 10, 19, 28, 37, 46, 55 and 64 which form a diagonal of the plot area (see Figure 6-3). The samples were analysed according to Section 2.5 separately. The percentage data was then averaged and used to determine the soil textual classification.

6.2.2 Field trial applications

There was one application of rockdust at the start of the field trial while compost, manure and NPK fertilizer were applied annually.

6.2.2.1 Rockdust application rate

Rockdust for the field trial was supplied by Tayside Contracts from Collace quarry (Collace by Kinrossie, Perthshire). The rockdust was applied by the SEER Centre to the plot surface in October 2003 at an application rate of 40 t ha^{-1} which, according to the SEER Centre, was designed to last for at least 5 years before re-application. The rockdust was applied on top of established grassland so no further re-seeding was necessary.

6.2.2.2 Inorganic fertilizer application rate

The inorganic fertilizer used in the field trial was NPK 20:10:10. The SEERAD (Scottish Executive Environment and Rural Affairs Department, 2003) recommended maximum application of 110 kg inorganic N ha^{-1} was added each year. This figure was obtained from the SEERAD booklet 'Guidelines for farmers in nitrate vulnerable zones' based on site class 2 (sandy loam soil with medium/high rainfall) and previous crop group 6 (permanent grass). This gives a total N requirement of 170 kg N ha^{-1} but 60 kg N ha^{-1} must be subtracted from this because of the 1 hay cut, 1 simulated graze management leaving an application rate of 110 kg N ha^{-1}. This was added in two applications: 60 kg N ha^{-1} in spring and 50 kg N ha^{-1} after the summer harvest each year.

6.2.2.3 Compost and manure application rates

Each spring, farmyard manure and compost were delivered to the field trial and samples brought back to the laboratory for analysis. The application rates for compost and manure samples were based on a matched total (Kjeldahl) nitrogen addition. The farmyard manure application rate was set at 25 t ha^{-1} and the compost application rate varied each year to match the total-N applied in the farmyard manure treatment.

6.2.2.4 Compost and manure sample preparation for Kjeldahl-N digestion

Compost and manure field trial application samples were analysed annually to calculate the rate of compost addition.

The manure samples typically had high moisture contents, so it was necessary to dry the samples before grinding them to < 4 mm in a small mill. This was also necessary to obtain a more representative sample of manure. The compost samples were not typically as moist, so only needed to be passed through a 4 mm sieve prior to analysis.

Kjeldahl-N in compost was measured directly on the fresh samples on an 'as received' basis. However, as the manure had to be analysed in the air dry ground-up state, moisture loss had to be taken into account before backwards calculating Kjeldahl-N in manure to the 'as received' state. To do this, two moisture contents had to be calculated on the manure samples.

Moisture contents on manure:

- ~ 70 g sample fresh – oven dry
- ~ 2.5 g sample air dry (ground-up sample) – oven dry

Section 2.9.1 describes the Kjeldahl-N digestion procedure. Since the manure analysis was on air dry ground-up sample, the Kjeldahl-N content was calculated to oven dry state from air dry and then back to fresh basis using these moisture contents.

6.2.2.5 Compost and manure nutrient analysis

A dilute sulphuric acid extraction was used to give information on the 'plant available' nutrients that could be extracted from organic amendments.

The method in Section 2.8 was used to perform the extraction on fresh compost and manure samples.

Nutrient analyses carried out on the extracts included:

- Nitrate-N (Section 2.11.2)
- Ammonium-N (Section 2.11.1)
- Phosphate- P (Section 2.11.3)
- Potassium (Section 2.12.2)

6.2.3 Field trial harvests

The summer field trial harvests took place in July 2004, 2005 and 2006. Autumn harvests were in October 2004 and 2005. There was no autumn 2006 harvest as sheep from the adjacent field breached the perimeter fence and grazed the field trial grass. The plots were harvested individually using motorized power scythes with a cutter bar width of approximately 1 m. The freshly cut grass was raked into large bags and weighed on a tripod mounted spring balance. Fresh yield per plot was recorded to be converted to dry yield using moisture content data.

A sub-sample of material was taken back to the lab for analysis. The sub-sample was dried in the oven at ~ 70 °C for several days to calculate dry matter content. This was used to determine plot dry matter yields from the fresh weights.

6.2.4 Analysis of plant material

The dried harvested grass samples nutrient contents were analysed using two digestion techniques:

- Kjeldahl digestion – total nitrogen and phosphorus analysis (Section 2.9.1)
- Nitric Acid digestion – total metal content including trace metal digestion (see Sections 2.10 and 3.3.2.1)

6.2.5 Field trial soil analysis

6.2.5.1 Soil core sampling

After the initial 32 baseline data plots were sampled in October 2003 (Section 6.2.1), all 64 plots were sampled in January 2005 then in January 2007. Section 6.2.1 describes the corer in detail. Once brought back to the laboratory, the cores were stored at 4 °C until they could be processed for chemical analysis. As was described in Section 6.2.1, topsoil < 25 cm was used for analysis. The sample was halved: half for fresh soil analyses and half for air dry soil analyses.

6.2.5.2 Fresh soil preparation

Plant tissue was removed from the top of the core and fresh soil was sieved to 4 mm in a stainless steel sieve using firm crushing by hand. Any stones > 4 mm were discarded as stones have little effect on soil fertility. Fine earth < 4 mm was kept for analysis. The soil was stored in the cold room at 4 °C until analysis and was extracted as soon as possible to minimise changes in nitrogen during storage.

6.2.5.3 Fresh soil analysis

- Moisture content (%)

The moisture content on all 64 samples was determined as in Section 2.3.1.

- Available nitrogen

The available nitrogen was determined on 0.5 M K_2SO_4 extracts (see Section 2.7.1 for method) for all 64 samples. The methods of analysis are described in Section 2.11.1 and 2.11.2.

6.2.5.4 Air dry soil preparation

The other core half was air dried for several days then sieved to 2 mm in a stainless steel sieve. Stones > 2 mm were weighed and discarded. Fine earth < 2 mm was weighed and kept for analysis.

6.2.5.5 Air dry soil analysis

- Moisture content (%)

The moisture content on all 64 samples was determined as in Section 2.3.2.

- pH

The pH on all 64 samples was determined as in Section 2.1.2.

- Organic matter content (%)

The soil organic matter content was determined on all 64 samples as in Section 2.4.

- Extractable P and K

Extractable P and K were determined in modified Morgan's solution extracts of all 64 samples as described in Section 2.7.2.

- EDTA Extractable metals

Extractable metals were determined in 0.05 M ammonium EDTA solution extracts of all 64 samples as described in Section 2.7.3.

6.3 Results

6.3.1 Baseline soil analysis

6.3.1.1 Recorded topsoil depth

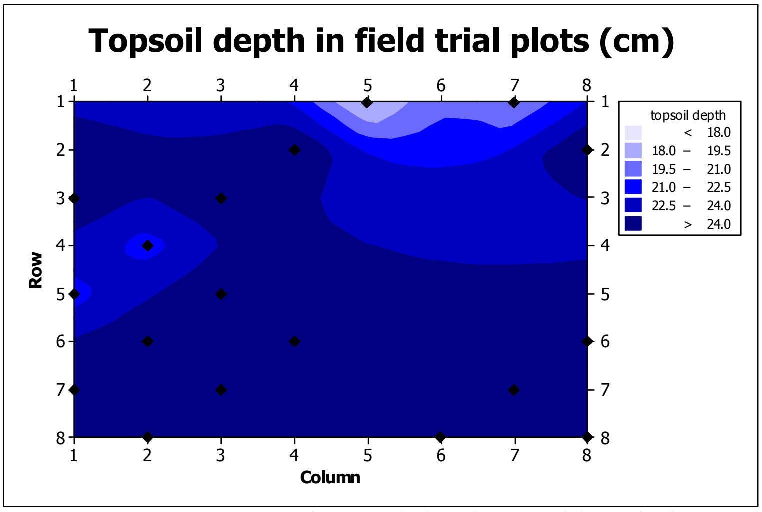


Figure 6-6 Measured topsoil depth in field trial plots

Initial cores only reached the subsoil in 5 out of the initial 32 samples. Interface material was recorded in a further 16 samples and the remaining 11 samples reached the topsoil only. These results are shown in Figure 6-6. Average recorded topsoil depth was approximately 24 cm although this was slightly shallower towards the North-East corner.

6.3.1.2 Soil chemical analysis

The mean, minimum and maximum results of baseline soil analysis are summarized in Table 6-4 below:

Baseline soil analysis – October 2003			
	Mean	Minimum	Maximum
pH (1:2.5 in water)	6.2	5.7	6.8
Organic matter (% in topsoil)	7.7	6.9	8.8
Extractable P (mg kg^{-1})*	6.8	3.4	11.7
Extractable K (mg kg^{-1})*	56.2	23	101

* Extractable with modified Morgan's solution

Table 6-4 Baseline soil analysis of SEER field trial

The measured values for each plot are shown on contour diagrams in Figure 6-7 – 6-10.

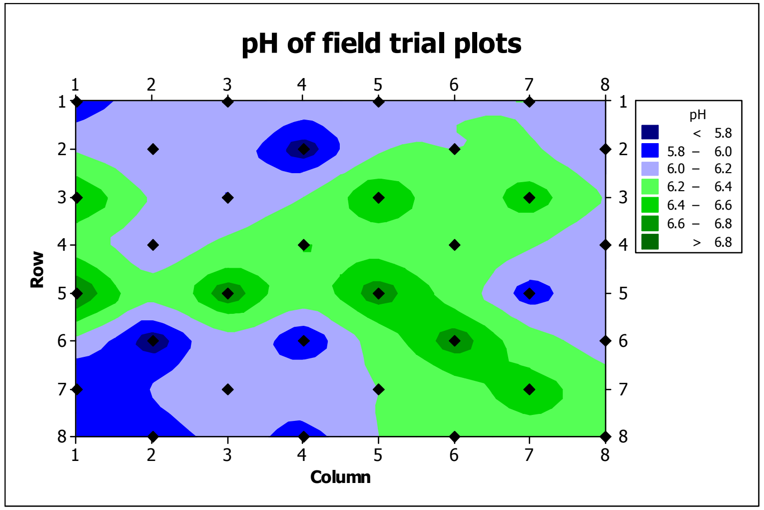


Figure 6-7 Baseline pH in field trial plots

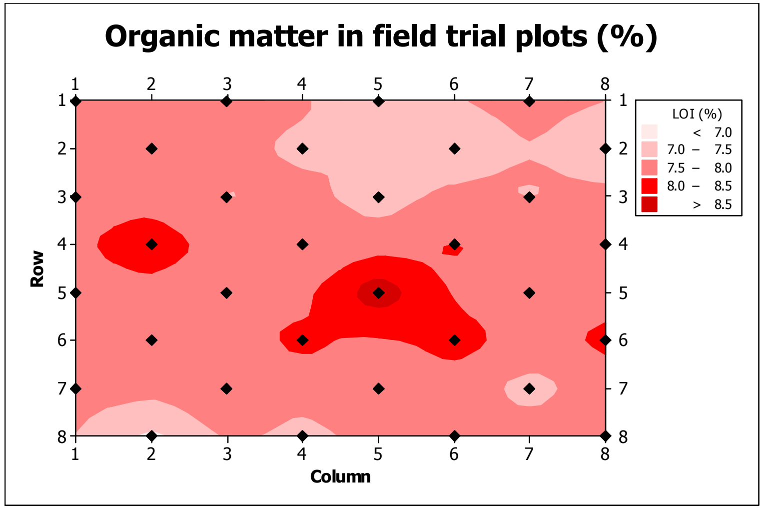


Figure 6-8 Baseline organic matter content of field trial plots

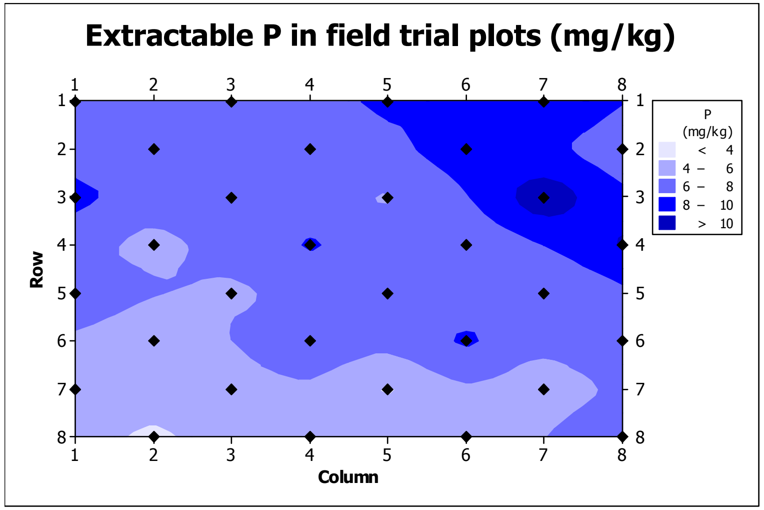


Figure 6-9 Baseline extractable phosphate-P in field trial plots

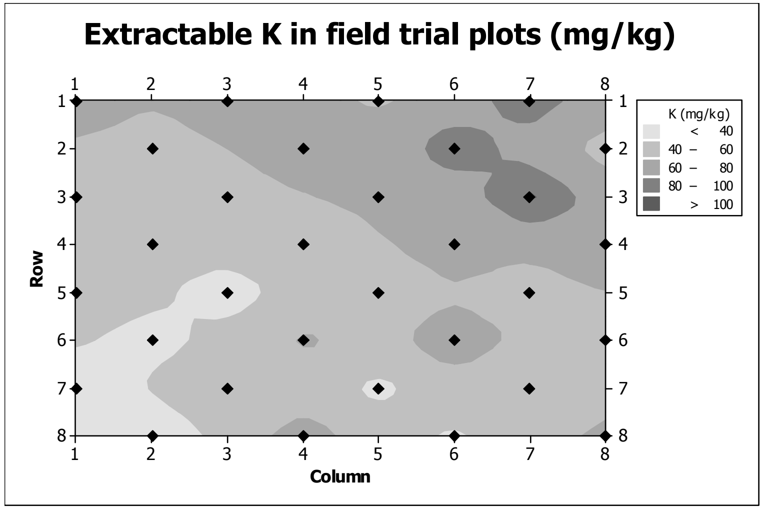


Figure 6-10 Baseline extractable K in field trial plots

The pH of the soil was within a relatively small range and the mean was close to the Agricultural Lime Association's target value of pH 6.5 for grassland soils (Agricultural Lime Association, 2007). There was no apparent trend across the plot area with regard to high or low values. Organic matter content was quite variable but is about average for cultivated soil in Scotland (Towers *et al.*, 2006). The extractable P levels were average to low (soil nutrient index value 2) according to fertilizer recommendations (ADAS, 1973) while the K index was low (soil nutrient index value 1) indicating that potash should be applied to this soil (Cooke, 1982; MAFF, 2000). There was systematic variation of P and K concentrations in the North-East corner of the field trial area with lower values in the South-West corner (see Figure 6-9 and 6-10). This may be related to the previous fertilizing programme undertaken prior to set-up of the field trial.

6.3.1.3 EDTA extractable metals

Baseline extractable metals in the field trial soil are summarized in Table 6-5.

Metal	Mean (mg kg^{-1})	Minimum (mg kg^{-1})	Maximum (mg kg^{-1})
Ba	10.2	8.4	13.8
Ca	1478	1044	2056
Cd	0.104	0.070	0.140
Cu	2.60	1.80	3.90
Fe	101.9	61.0	147.0
Mg	220.5	94.0	358.0
Mn	30.84	11.00	79.00
Ni	0.816	0.700	1.100
Pb	4.34	2.50	15.00
Zn	2.21	1.40	5.90

Table 6-5 EDTA extractable metals in baseline soil samples

The individual values measured in each plot are plotted as surface diagrams in Figure 6-11 – Figure 6-20.

Baseline EDTA extractable metals in the field trial area were variable and only showed clear trends in barium, iron, manganese and nickel levels. Iron, manganese and nickel concentrations were highest at the North end of the field trial (rows 1 – 4) while barium levels peaked at the South West corner of the field (column 1, row 8). Baseline lead and zinc were overall low but with spot, high concentrations. Overall, baseline soil analysis showed that the field trial plots were low to moderate in most extractable metals. Despite some high spike concentrations, and some trends across the field, the variation was within reasonable levels.

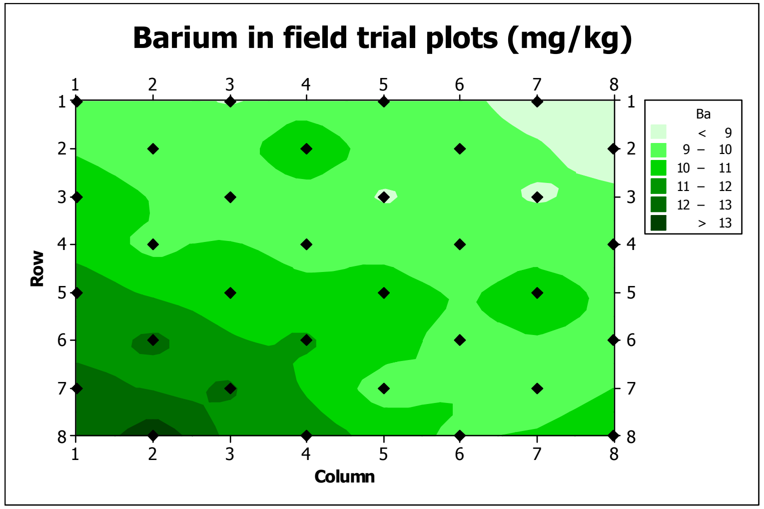


Figure 6-11 Baseline EDTA extractable barium in field trial plots

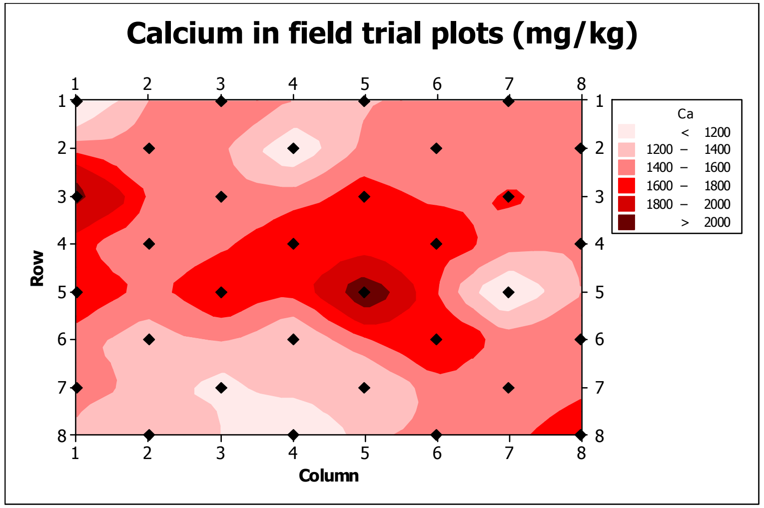


Figure 6-12 Baseline EDTA extractable calcium in field trial plots

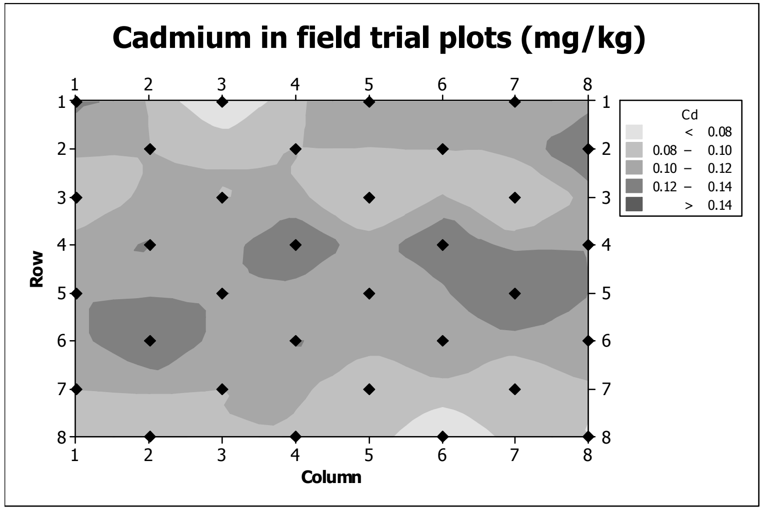


Figure 6-13 Baseline EDTA extractable cadmium in field trial plots

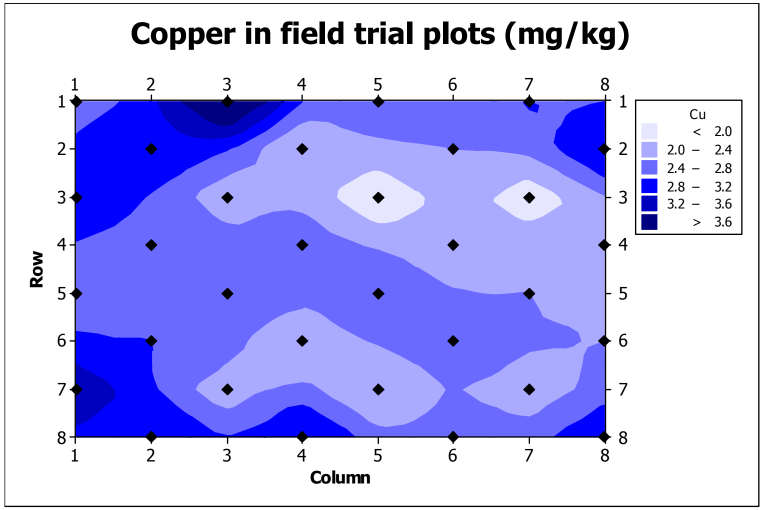


Figure 6-14 Baseline EDTA extractable copper in field trial plots

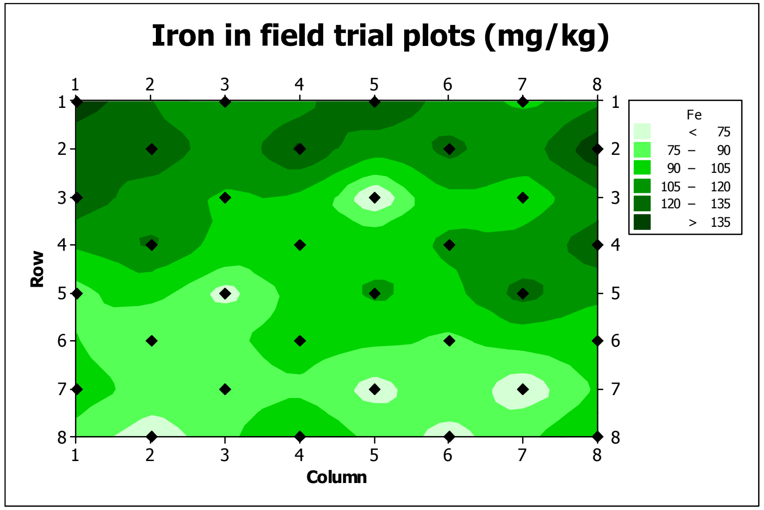


Figure 6-15 Baseline EDTA extractable iron in field trial plots

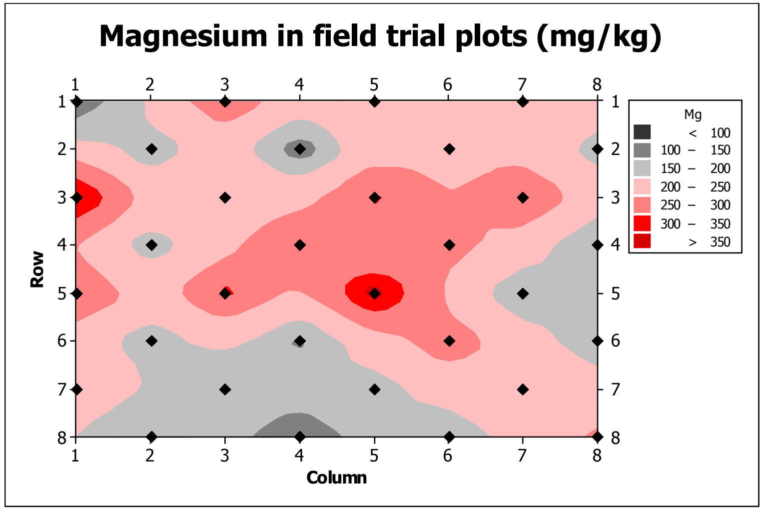


Figure 6-16 Baseline EDTA extractable magnesium in field trial plots

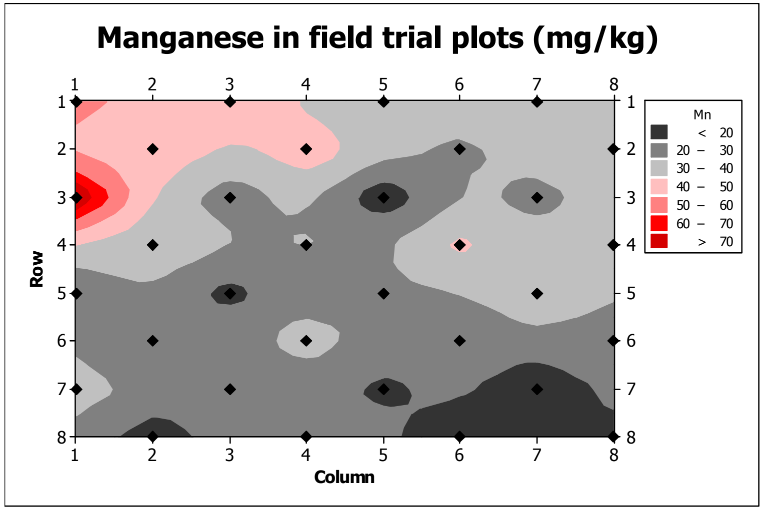


Figure 6-17 Baseline EDTA extractable manganese in field trial plots

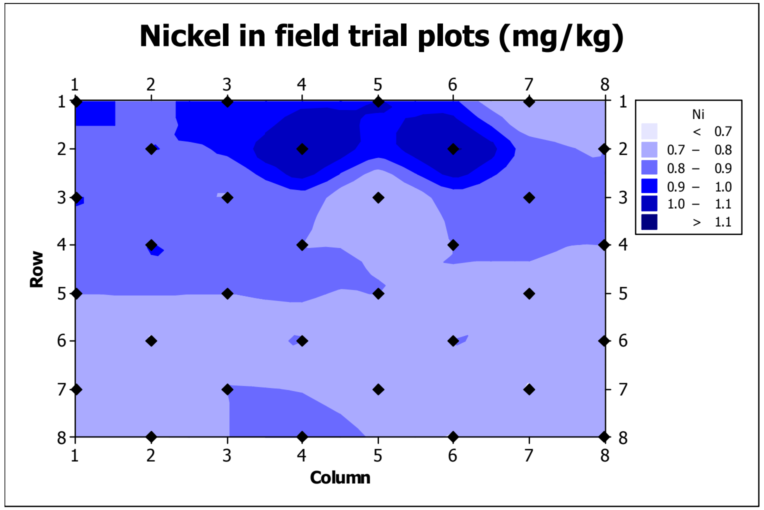


Figure 6-18 Baseline EDTA extractable nickel in field trial plots

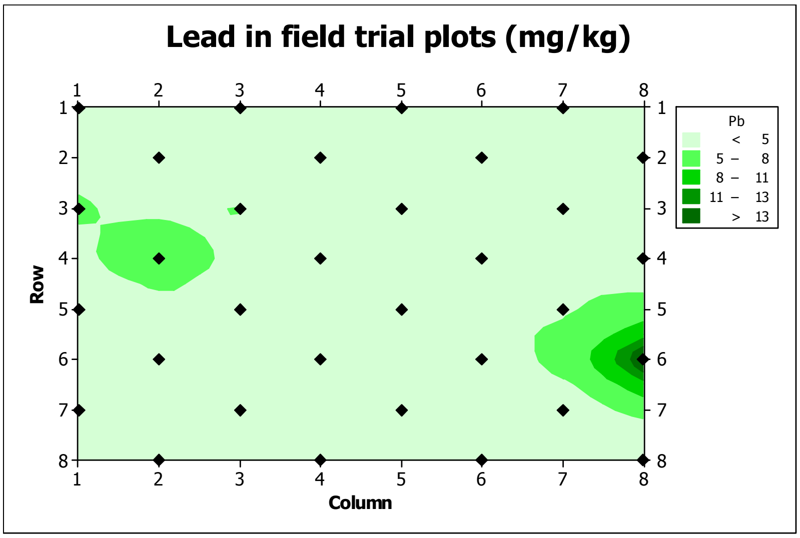


Figure 6-19 Baseline EDTA extractable lead in field trial plots

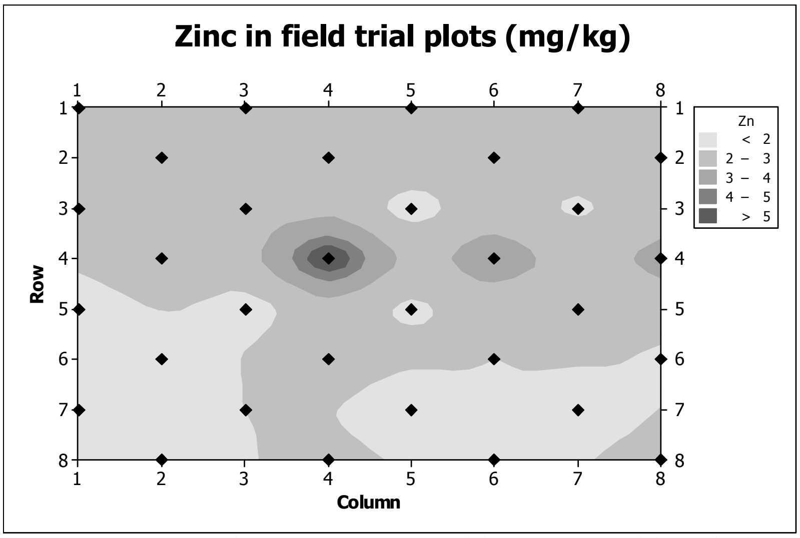


Figure 6-20 Baseline EDTA extractable zinc in field trial plots

6.3.1.4 Soil textural classification

Averaged data from the 8 replicates is shown in Table 6-6 below:

Soil fraction	Fraction percentage (%)
Sand (2 mm - 53 µm)	72.64
Silt (53 µm - 2 µm)	21.52
Clay (< 2 µm)	5.84

Table 6-6 Particle size fractionation of SEER field trial soil

Figure 6-21 shows the data from Table 6-6 plotted into a soil textural diagram. It can be seen that the lines intersect at a point in the 'sandy loam' section of the diagram. This information was used when determining the recommended N application (see Section 6.2.2.2).

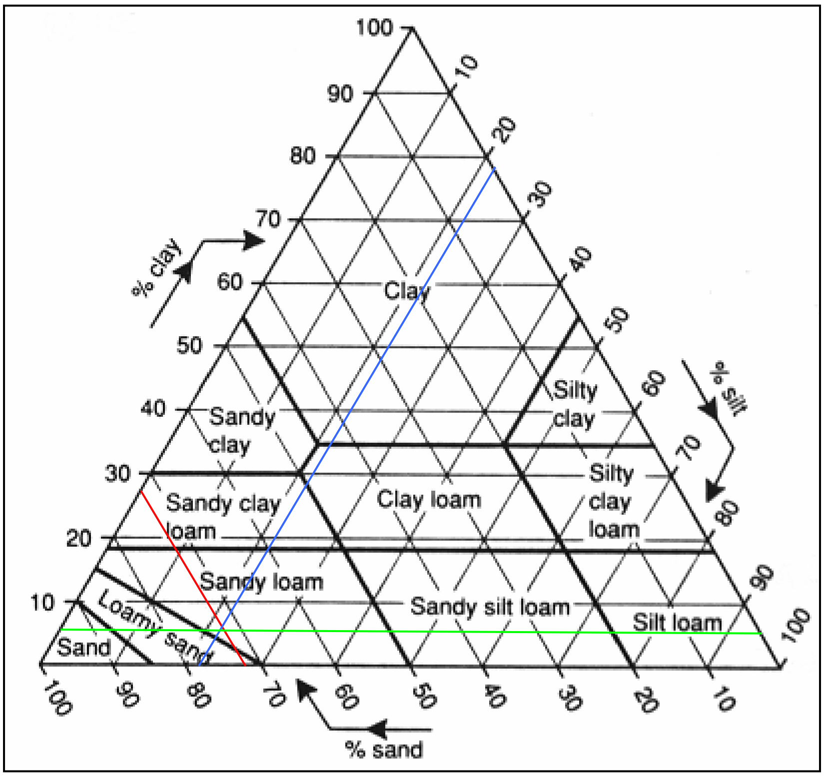


Figure 6-21 Soil textural diagram: SEER field trial soil

6.3.2 Field trial applications

6.3.2.1 2004 applications

Manure applied to 16 plots at rate of 25 t ha^{-1} = 62.5 kg plot^{-1}

Compost applied to 16 plots at rate of 18 t ha^{-1} = 45 kg plot^{-1}

Total NPK applied to 16 plots at rate of 110 kg N ha^{-1} = 1375 g plot^{-1}

	Total N (kg tonne^{-1})	Available N (kg tonne^{-1})	Available P (kg tonne^{-1})	Available K (kg tonne^{-1})
Manure	5.18	0.60	1.06	7.36
Compost	7.22	0.19	1.21	5.06

Table 6-7 Nutrient analysis of compost and manure in 2004 (kg tonne^{-1})

	Total N (kg ha^{-1})	Available N (kg ha^{-1})	Available P (kg ha^{-1})	Available K (kg ha^{-1})
Manure	129	15	27	184
Compost	129	3.4	22	91
NPK	110	110	55	55

Table 6-8 Nutrients added in 2004 (kg ha^{-1})

6.3.2.2 2005 applications

Manure applied to 16 plots at rate of 25 t ha^{-1} = 62.5 kg plot^{-1}

Compost applied to 16 plots at rate of 30 t ha^{-1} = 75 kg plot^{-1}

Total NPK applied to 16 plots at rate of 110 kg N ha^{-1} = 1375 g plot^{-1}

	Total N (kg tonne^{-1})	Available N (kg tonne^{-1})	Available P (kg tonne^{-1})	Available K (kg tonne^{-1})
Manure	7.22	0.05	0.54	7.60
Compost	5.30	0.20	1.10	3.15

Table 6-9 Nutrient analysis of compost and manure in 2005 (kg tonne^{-1})

	Total N (kg ha^{-1})	Available N (kg ha^{-1})	Available P (kg ha^{-1})	Available K (kg ha^{-1})
Manure	180.5	1.2	14	190
Compost	159	5.8	33	94
NPK	110	110	55	55

Table 6-10 Nutrients added in 2005 (kg ha^{-1})

6.3.2.3 2006 applications

Manure applied to 16 plots at rate of 25 t ha^{-1} = 62.5 kg plot^{-1}

Compost applied to 16 plots at rate of 19.7 t ha^{-1} = 49.5 kg plot^{-1}

Total NPK applied to 16 plots at rate of 110 kg N ha^{-1} = 1375 g plot^{-1}
(Total NPK recovered in harvested material = 60 kg N ha^{-1} = 750 g plot^{-1})

	Total N (kg tonne^{-1})	Available N (kg tonne^{-1})	Available P (kg tonne^{-1})	Available K (kg tonne^{-1})
Manure	5.7	0.15	0.55	2.78
Compost	7.2	0.20	1.14	3.30

Table 6-11 Nutrient analysis of compost and manure in 2006 (kg tonne^{-1})

	Total N (kg ha^{-1})	Available N (kg ha^{-1})	Available P (kg ha^{-1})	Available K (kg ha^{-1})
Manure	142	3.8	14	69
Compost	142	3.9	22	65
NPK	110	110	55	55
NPK (recovered in harvested material)	60	60	30	30

Table 6-12 Nutrients added in 2006 (kg ha^{-1})

6.3.2.4 Annual application analysis

The compost application rate in 2004 and 2006 were similar (18 t ha^{-1} compared with 19.7 t ha^{-1}). Differences in application rate occurred because of differences in total-nitrogen analysis each year in compost and manure samples (Table 6-7, Table 6-9 and Table 6-11). Due to problems with the Kjeldahl-N Technicon system in 2005 (see Section 3.2), there was a small error in total-N of compost and manure samples. As a result, the compost application of total-N did not match the manure total-N in 2005 (Table 6-10). In the revised analysis of the materials in this year (Table 6-9), manure samples were shown to be higher in total-N and compost was lower in total-N compared with 2004 and 2006. Despite these differences in total-N, the available nutrients added in 2005 were similar to those in 2004 and 2006 (Table 6-8, 6-10 and 6-12). In general, the analysis of these organic materials showed that compost was higher than manure in available P, manure was higher in available K and available N levels were variable but low in both materials. As there was no autumn harvest in 2006, only the NPK added in spring 2006 was recovered in harvested grass shown in Table 6-12.

6.3.3 Field trial harvests

6.3.3.1 Harvest 1

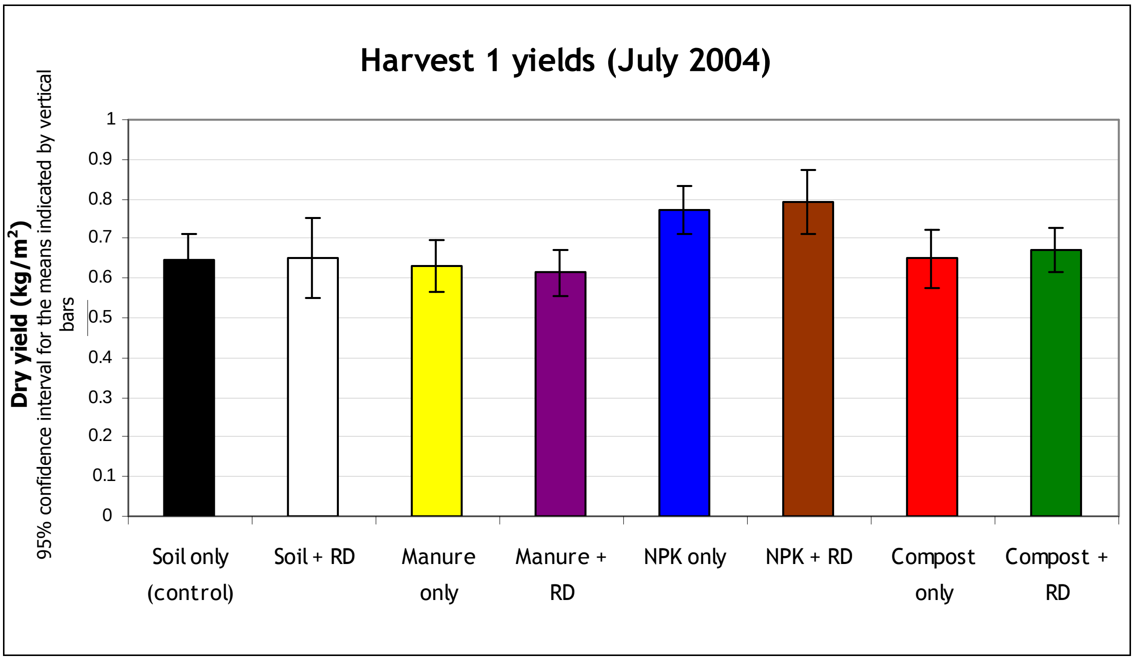


Figure 6-22 Harvest 1 dry yields (July 2004)

6.3.3.2 Harvest 2

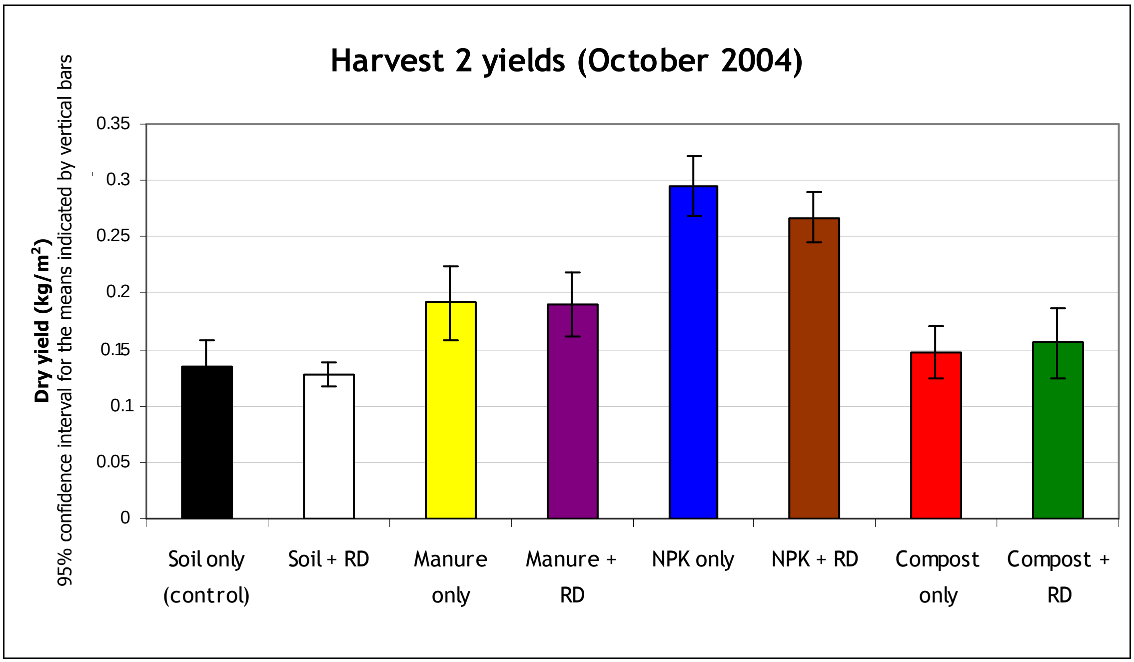


Figure 6-23 Harvest 2 dry yields (October 2004)

6.3.3.3 Harvest 3

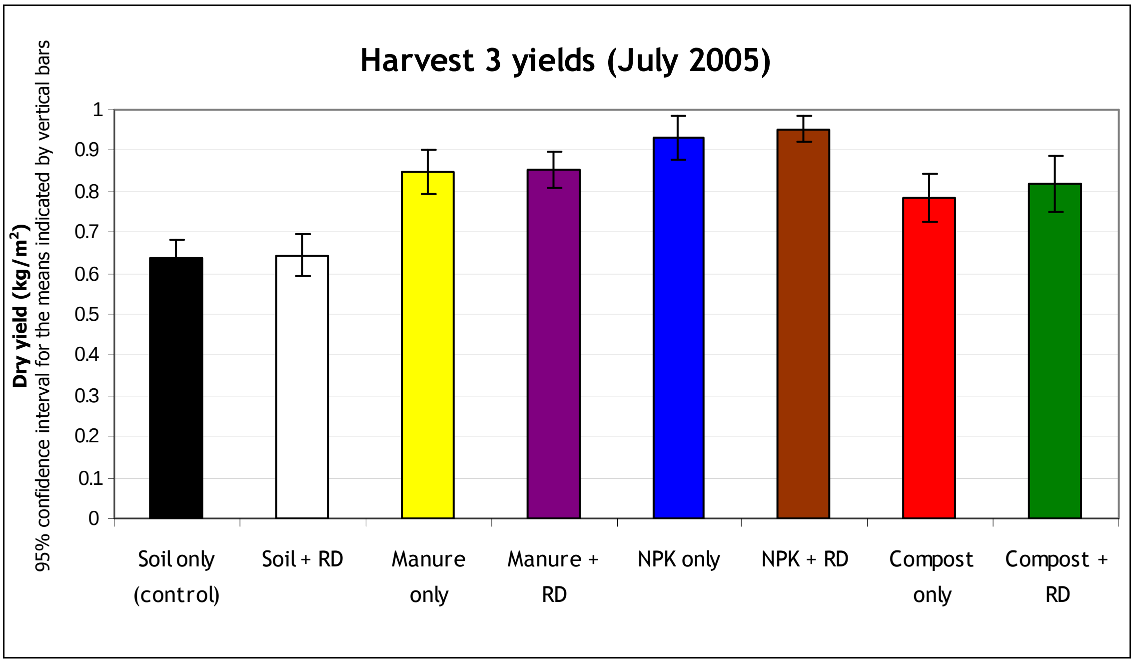


Figure 6-24 Harvest 3 dry yields (July 2005)

6.3.3.4 Harvest 4

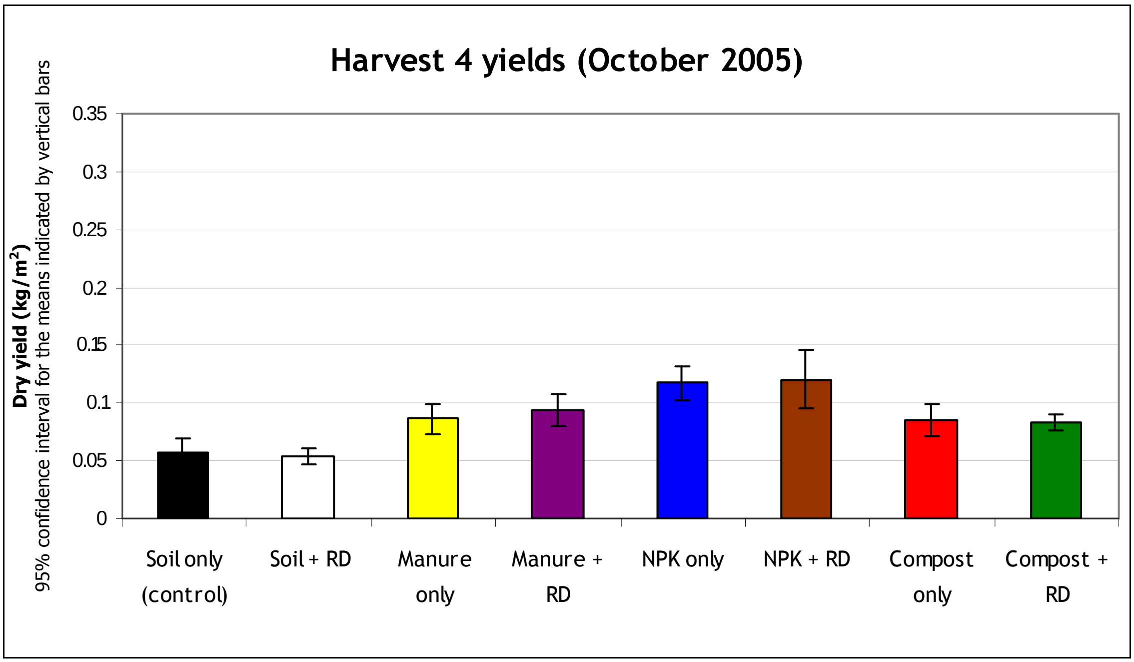


Figure 6-25 Harvest 4 dry yields (October 2005)

6.3.3.5 Harvest 5

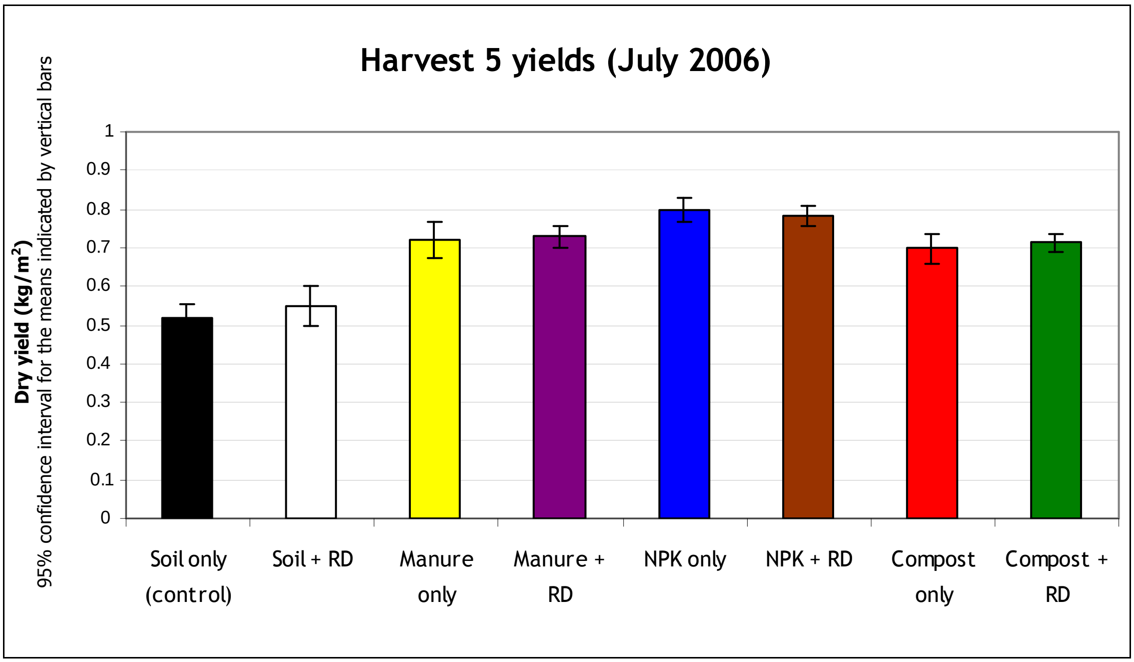


Figure 6-26 Harvest 5 dry yields (July 2006)

6.3.3.6 Total harvest yields

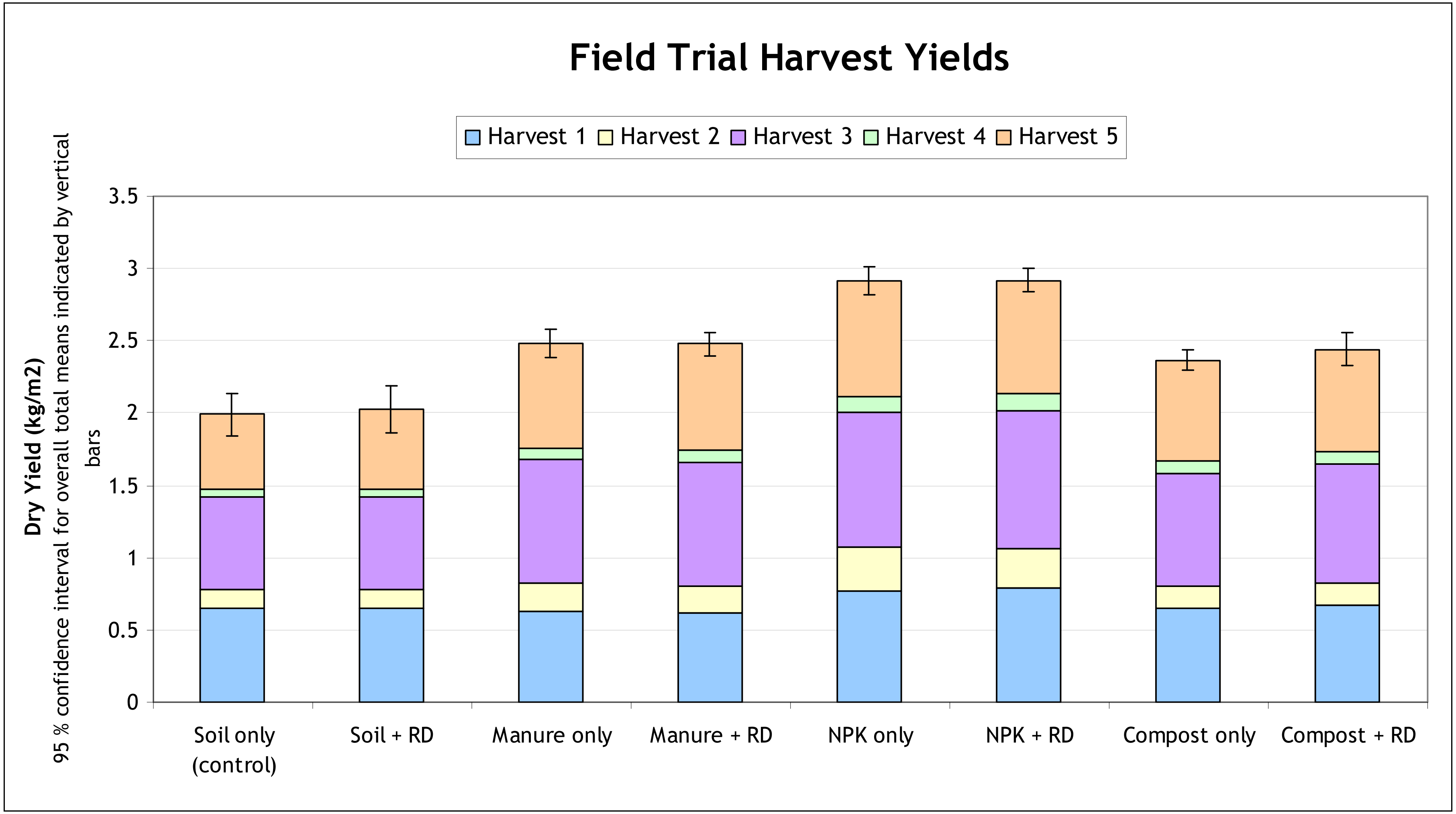


Figure 6-27 Total field trial harvest yields (harvests 1 - 5)

6.3.4 Statistical analysis of harvest data

Harvest data was analysed with Minitab statistical software (version 15.1) using the general linear model command. Factors included: column, row, amendment, rockdust and an amendment/rockdust interaction. This meant that differences within the field trial from one end to the other could be taken into account when analysing the data and was the main reason for using a Latin Square design when setting up the trial.

6.3.4.1 Individual harvest analysis

Figure 6-22 – 6-26 show the individual harvest yields. The effects of amendment, rockdust and amendment/rockdust interaction from the GLM output are summarised in Table 6-13 below:

	Effect		
	Amendment	Rockdust	Amendment/rockdust interaction
Harvest 1	***	NS	NS
Harvest 2	***	NS	NS
Harvest 3	***	NS	NS
Harvest 4	***	NS	NS
Harvest 5	***	NS	NS

Table 6-13 Effect of 3 factors on individual harvest yields
(NS = not significant; * = highly significant effect at $p \leq 0.01$ level)**

The individual harvest yields were further analysed using Tukey's least significant differences test at the 5 % level to find differences due to organic/inorganic amendment as indicated in the GLM. Table 6-14 summarises these differences.

Amendment	Individual harvest average yields (kg dry matter m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	0.650 a	0.126 a	0.640 a	0.056 a	0.532 a
Manure	0.624 a	0.186 b	0.851 b	0.090 b	0.724 b
NPK	0.784 b	0.275 c	0.942 c	0.119 c	0.791 c
Compost	0.660 a	0.146 a	0.803 b	0.084 b	0.705 b

Table 6-14 Effect of organic/inorganic amendments on individual harvest average yields
Average yields in the same harvest (column) followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test.

The statistical analysis shows the immediate effect of soluble fertilizer on plant yield. The first harvest occurred 3 months after application of organic/inorganic amendments and the data in Table 6-14 supports the theory that organic amendments need time to mineralize organic nutrients after addition. Since the NPK fertilizer was added in a soluble form, it could be easily utilized by the growing grass. Neither of the two organic treatments 'caught up' with the yields in the NPK treatments over the duration of the field trial. However, by the second harvest (for manure) and by the third harvest (for compost) the organic treatments produced significantly higher yields than the control and this remained true for the rest of the trial. By the third harvest, manure and compost produced statistically the same yields.

6.3.4.2 Total harvest yields

Figure 6-27 shows the total harvest yields. The effects of amendment, rockdust and amendment/rockdust interaction from the GLM output are summarised in Table 6-15 below:

	Effect		
	Amendment	Rockdust	Amendment/rockdust interaction
Total harvest yields (harvests 1 – 5)	***	NS	NS

Table 6-15 Effect of 3 factors on Total (Combined) Harvest Yields
(NS = not significant; * = highly significant effect at p ≤ 0.01 level)**

Amendment	Total harvest yields (kg dry matter m^{-2})
Control	2.002 a
Manure	2.474 b
NPK	2.910 c
Compost	2.398 b

Table 6-16 Effect of organic/inorganic amendments on total harvest yields
Yields followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

The data in Table 6-16 shows that the NPK treatment gave the highest yields overall. The manure and compost treatments gave statistically the same yields and the control produced the lowest yields. Although the compost treatment took longer than the manure treatment to outperform the control (Table 6-14), Table 6-16 shows that over the 3 years of the trial they did not perform differently to each other.

6.3.5 Analysis of plant material

Total nitrogen and phosphorus in the harvested plant material was determined on Kjeldahl digests. Total metals in the plant material were determined on nitric acid digests. Harvests 1 – 4 were digested as in Section 2.10.1 while samples from harvest 5 were digested as in Section 3.3.2.1 for trace element analysis. A certified reference material was also digested and analysed using the same methods to validate the techniques.

Nutrient uptake was calculated per plot from the yield data and the nutrient content data. This combines the two factors to give a measurement of quality of plant material as a function of the weight of material produced and is more useful for determining the fertilizer effectiveness than nutrient content data alone.

Plant nutrient content and nutrient uptake data were analysed with Minitab statistical software (version 15.1) using the general linear model command. The effects of amendment, rockdust and the amendment/rockdust interaction on metal content of plant material were investigated.

6.3.5.1 Certified reference material analysis

Element	Bush branches & leaves certified reference material analysis			
	Measured mean value (%)	Measured 95 % confidence interval	Certified value (%)	Statistical t-test result
Nitrogen	1.19	1.17 – 1.20	1.20	NS
Phosphorus	0.826	0.812 – 0.839	0.830	NS

Table 6-17 Measured and certified values from Kjeldahl digestion with results from statistical t-test (assuming equal variances) at 95 % confidence level (NS = no significant difference)

Table 6-17 shows that the measured values for N and P in the certified reference material were not significantly different to the certified values; this technique was therefore suitable for measurement of N and P in plant material.

Element	Bush branches and leaves certified reference material analysis			
	Measured mean value (mg kg^{-1})	Measured 95 % confidence interval	Certified value (mg kg^{-1})	Statistical t-test result
Ba	12.8	11.8 – 13.8	19	***
Ca	20481	20260 - 20704	22200	***
Co	0.36	0.22 – 0.50	0.39	NS
Fe	776	742 - 810	1020	***
K	7573	7396 - 7750	8500	***
Li	3.16	2.98 – 3.33	2.4	***
Mg	2679	2648 - 2711	2870	***
Mn	62.9	50.8 – 75.0	58	NS
Pb	5.8	4.0 – 7.6	7.1	NS
Zn	25.5	19.1 – 31.9	20.6	NS

Table 6-18 Measured and certified values from standard nitric acid digestion with results from statistical t-test (assuming equal variances) at 95 % confidence level (NS = no significant difference; * = highly significant difference at $p \leq 0.01$ level)**

The analysis of the Bush branches and leaves certified reference material (NCS DC 73348) in Table 6-18 shows that the recoveries of some elements (barium, calcium, iron potassium and magnesium) were lower than the certified values while lithium recovery was higher than the certified value. Cobalt, manganese, lead and zinc recoveries were not significantly different to the certified values. As was discussed in Section 3.3, a single acid digestion might not be suitable for quantitative recovery of all elements. Despite the large excess of nitric acid and long boiling period used in this procedure, further digestion with perchloric acid could be required to obtain better recoveries.

The trace element digest used to analyse harvest 5 data was investigated in Chapter 3. The effectiveness of this digestion technique was discussed in Section 3.3.4).

6.3.5.2 Total nitrogen content of plant material

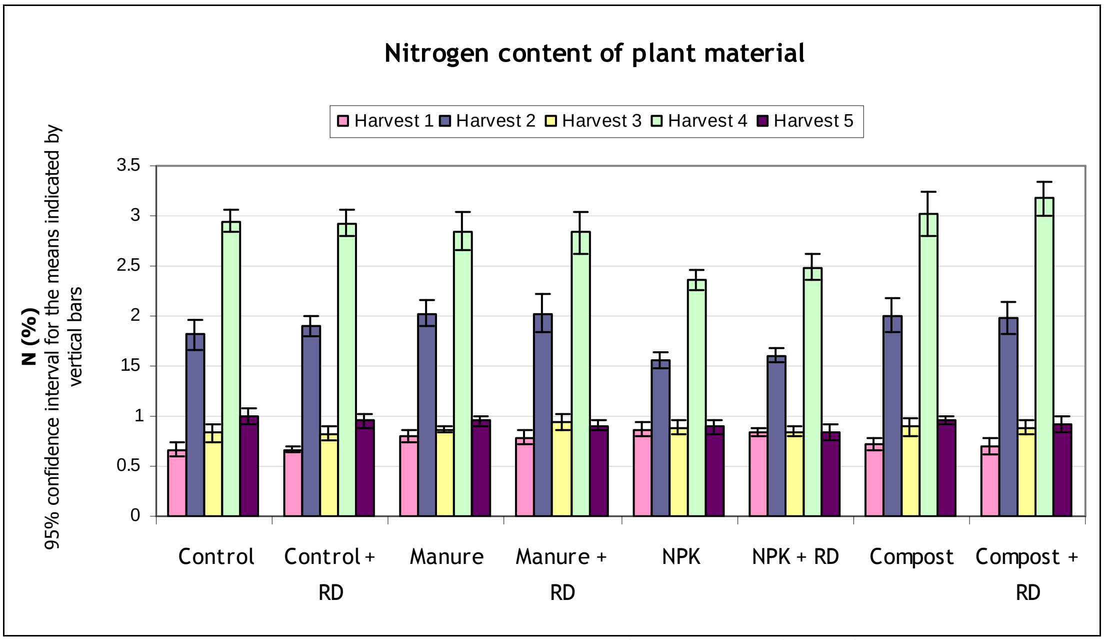


Figure 6-28 Nitrogen content (%) of plant material at 5 harvests

6.3.5.3 Statistical analysis of N content of plant material

Nitrogen content data was analysed with Minitab statistical software (version 15.1) using the general linear model command. The effects of amendment, rockdust and the amendment/rockdust interaction are summarized in Table 6-19.

	Nitrogen content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	NS	***	**
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-19 Effect of 3 factors on nitrogen content of plant material at individual harvests (NS = not significant; ** = significant effect at p ≤ 0.05 level; * = highly significant effect at p ≤ 0.01 level)**

The significant effects of amendment were further analysed using Tukey's least significant differences test at the 5 % level to find differences due to organic/inorganic amendment. Results are summarized in Table 6-20:

Amendment	Nitrogen content of plant material (%)				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	0.67 a	1.86 b	0.83 a	2.94 b	0.98 b
Manure	0.79 b	2.03 c	0.90 a	2.84 b	0.93 ab
NPK	0.85 b	1.58 a	0.87 a	2.42 a	0.87 a
Compost	0.71 a	1.99 bc	0.89 a	3.10 b	0.94 ab

Table 6-20 Effect of organic/inorganic amendments on nitrogen content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

These results show that there were differences in the N content of plant material due to amendment addition from the first harvest. In this harvest, the manure and NPK treatments produced higher plant N contents than the control and compost treated soil. In harvest 2, the manure treatment continued to produce the highest N contents whereas the NPK treated grass had the lowest levels. In harvest 3 there were no significant differences between treatments. At harvest 4 the NPK treatment gave lower N levels than all other treatments. In the final harvest, the control grass had the highest N content while the NPK treatment had the lowest.

6.3.5.4 Nitrogen uptake by plant material

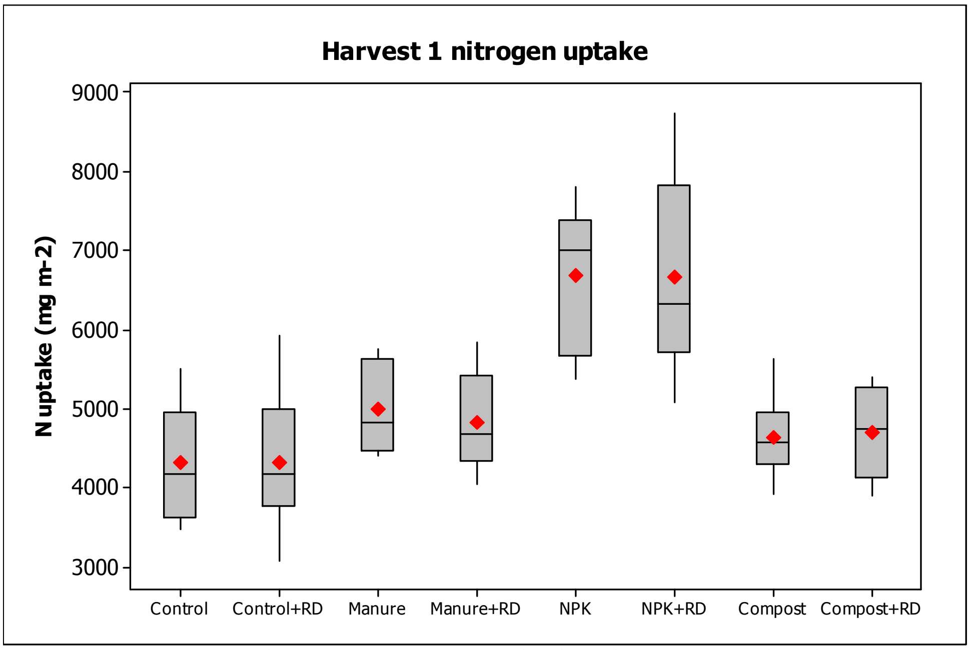


Figure 6-29 Boxplots of nitrogen uptake by plant material at harvest 1
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

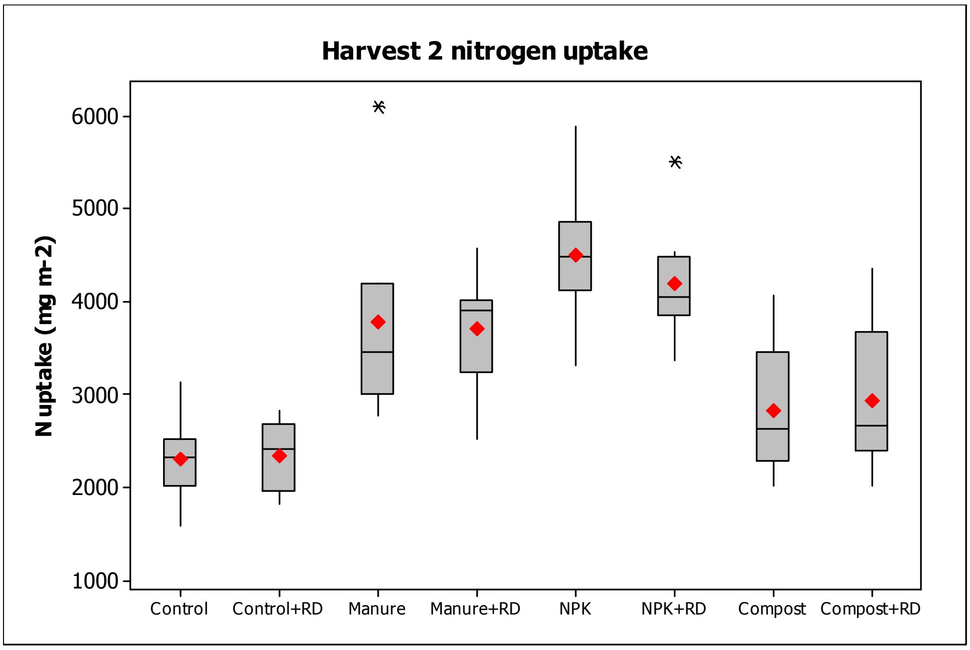


Figure 6-30 Boxplots of nitrogen uptake by plant material at harvest 2
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

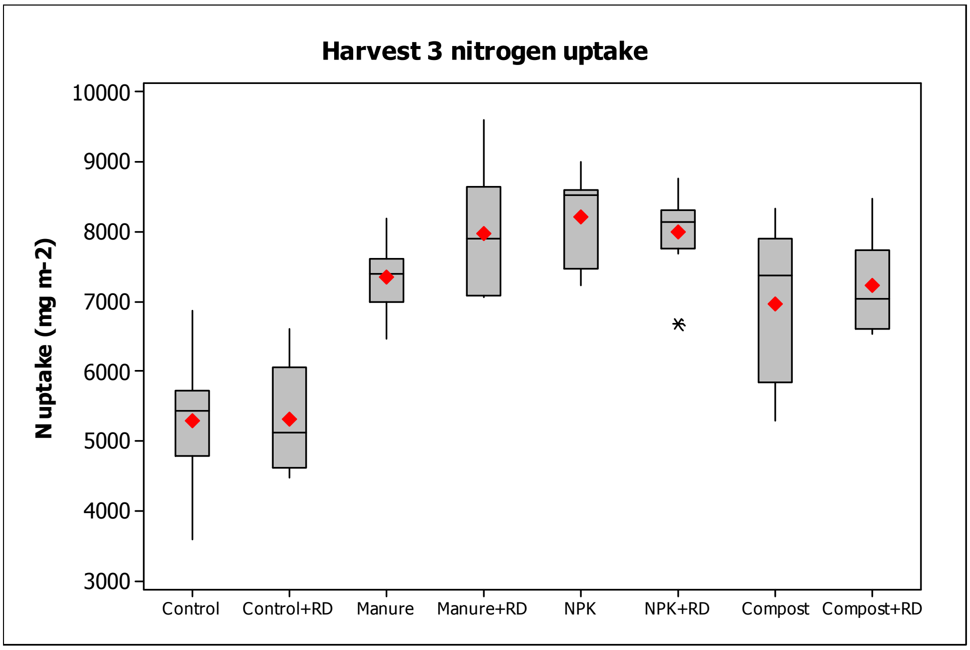


Figure 6-31 Boxplots of nitrogen uptake by plant material at harvest 3
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

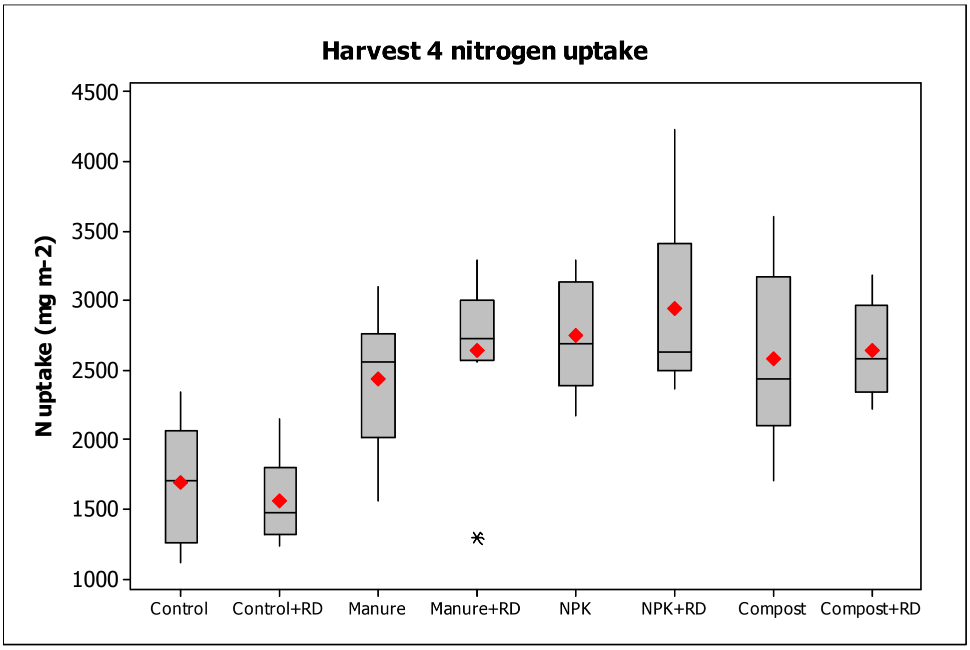


Figure 6-32 Boxplots of nitrogen uptake by plant material at harvest 4
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

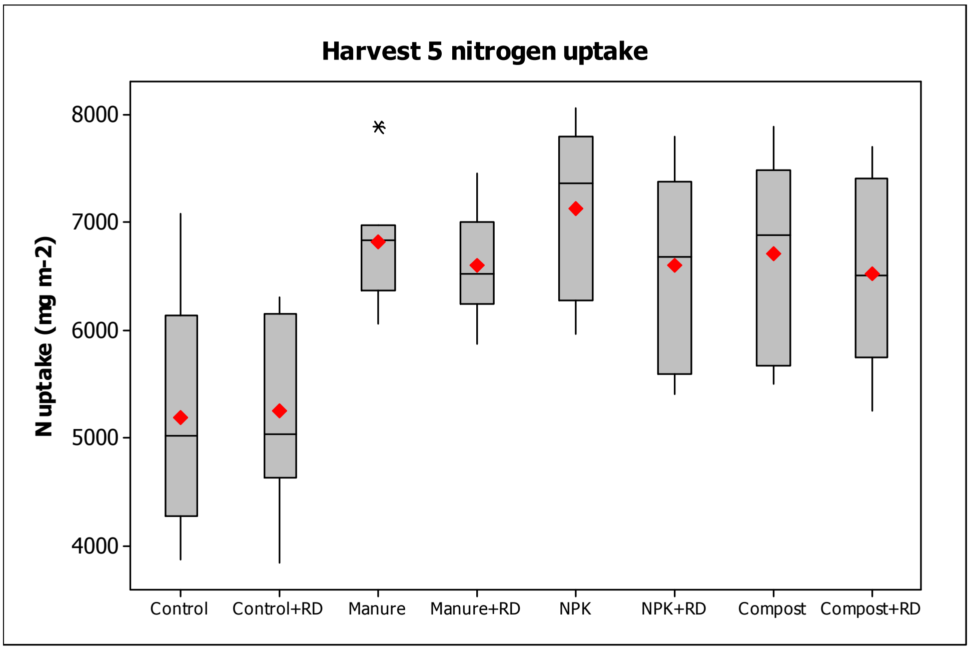


Figure 6-33 Boxplots of nitrogen uptake by plant material at harvest 5
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

6.3.5.5 Statistical analysis of N uptake by plant material

Nitrogen uptake was calculated using the yield and nutrient contents. The data was analysed with Minitab statistical software (version 15.1) using the general linear model command. The effects of amendment, rockdust and the amendment/rockdust interaction are summarized in Table 6-21.

	Nitrogen uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	***	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-21 Effect of 3 factors on nitrogen uptake by plant material at individual harvests (NS = not significant; * = highly significant effect at p ≤ 0.01 level)**

The significant effects of amendment were further analysed using Tukey's least significant differences test at the 5 % level to find differences due to organic/inorganic amendment. Results are summarized in Table 6-22:

Amendment	Nitrogen uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	4315 a	2315 a	5309 a	1631 a	5220 a
Manure	4907 a	3732 b	7667 bc	2545 b	6706 b
NPK	6679 b	4347 b	8119 c	2842 b	6862 b
Compost	4663 a	2875 a	7114 b	2611 b	6613 b

Table 6-22 Effect of organic/inorganic amendments on nitrogen uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-22 shows that the control treatment always gave statistically the lowest plant uptake of nitrogen while the NPK treatment always higher N uptake than the control. The manure treatment gave statistically the same N uptake as the control in the first harvest but significantly higher plant uptake from harvest 2 onwards. Plants grown on compost treated soil required until the third harvest to give higher uptake of N than the control. After harvest 4, plants grown on manure, NPK and compost treated soil produced the same level of N uptake.

6.3.5.6 Total phosphorus in plant material

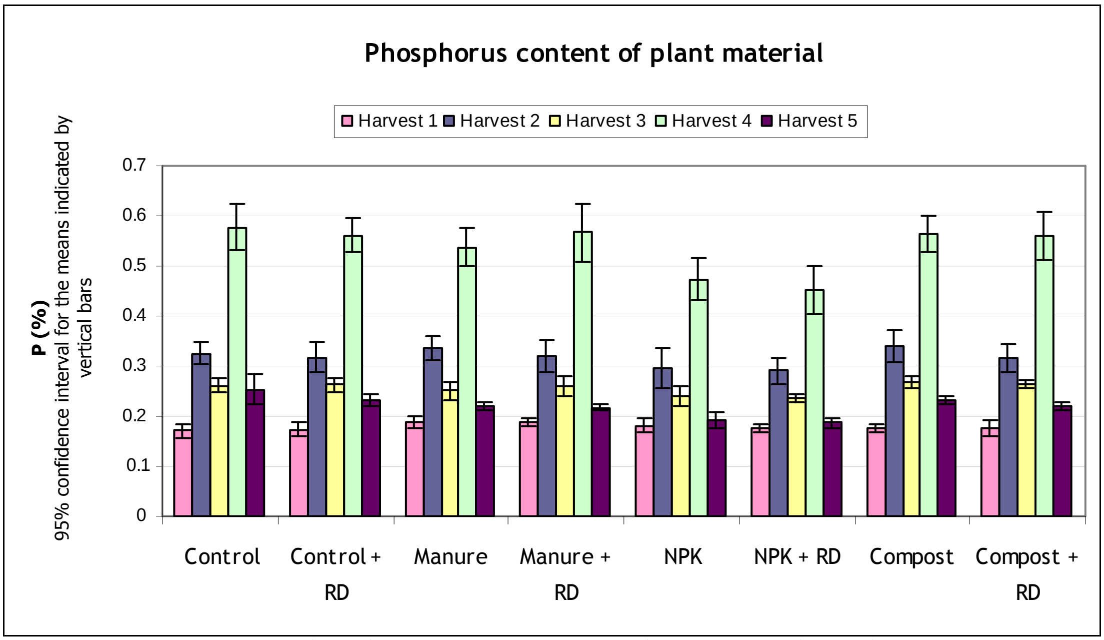


Figure 6-34 Phosphorus content (%) of plant material at 5 harvests

6.3.5.7 Statistical analysis of P content of plant material

Phosphorus content data was analysed with Minitab statistical software (version 15.1) using the general linear model command. The effects of amendment, rockdust and the amendment/rockdust interaction are summarized in Table 6-23.

	Phosphorus content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	**	NS	***	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-23 Effect of 3 factors on phosphorus content of plant material at individual harvests (NS = not significant; ** = significant effect at p ≤ 0.05 level; * = highly significant effect at p ≤ 0.01 level)**

The significant effect of amendment was further analysed using Tukey's least significant differences test at the 5 % level to find differences due to organic/inorganic amendment. Results are summarized in Table 6-24.

Amendment	Phosphorus content of plant material (%)				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	0.172 a	0.321 a	0.262 b	0.569 b	0.235 c
Manure	0.188 b	0.328 a	0.255 ab	0.552 b	0.218 b
NPK	0.178 ab	0.294 a	0.239 a	0.462 a	0.189 a
Compost	0.177 ab	0.327 a	0.266 b	0.562 b	0.225 bc

Table 6-24 Effect of organic/inorganic amendments on phosphorus content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test

The results in Table 6-24 show that at the first harvest, the manure treatment produced higher plant P content than the control. In harvest 2 there were no significant differences due to amendment type. At harvest 3, the control and compost treatments had higher P content in plant material than the NPK treatment. In harvest 4 the plant material had significantly low P content in the NPK treatment compared to all other treatments. At the last harvest, the NPK treatment had lowest plant P contents and the control had the highest while compost and manure were intermediate between the two extremes.

6.3.5.8 Phosphorus uptake by plant material

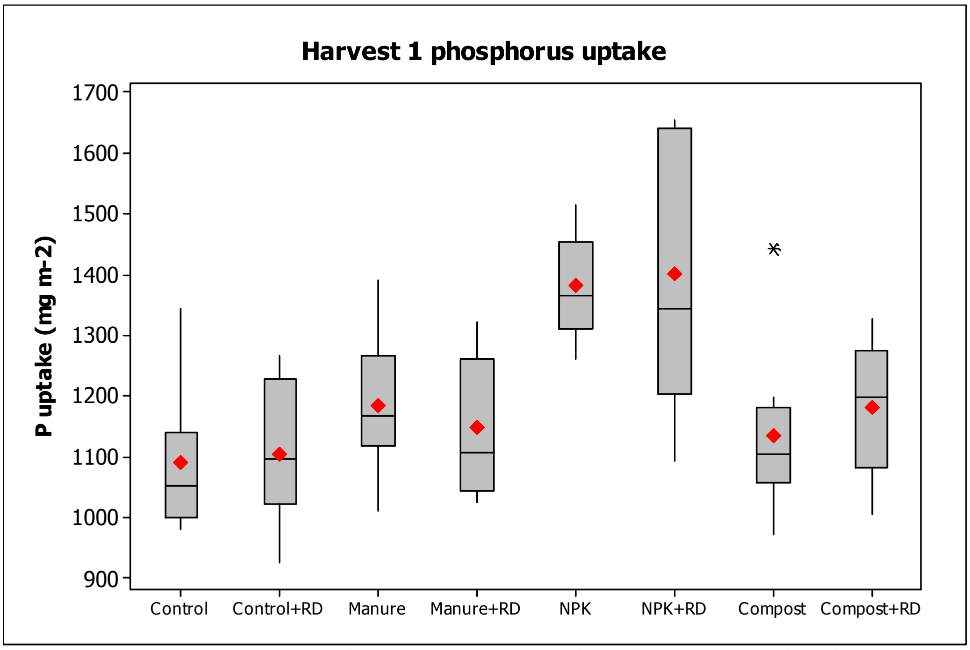


Figure 6-35 Boxplots of phosphorus uptake by plant material at harvest 1
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

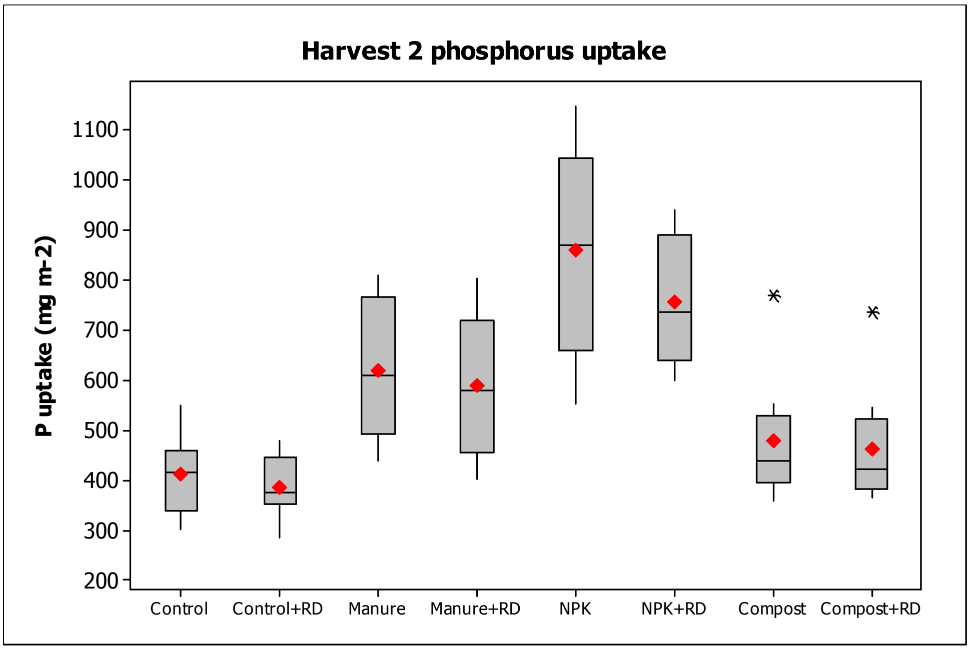


Figure 6-36 Boxplots of phosphorus uptake by plant material at harvest 2
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

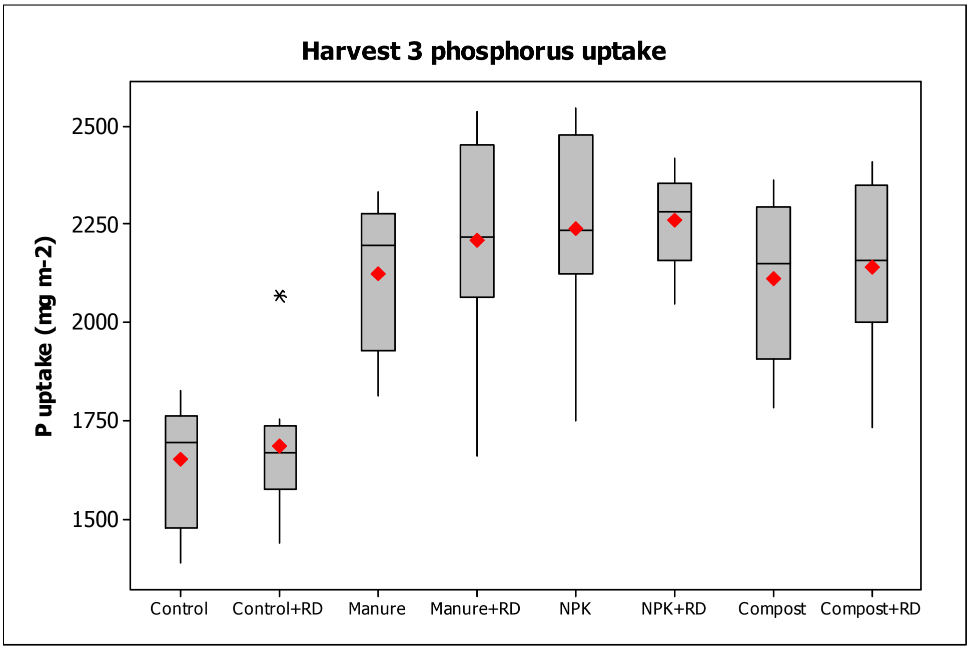


Figure 6-37 Boxplots of phosphorus uptake by plant material at harvest 3
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

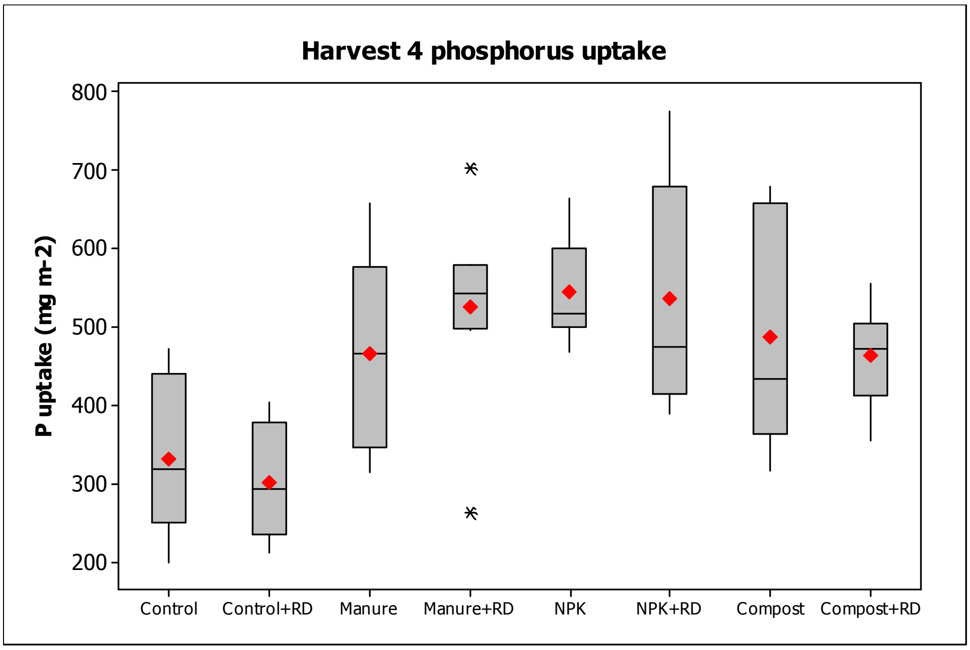


Figure 6-38 Boxplots of phosphorus uptake by plant material at harvest 4
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

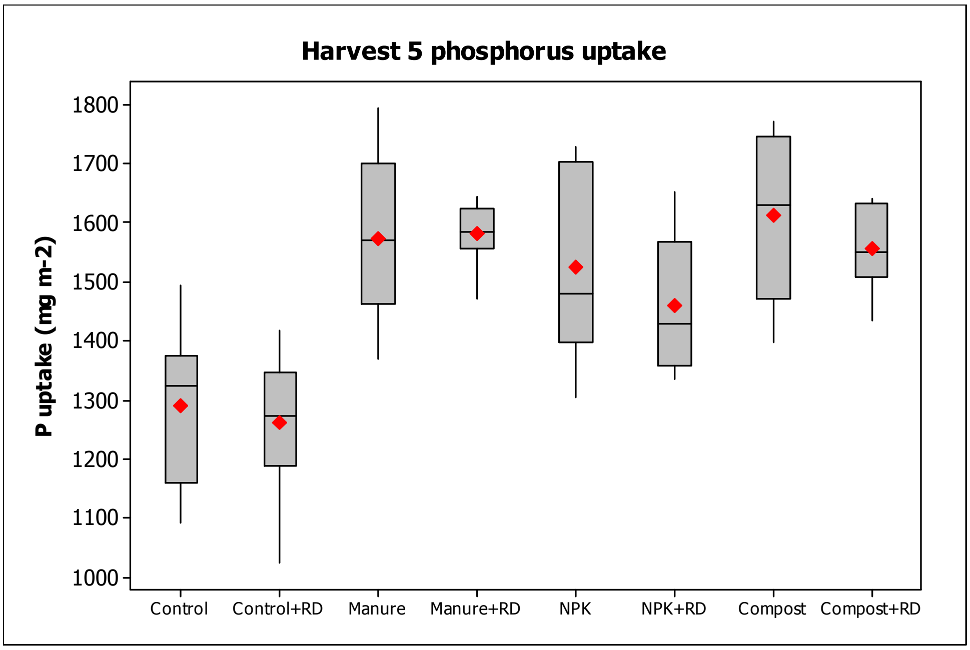


Figure 6-39 Boxplots of phosphorus uptake by plant material at harvest 5
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

6.3.5.9 Statistical analysis of P uptake by plant material

Phosphorus uptake was calculated using the yield and nutrient contents. The data was analysed with Minitab statistical software (version 15.1) using the general linear model command. The effects of amendment, rockdust and the amendment/rockdust interaction are summarized in Table 6-25.

	Phosphorus uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	***	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-25 Effect of 3 factors on phosphorus uptake by plant material at individual harvests (NS = not significant; * = highly significant effect at p ≤ 0.01 level)**

The significant effects of amendment were further analysed using Tukey's least significant differences test at the 5 % level to find differences due to organic/inorganic amendment. Results are summarized in Table 6-26:

Amendment	Phosphorus uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	1098 a	399 a	1669 a	318 a	1261 a
Manure	1168 a	604 b	2168 b	496 b	1577 b
NPK	1392 b	808 c	2249 b	541 b	1493 b
Compost	1159 a	471 a	2127 b	476 b	1584 b

Table 6-26 Effect of organic/inorganic amendments on phosphorus uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-26 shows that the control gave lowest level of plant uptake of phosphorus across all harvests. The NPK treatment gave the highest P uptake from the first harvest and continued throughout the trial. The plants grown on manure treated soil required until the second harvest to 'catch up' with those in the NPK treatment. The uptake of P in compost treated soil took even longer than the manure treatment to reach a level of uptake similar to that of the NPK treatment. After harvest 3, the manure, NPK and compost treated soils all had statistically the same plant P uptake and were all significantly higher than the control.

6.3.5.10 Total potassium in plant material

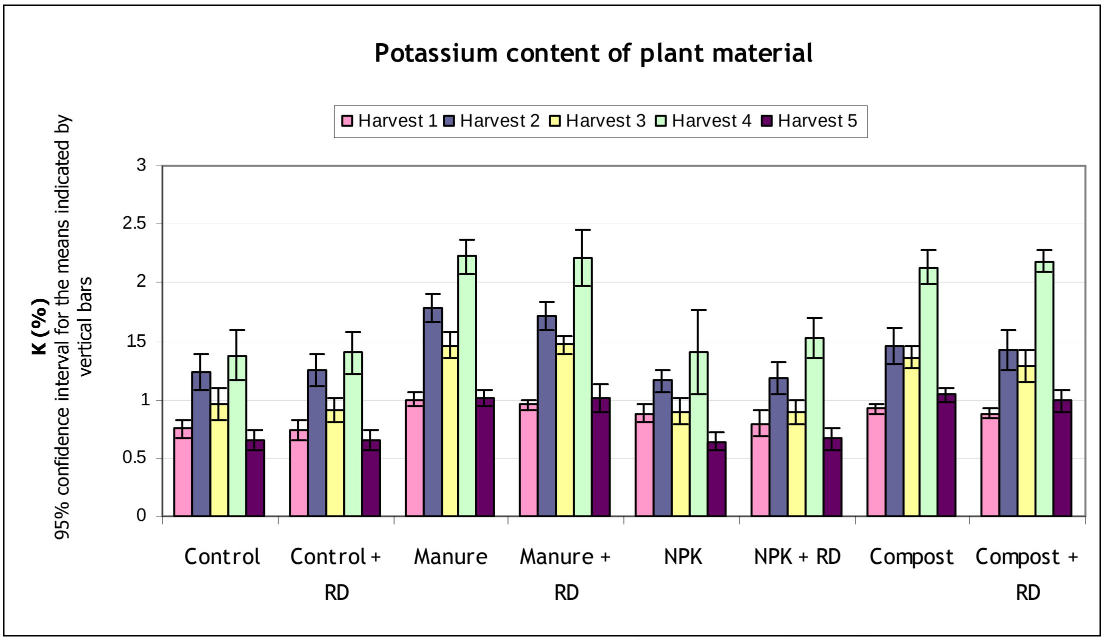


Figure 6-40 Potassium content (%) of plant material at 5 harvests

6.3.5.11 Statistical analysis of K content of plant material

Potassium content data was analysed with Minitab statistical software (version 15.1) using the general linear model command. The effects of amendment, rockdust and the amendment/rockdust interaction are summarized in Table 6-27.

	Potassium content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	***	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-27 Effect of 3 factors on potassium content of plant material at individual harvests (NS = not significant; * = highly significant effect at p ≤ 0.01 level)**

The significant effects of amendment were further analysed using Tukey's least significant differences test at the 5 % level to find differences due to organic/inorganic amendment. Results are summarized in Table 6-28:

Amendment	Potassium content of plant material (%)				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	0.743 a	1.251 a	0.938 a	1.385 a	0.654 a
Manure	0.976 c	1.749 c	1.465 c	2.217 b	1.010 b
NPK	0.836 b	1.171 a	0.893 a	1.467 a	0.652 a
Compost	0.900 bc	1.442 b	1.322 b	2.158 b	1.012 b

Table 6-28 Effect of organic/inorganic amendments on potassium content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-28 shows that the control plots always gave plants with the lowest potassium levels. In the first 3 harvests, potassium content was significantly highest in manure treated plots. The compost treatment gave plants with higher K content than the control in all harvests and by harvest 4, the K content of plants grown on compost and manure treated plots was statistically the same. The NPK treatment gave plant K contents that were higher than the control at harvest 1 only. After this, the K content of plants was statistically the same as the control and significantly lower than plants grown on soil treated with both compost and manure.

6.3.5.12 Potassium uptake by plant material

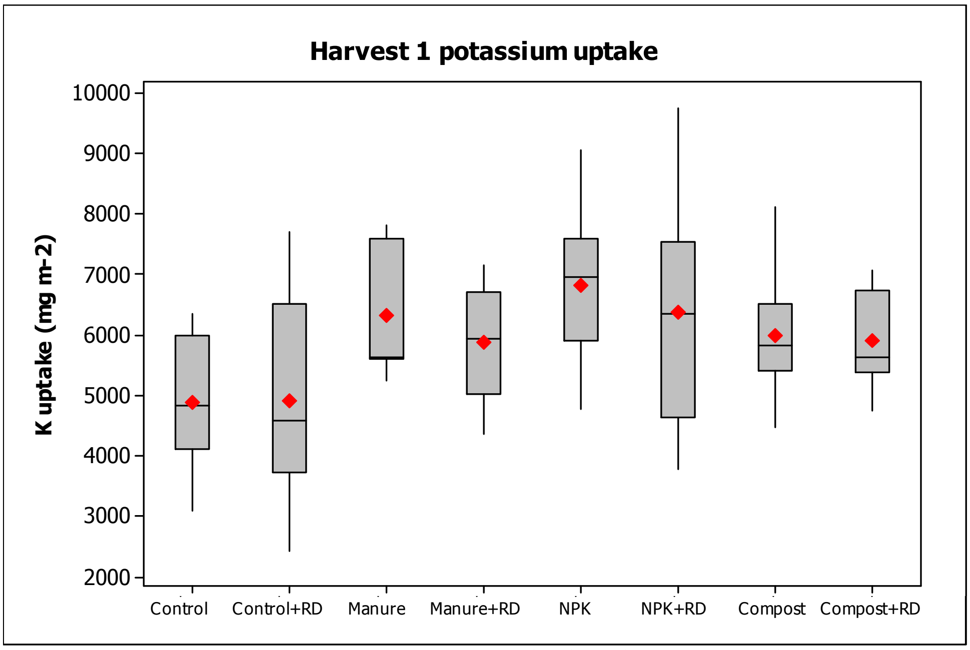


Figure 6-41 Boxplots of potassium uptake by plant material at harvest 1
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

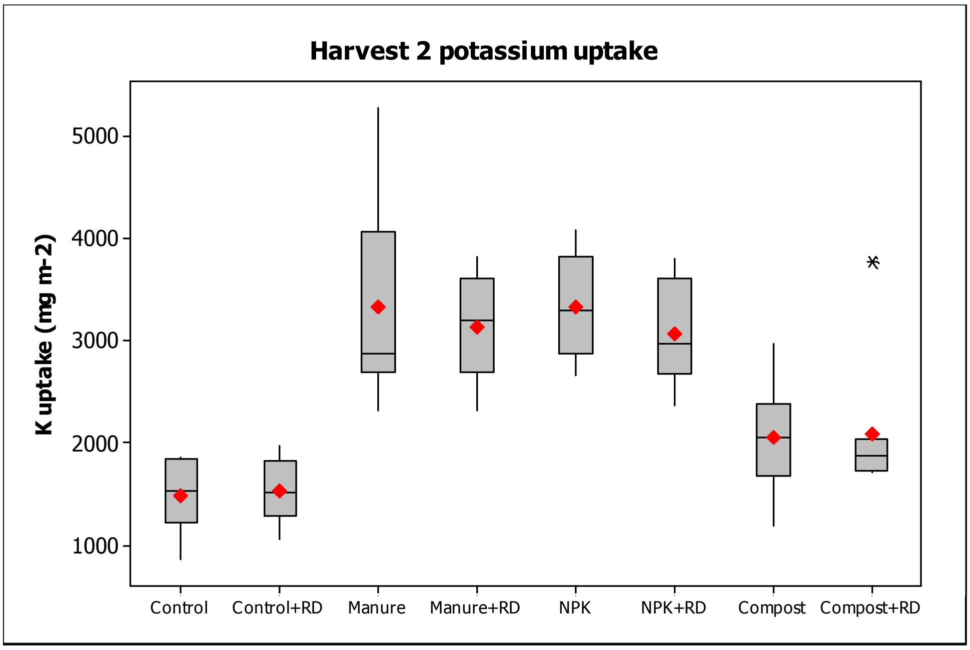


Figure 6-42 Boxplots of potassium uptake by plant material at harvest 2
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

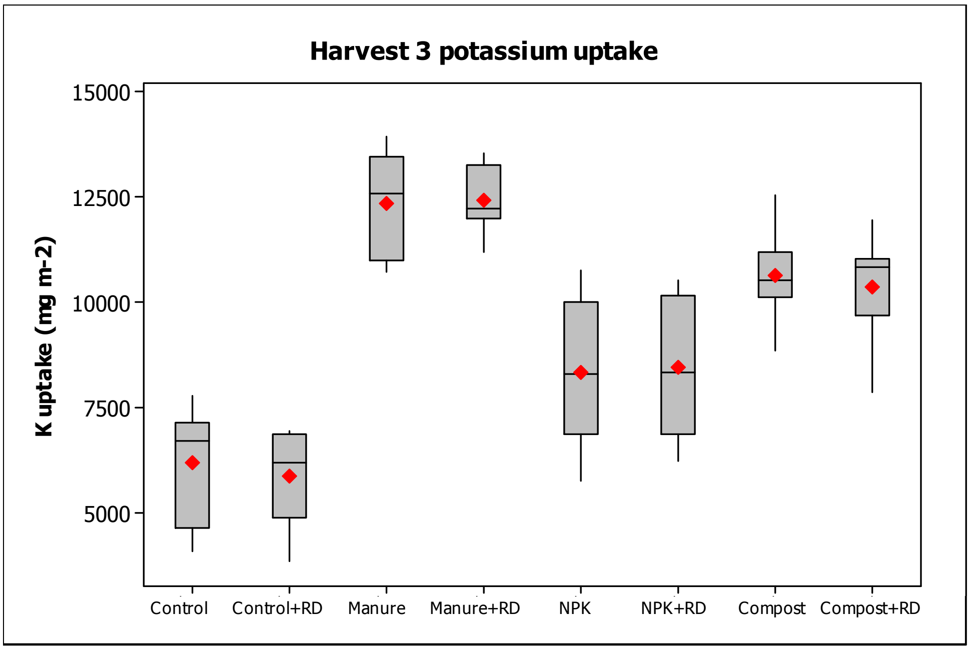


Figure 6-43 Boxplots of potassium uptake by plant material at harvest 3
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

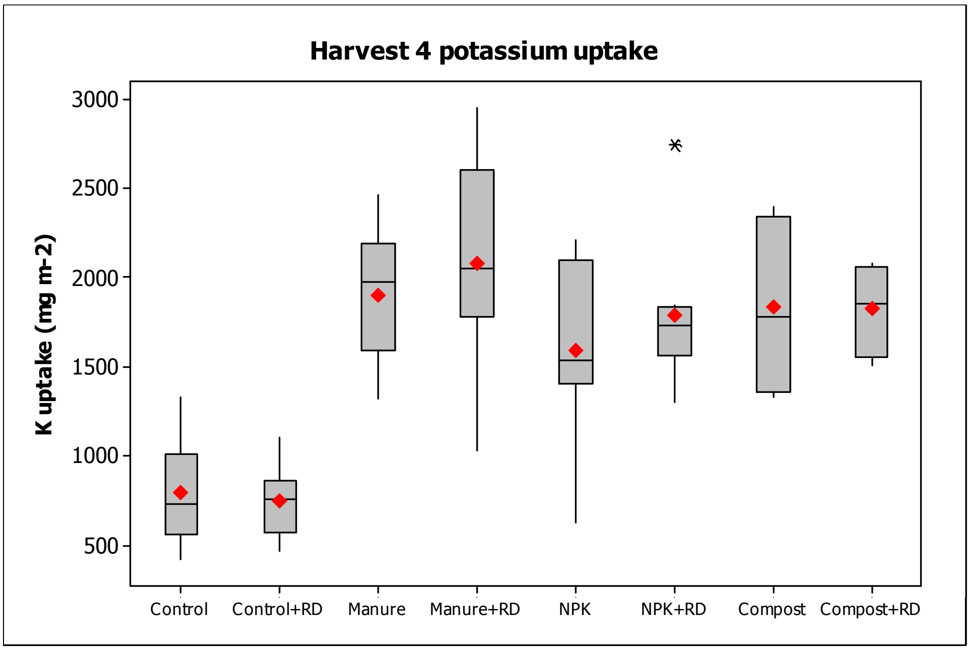


Figure 6-44 Boxplots of potassium uptake by plant material at harvest 4
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

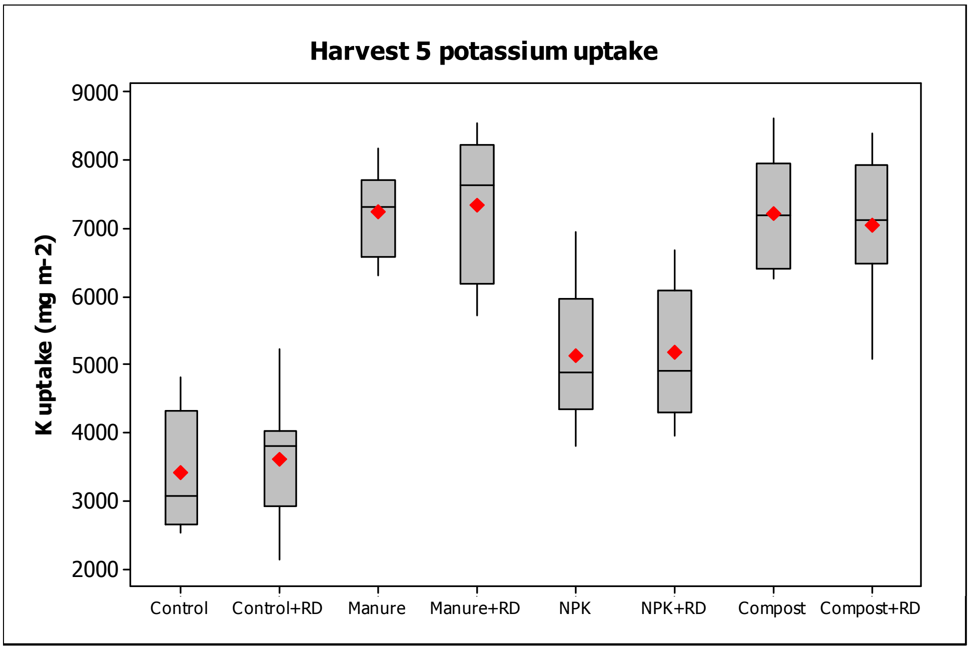


Figure 6-45 Boxplots of potassium uptake by plant material at harvest 5
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

6.3.5.13 Statistical analysis of K uptake by plant material

Potassium uptake was calculated using the yield and nutrient contents. The data was analysed with Minitab statistical software (version 15.1) using the general linear model command. The effects of amendment, rockdust and the amendment/rockdust interaction are summarized in Table 6-29.

	Potassium uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	***	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-29 Effect of 3 factors on potassium uptake by plant material at individual harvests (NS = not significant; * = highly significant effect at $p \leq 0.01$ level)**

The significant effects of amendment were further analysed using Tukey's least significant differences test at the 5 % level to find differences due to organic/inorganic amendment. Results are summarized in Table 6-30:

Amendment	Potassium uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	4900 a	1512 a	6041 a	773.1 a	4199 a
Manure	6096 b	3231 b	12422 d	1991 b	7289 b
NPK	6604 b	3197 b	8433 b	1690 b	5159 a
Compost	5945 b	2079 a	10524 c	1828 b	7138 b

Table 6-30 Effect of organic/inorganic amendments on potassium uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-30 shows that the control treatment gave statistically the lowest plant potassium uptakes across all harvests. The manure treatment always gave higher uptake compared to the control. P uptake by plants grown in NPK treated soil was significantly higher than the control in all harvests until harvest 5. The compost treatment gave higher plant potassium uptake than the control except in harvest 2 when they were not statistically different. Table 6-30 also shows that the manure and compost treatments gave significantly higher P uptake than the NPK treatment in harvests 3 and 5.

6.3.5.14 Barium content of plant material

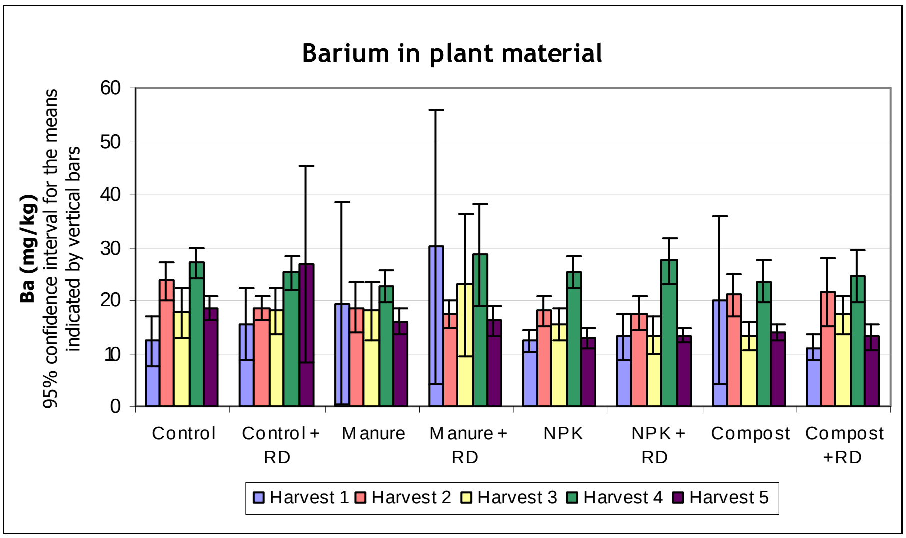


Figure 6-46 Barium in plant material at 5 harvests

6.3.5.15 Statistical analysis of Ba content of plant material

	Barium content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	NS	NS	NS	NS	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-31 Effect of 3 factors on barium content of plant material at individual harvests (NS = not significant; * = highly significant effect at $p \leq 0.01$ level)**

Amendment	Barium content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	13.92 a	20.96 a	17.85 a	26.15 a	22.66 b
Manure	24.72 a	18.02 a	20.44 a	25.63 a	16.02 b
NPK	12.72 a	17.76 a	14.39 a	26.39 a	13.15 a
Compost	15.47 a	21.21 a	15.19 a	24.09 a	13.49 ab

Table 6-32 Effect of organic/inorganic amendments on barium content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test

Table 6-31 shows that there was no significant effect of amendment on barium content of plant material until harvest 5. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest. Table 6-32 shows that the NPK treated plots produced lower plant Ba contents than the control and manure treatments at harvest 5.

6.3.5.16 Statistical analysis of Ba uptake by plant material

	Barium uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	NS	***	**	***	NS
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-33 Effect of 3 factors on barium uptake by plant material at individual harvests (NS = not significant; ** = significant effect at p ≤ 0.05 level; * = highly significant effect at p ≤ 0.01 level)**

Amendment	Barium uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	9.07 a	2.53 a	11.34 a	1.46 a	11.89 a
Manure	15.45 a	3.37 a	17.31 b	2.37 bc	11.56 a
NPK	9.98 a	4.93 b	13.42 ab	3.13 c	10.38 a
Compost	10.03 a	3.11 a	12.08 ab	2.02 ab	9.43 a

Table 6-34 Effect of organic/inorganic amendments on barium uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-33 shows that barium uptake was significantly affected by amendment addition in harvests 2, 3 and 4. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest. Table 6-34 shows that the NPK treatment gave a significantly higher barium uptake than the control in harvests 2 and 4. At harvests 3 and 4, the plant material grown on manure treated soil gave significantly higher uptake than the control. The compost treatment never increased plant uptake of barium higher than the uptake shown in the control.

6.3.5.17 Calcium content of plant material

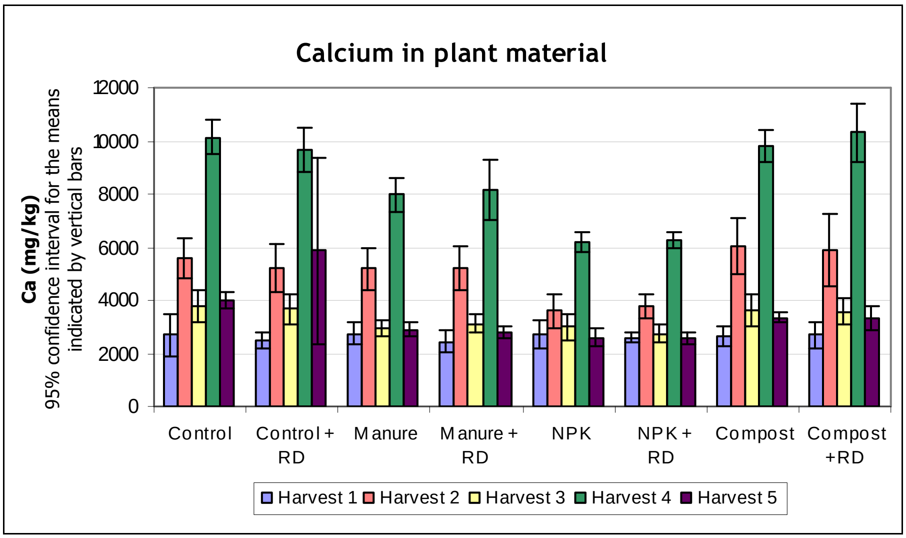


Figure 6-47 Calcium in plant material at 5 harvests

6.3.5.18 Statistical analysis of Ca content of plant material

	Calcium content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	NS	***	***	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-35 Effect of 3 factors on calcium content of plant material at individual harvests (NS = not significant; * = highly significant effect at p ≤ 0.01 level)**

Amendment	Calcium content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	2594 a	5372 b	3723 b	9897 c	4924 c
Manure	2591 a	5192 b	3027 a	8065 b	2826 a
NPK	2652 a	3709 a	2868 a	6229 a	2588 a
Compost	2660 a	5965 b	3589 b	10054 c	3334 b

Table 6-36 Effect of organic/inorganic amendments on calcium content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-35 shows that calcium content of plant material was significantly affected by amendment addition in harvests 2 – 5. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest. Table 6-36 shows that the NPK treatment produced plant material with significantly lower calcium content than the control after harvest 1. The manure treatment gave lower plant calcium content than the control in harvests 3, 4 and 5. Compost treated soil produced plant material with statistically the same calcium content as the control in harvests 1, 2, 3 and 4.

6.3.5.19 Statistical analysis of Ca uptake by plant material

	Calcium uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	NS	***	NS
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-37 Effect of 3 factors on calcium uptake by plant material at individual harvests (NS = not significant; * = highly significant effect at p ≤ 0.01 level)**

Amendment	Calcium uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	1632 a	649.6 a	2373 a	551.3 a	2608 a
Manure	1584 a	951.0 b	2564 a	721.5 b	2041 a
NPK	2063 b	1021 b	2681 a	734.0 b	2044 a
Compost	1723 a	852.6 ab	2854 a	846.4 b	2346 a

Table 6-38 Effect of organic/inorganic amendments on calcium uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-37 shows that calcium uptake by plant material was significantly affected by amendment addition in harvests 1, 2 and 4. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest. The differences due to amendment are shown in Table 6-38. This analysis shows that calcium uptake by plants grown on NPK treated soil was higher than the uptake in the control in harvests 1, 2 and 4. The manure treatment gave higher calcium uptake than the control in the autumn harvests only (harvest 2 and 4). The compost treatment produced higher calcium uptakes than the control in harvest 4 only.

6.3.5.20 Copper content of plant material

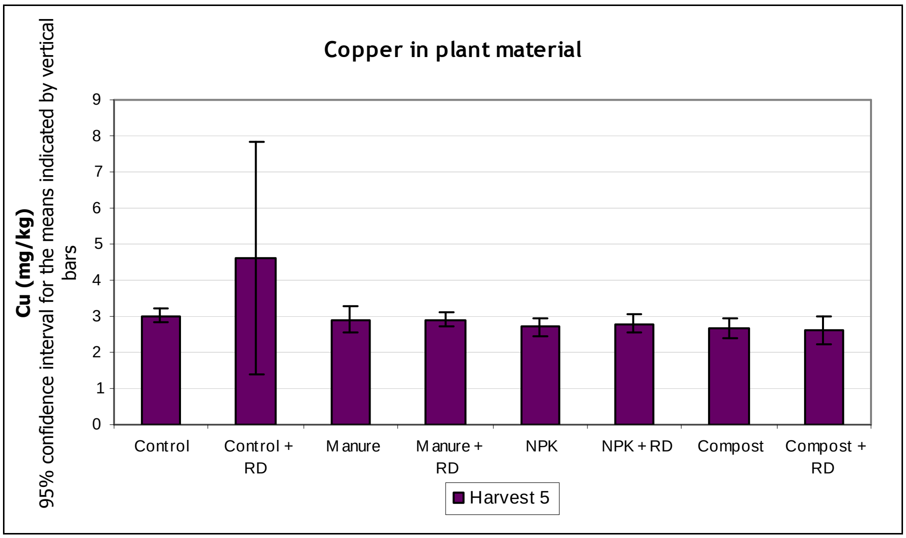


Figure 6-48 Copper in plant material at Harvest 5

6.3.5.21 Statistical analysis of Cu content of plant material

	Copper content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	bdl	bdl	bdl	bdl	**
Rockdust	bdl	bdl	bdl	bdl	NS
Amendment*rockdust	bdl	bdl	bdl	bdl	NS

Table 6-39 Effect of 3 factors on copper content of plant material at individual harvests (NS = not significant; ** = significant effect at $p \le 0.05$ level; bdl = below detection limit)

Amendment	Copper content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	< 5.00	< 5.00	< 5.00	< 5.00	3.81 b
Manure	< 5.00	< 5.00	< 5.00	< 5.00	2.90 ab
NPK	< 5.00	< 5.00	< 5.00	< 5.00	2.75 ab
Compost	< 5.00	< 5.00	< 5.00	< 5.00	2.65 a

Table 6-40 Effect of organic/inorganic amendments on copper content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-39 shows that copper was only measurable in the trace element digest that was used to analyse harvest 5 plant material. In this harvest, there was a significant effect of amendment on the copper content of plant material. Rockdust addition did not significantly affect copper in plant material and there was no significant interaction on amendment and rockdust. The analysis in Table 6-40 shows that the control gave plant material with significantly higher copper contents than the compost treated plots.

6.3.5.22 Statistical analysis of Cu uptake by plant material

	Copper uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	bdl	bdl	bdl	bdl	NS
Rockdust	bdl	bdl	bdl	bdl	NS
Amendment*rockdust	bdl	bdl	bdl	bdl	NS

Table 6-41 Effect of 3 factors on copper uptake by plant material at individual harvests (NS = not significant; bdl = below detection limit)

Amendment	Copper uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	bdl	bdl	bdl	bdl	2.02 a
Manure	bdl	bdl	bdl	bdl	2.10 a
NPK	bdl	bdl	bdl	bdl	2.18 a
Compost	bdl	bdl	bdl	bdl	1.87 a

Table 6-42 Effect of organic/inorganic amendments on copper uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test (bdl = below detection limit)

Table 6-41 shows that copper uptake by plant material could not be measured in harvests 1 – 4. Copper uptake by plant material was not significantly affected by any of the three factors investigated in Table 6-41.

6.3.5.23 Iron content of plant material

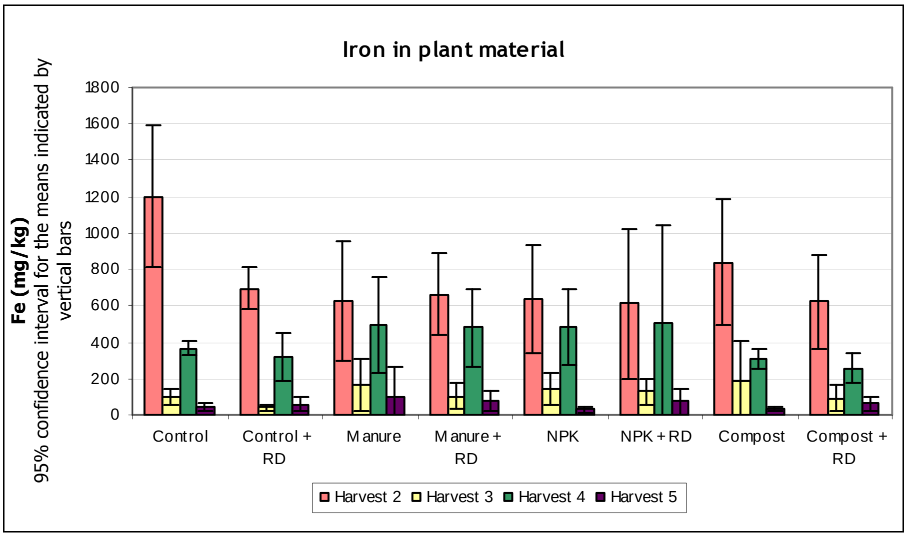


Figure 6-49 Iron in plant material at 4 harvests

6.3.5.24 Statistical analysis of Fe content of plant material

	Iron content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	bdl	NS	NS	NS	NS
Rockdust	bdl	NS	NS	NS	NS
Amendment*rockdust	bdl	NS	NS	NS	NS

Table 6-43 Effect of 3 factors on iron content of plant material at individual harvests (NS = not significant; bdl = below detection limit)

Amendment	Iron content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	< 5.5	930 a	69.8 a	340 a	50.8 a
Manure	< 5.5	643 a	133 a	484 a	90.5 a
NPK	< 5.5	622 a	135 a	496 a	51.4 a
Compost	< 5.5	730 a	138 a	281 a	49.2 a

Table 6-44 Effect of organic/inorganic amendments on iron content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-43 shows that the plant iron content was not measurable in harvest 1. In harvests 2 – 5, there were no significant effects of amendment or rockdust on iron content of plant material.

6.3.5.25 Statistical analysis of Fe uptake by plant material

	Iron uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	bdl	NS	NS	NS	NS
Rockdust	bdl	NS	NS	NS	NS
Amendment*rockdust	bdl	NS	NS	NS	NS

Table 6-45 Effect of 3 factors on iron uptake by plant material at individual harvests (NS = not significant; bdl = below detection limit)

Amendment	Iron uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	bdl	113 a	44.5 a	19.0a	4199 a
Manure	bdl	122 a	109 a	40.2 a	7289 a
NPK	bdl	180 a	131 a	71.0 a	5159 a
Compost	bdl	110 a	112 a	23.4 a	7138 a

Table 6-46 Effect of organic/inorganic amendments on iron uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test (bdl = below detection limit)

Table 6-45 shows that uptake of iron was not measurable in harvest 1 plant material. In harvests 2 – 5, there were no significant effects of amendment or rockdust on iron uptake by plant material.

6.3.5.26 Lithium content of plant material

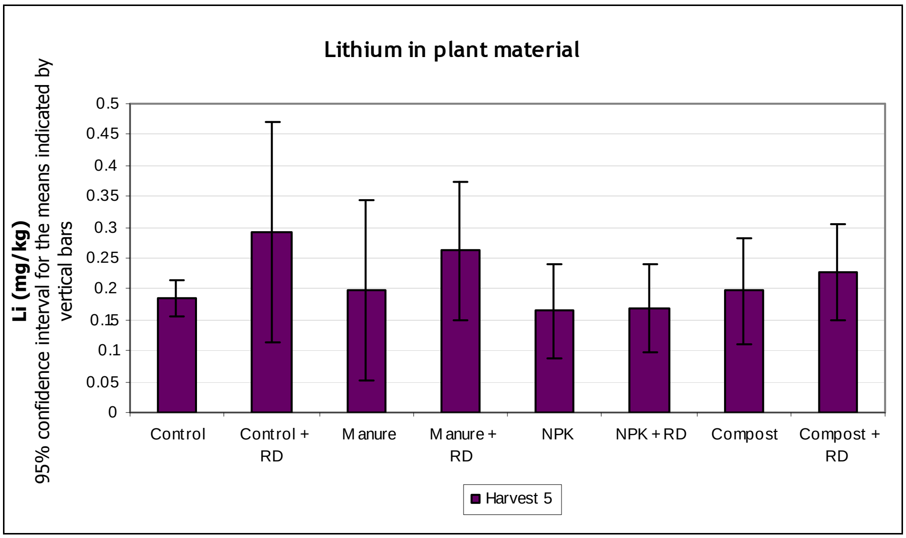


Figure 6-50 Lithium in plant material at Harvest 5

6.3.5.27 Statistical analysis of Li content of plant material

	Lithium content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	bdl	bdl	bdl	bdl	NS
Rockdust	bdl	bdl	bdl	bdl	NS
Amendment*rockdust	bdl	bdl	bdl	bdl	NS

Table 6-47 Effect of 3 factors on lithium content of plant material at individual harvests (NS = not significant; bdl = below detection limit)

Amendment	Lithium content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	< 0.50	< 0.50	< 0.50	< 0.50	0.24 a
Manure	< 0.50	< 0.50	< 0.50	< 0.50	0.23 a
NPK	< 0.50	< 0.50	< 0.50	< 0.50	0.17 a
Compost	< 0.50	< 0.50	< 0.50	< 0.50	0.21 a

Table 6-48 Effect of organic/inorganic amendments on lithium content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-47 shows that the plant lithium content was only measurable in the trace element digest used to analyse harvest 5 plant material. In harvests 5, there were no significant effects of amendment or rockdust on lithium content of plant material.

6.3.5.28 Statistical analysis of Li uptake by plant material

	Lithium uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	bdl	bdl	bdl	bdl	NS
Rockdust	bdl	bdl	bdl	bdl	NS
Amendment*rockdust	bdl	bdl	bdl	bdl	NS

Table 6-49 Effect of 3 factors on lithium uptake by plant material at individual harvests (NS = not significant; bdl = below detection limit)

Amendment	Lithium uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	bdl	bdl	bdl	bdl	0.13 a
Manure	bdl	bdl	bdl	bdl	0.17 a
NPK	bdl	bdl	bdl	bdl	0.13 a
Compost	bdl	bdl	bdl	bdl	0.15 a

Table 6-50 Effect of organic/inorganic amendments on lithium uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey’s LSD test (bdl = below detection limit)

Table 6-49 shows that plant uptake of lithium was only measurable in the trace element digest used to analyse harvest 5 plant material. In harvests 5, there were no significant effects of amendment or rockdust on lithium uptake by plant material.

6.3.5.29 Magnesium content of plant material

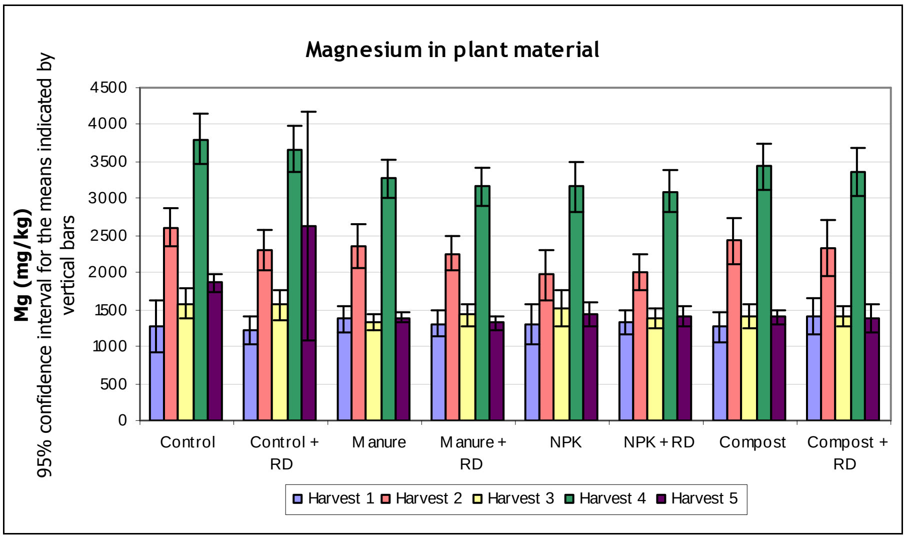


Figure 6-51 Magnesium in plant material at 5 harvests

6.3.5.30 Statistical analysis of Mg content of plant material

	Magnesium content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	NS	***	**	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-51 Effect of 3 factors on magnesium content of plant material at individual harvests (NS = not significant; ** = significant effect at p ≤ 0.05 level; * = highly significant effect at p ≤ 0.01 level)**

Amendment	Magnesium content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	1244 a	2451 b	1572 b	3738 b	2251 b
Manure	1340 a	2307 ab	1374 a	3214 a	1356 a
NPK	1316 a	1989 a	1446 ab	3134 a	1429 a
Compost	1339 a	2379 b	1406 ab	3399 ab	1391 a

Table 6-52 Effect of organic/inorganic amendments on magnesium content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-51 shows that the magnesium content of plant material was significantly affected by amendment type in harvests 2 – 5. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest. Table 6-52 shows that the NPK treatment produced plants with lower magnesium contents than the control in harvests 2, 4 and 5. Manure treated soil gave lower plant Mg contents than the control in harvests 3 – 5. The compost treatment only gave plant material with lower magnesium contents than the control in harvest 5.

6.3.5.31 Statistical analysis of Mg uptake by plant material

	Magnesium uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	***	***	NS
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-53 Effect of 3 factors on magnesium uptake by plant material at individual harvests (NS = not significant; * = highly significant effect at $p \leq 0.01$ level)**

Amendment	Magnesium uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	786.9 a	295.9 a	1003 a	207.6 a	1191 a
Manure	826.7 a	426.2 b	1165 a	288.7 b	980.0 a
NPK	1025 b	549.2 c	1351 b	373.0 c	1130 a
Compost	868.5 ab	346.6 ab	1127 a	286.9 b	980.2 a

Table 6-54 Effect of organic/inorganic amendments on magnesium uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test

Table 6-53 shows that magnesium uptake by plant material was significantly affected by amendment type in harvests 1 – 4. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest. Table 6-54 shows that the NPK treated plots gave higher plant uptake of magnesium in harvests 1 – 4. The manure treated plots gave significantly higher Mg uptake than the control in the autumn harvests (harvests 2 and 4) only. The compost treatment gave higher plant uptake of magnesium in harvest 4 only.

6.3.5.32 Manganese content of plant material

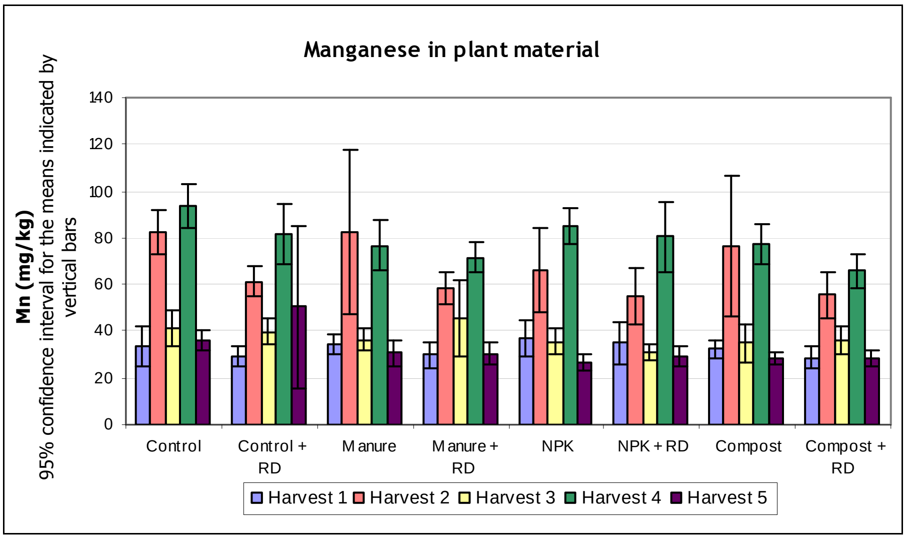


Figure 6-52 Manganese in plant material at 5 harvests

6.3.5.33 Statistical analysis of Mn content of plant material

	Manganese content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	NS	NS	NS	***	***
Rockdust	NS	***	NS	**	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-55 Effect of 3 factors on manganese content of plant material at individual harvests (NS = not significant; ** = significant effect at $p \leq 0.05$ level; * = highly significant effect at $p \leq 0.01$ level)**

Amendment	Manganese content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	31.24 a	71.23 a	40.62 a	87.65 b	43.45 b
Manure	32.23 a	70.30 a	40.95 a	74.23 ab	30.56 ab
NPK	36.00 a	60.45 a	33.29 a	82.64 ab	27.97 a
Compost	30.55 a	65.92 a	35.34 a	71.69 a	28.32 a

Table 6-56 Effect of organic/inorganic amendments on manganese content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Rockdust addition	Manganese content of plant material (mg kg^{-1})	
	Harvest 2	Harvest 4
No rockdust added	76.60 b	83.20 b
Rockdust added	57.52 a	74.90 a

Table 6-57 Effect of rockdust addition on manganese content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-55 shows that there were significant effects on manganese content of plant material due to amendment type in harvests 4 and 5 and due to rockdust in harvests 2 and 4. Table 6-56 shows that plants grown on the control were significantly higher in manganese than those grown on compost treated soil in harvests 4 and 5. The manganese content of the control plant material was also higher than the NPK treatment in harvest 5. Table 6-57 shows that in both harvest 2 and 4 the addition of rockdust gave significantly lower plant manganese contents than the plots that had no rockdust applied.

6.3.5.34 Statistical analysis of Mn uptake by plant material

	Manganese uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	***	***	**	***	NS
Rockdust	NS	***	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-58 Effect of 3 factors on manganese uptake by plant material at individual harvests (NS = not significant; ** = significant effect at p ≤ 0.05 level; * = highly significant effect at p ≤ 0.01 level)**

Amendment	Manganese uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	20.27 a	8.56 a	25.78 a	4.87 a	22.98 a
Manure	19.92 a	13.49 ab	34.65 b	6.53 a	22.17 a
NPK	27.95 b	16.98 b	31.40 ab	10.06 b	22.07 a
Compost	19.97 a	9.87 a	27.91 ab	6.02 a	19.88 a

Table 6-59 Effect of organic/inorganic amendments on manganese uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Rockdust addition	Manganese uptake by plant material (mg m^{-2})
	Harvest 2
No rockdust added	14.43 b
Rockdust added	10.20 a

Table 6-60 Effect of rockdust addition on manganese uptake by plant material at harvest 2 Values followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-58 shows that uptake of manganese was influenced by amendment type in harvests 1 – 4. Table 6-59 shows that the manure treatment only gave higher plant uptake of Mn than the control in harvest 3. The NPK treatment gave higher plant uptake compared to the control in harvests 1, 2 and 4. The compost treatment did not increase plant Mn uptake in any of the harvests compared to the control. Rockdust addition only affected manganese uptake in harvest 2 where it was shown to reduce plant manganese uptake (Table 6-60).

6.3.5.35 Lead content of plant material

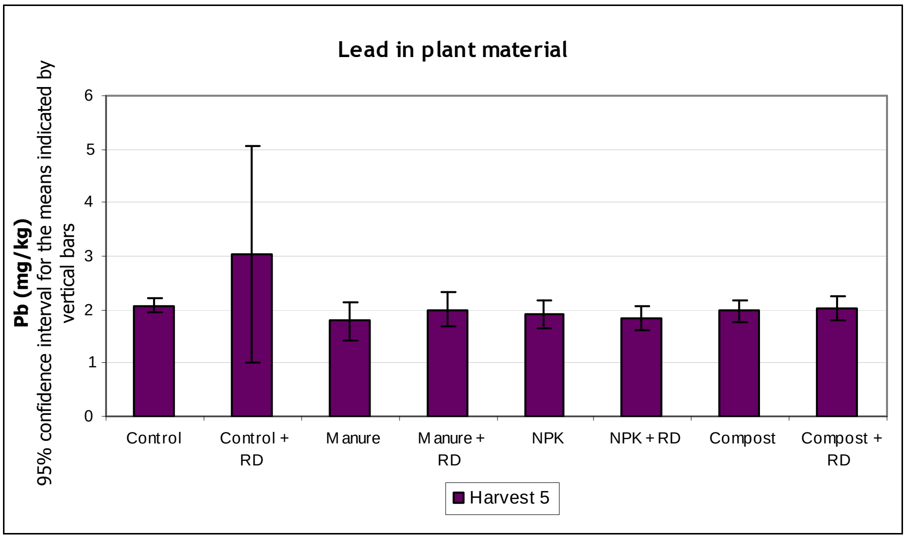


Figure 6-53 Lead in plant material at Harvest 5

6.3.5.36 Statistical analysis of Pb content of plant material

	Lead content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	nd	nd	nd	nd	NS
Rockdust	nd	nd	nd	nd	NS
Amendment*rockdust	nd	nd	nd	nd	NS

Table 6-61 Effect of 3 factors on magnesium content of plant material at individual harvests (NS = not significant; nd = not determined)

Amendment	Lead content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	nd	nd	nd	nd	2.56 a
Manure	nd	nd	nd	nd	1.90 a
NPK	nd	nd	nd	nd	1.87 a
Compost	nd	nd	nd	nd	2.01 a

Table 6-62 Effect of organic/inorganic amendments on lead content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test (nd = not determined)

Table 6-61 shows that lead content was only measurable in the trace element digest used to analyse harvest 5 plant material. However, Table 6-61 and 6-62 show that there were no significant differences due to amendment or rockdust at this harvest. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest.

6.3.5.37 Statistical analysis of Pb uptake by plant material

	Lead uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	nd	nd	nd	nd	NS
Rockdust	nd	nd	nd	nd	NS
Amendment*rockdust	nd	nd	nd	nd	NS

Table 6-63 Effect of 3 factors on lead uptake by plant material at individual harvests (NS = not significant; nd = not determined)

Amendment	Lead uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	nd	nd	nd	nd	1.36 a
Manure	nd	nd	nd	nd	1.38 a
NPK	nd	nd	nd	nd	1.48 a
Compost	nd	nd	nd	nd	1.42 a

Table 6-64 Effect of organic/inorganic amendments on lead uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test (nd = not determined)

Table 6-63 and 6-64 show that lead uptake was only measurable in harvest 5 plant material analysis. In this harvest there were no significant effects due to amendment or rockdust. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest.

6.3.5.38 Zinc content of plant material

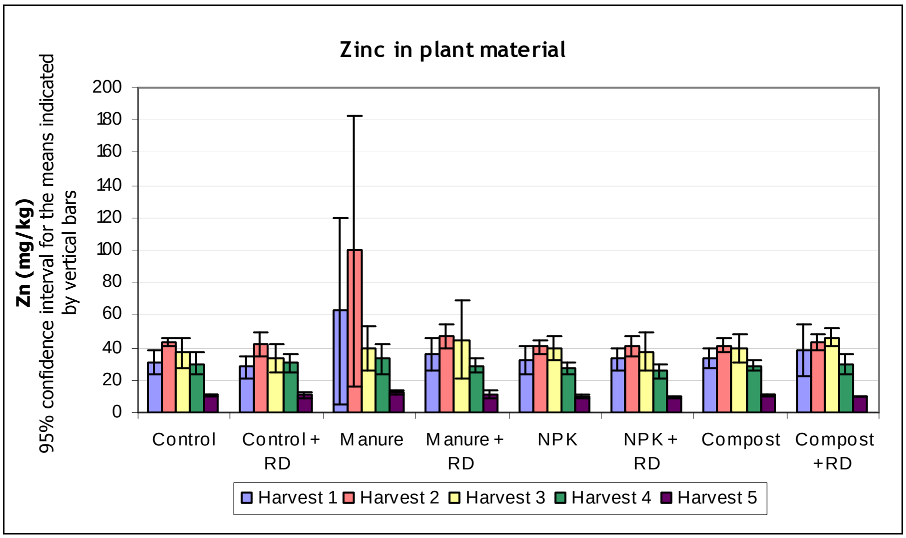


Figure 6-54 Zinc in plant material at 5 harvests

6.3.5.39 Statistical analysis of Zn content of plant material

	Zinc content of plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	NS	NS	NS	NS	**
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-65 Effect of 3 factors on magnesium content of plant material at individual harvests (NS = not significant; ** = significant effect at p ≤ 0.05 level)

Amendment	Zinc content of plant material (mg kg^{-1})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	29.52 a	42.66 a	35.20 a	30.29 a	10.66 ab
Manure	49.50 a	73.2 a	42.16 a	30.80 a	11.70 b
NPK	32.54 a	40.35 a	38.35 a	26.24 a	9.95 a
Compost	36.01 a	42.35 a	42.89 a	29.43 a	10.22 ab

Table 6-66 Effect of organic/inorganic amendments on zinc content of plant material Values in the same harvest (column) followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 6-65 shows that amendment type only had a significant effect on zinc content of plant material at harvest 5. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest. Table 6-66 shows that at harvest 5, the NPK treatment gave significantly lower plant zinc contents than the manure treatment.

6.3.5.40 Statistical analysis of Zn uptake by plant material

	Zinc uptake by plant material				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Amendment	NS	***	***	***	***
Rockdust	NS	NS	NS	NS	NS
Amendment*rockdust	NS	NS	NS	NS	NS

Table 6-67 Effect of 3 factors on zinc uptake by plant material at individual harvests (NS = not significant; * = highly significant effect at $p \leq 0.01$ level)**

Amendment	Zinc uptake by plant material (mg m^{-2})				
	Harvest 1	Harvest 2	Harvest 3	Harvest 4	Harvest 5
Control	18.93 a	5.15 a	22.59 a	1.67 a	5.67 a
Manure	30.06 a	12.66 b	35.81 b	2.77 b	8.48 b
NPK	25.39 a	11.05 ab	36.12 b	3.11 b	7.86 b
Compost	23.49 a	6.27 a	34.31 ab	2.51 b	7.22 b

Table 6-68 Effect of organic/inorganic amendments on zinc uptake by plant material Values in the same harvest (column) followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test

Table 6-67 shows that zinc uptake by plant material was significantly affected by amendment type in harvests 2 – 5. Table 6-68 shows that the control always gave lowest plant zinc uptakes. The manure treatment gave significantly higher Zn uptake than the control from harvest 2 onwards. The NPK treatment gave higher plant zinc uptake than the control from harvest 3 while the compost treatment took until harvest 4 to give higher uptake. There were no significant effects of rockdust addition nor were there any significant interactions of amendment and rockdust in any harvest.

6.3.6 Field trial soil analyses

6.3.6.1 January 2005 soil analysis

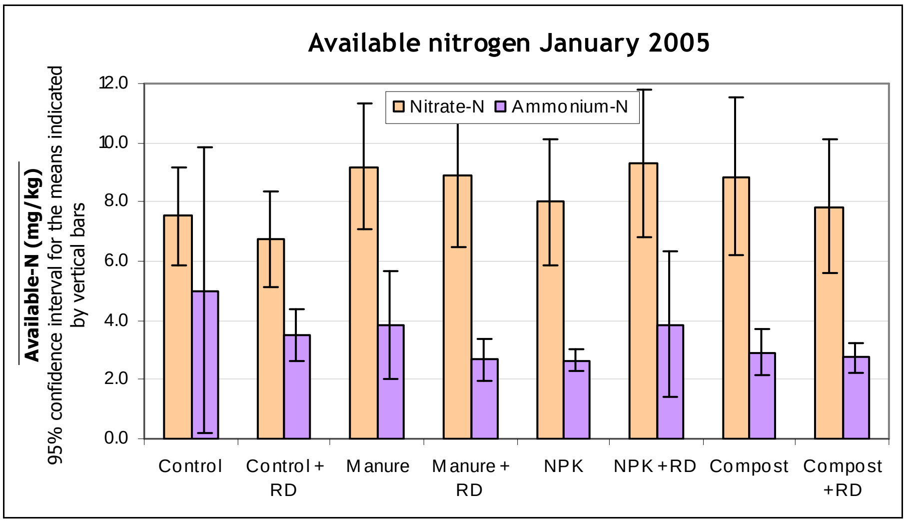


Figure 6-55 Available nitrogen in field trial soil samples at January 2005

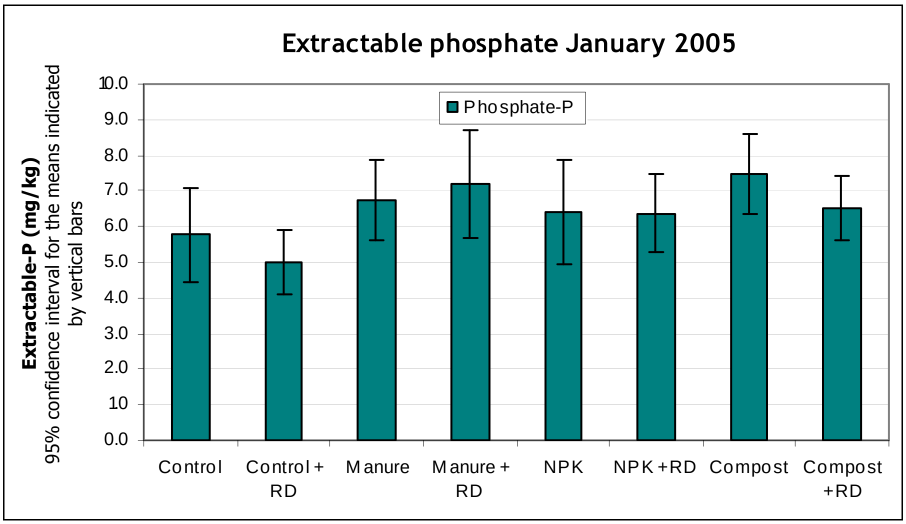


Figure 6-56 Extractable phosphate in field trial soil samples at January 2005

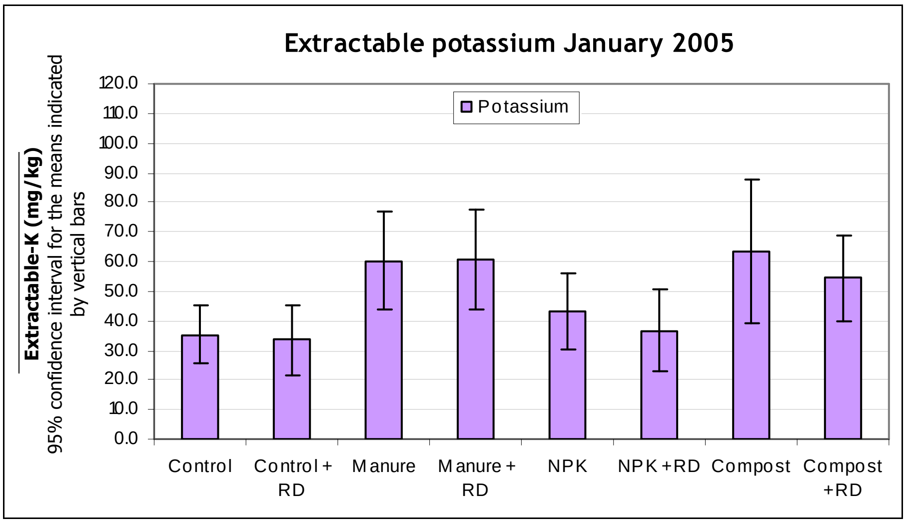


Figure 6-57 Extractable potassium in field trial soil samples at January 2005

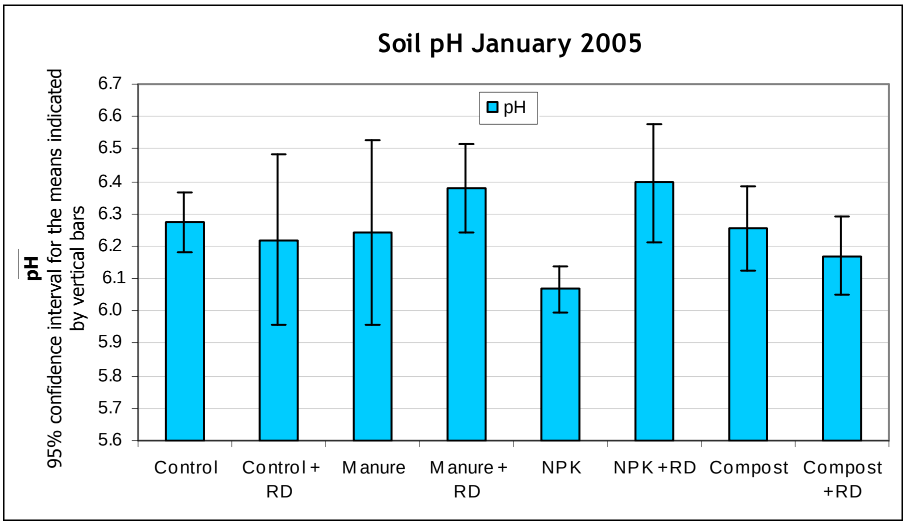


Figure 6-58 pH of field trial soil samples at January 2005

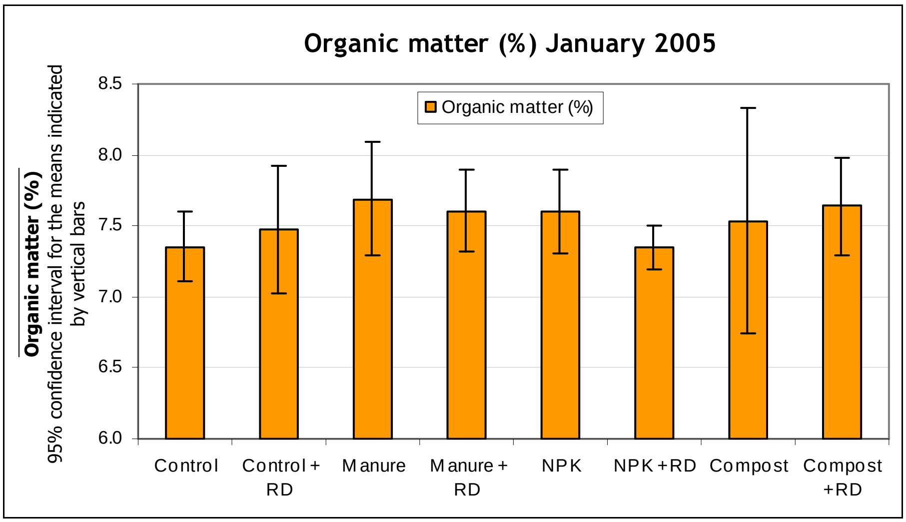


Figure 6-59 Organic matter content of topsoil in field trial soil samples at January 2005

6.3.6.2 January 2005 statistical analysis

	Effect		
	Amendment	Rockdust	Amendment/rockdust interaction
Available[δ] NO_3-N	NS	NS	NS
Available[δ] NH_4-N	NS	NS	NS
Available[δ] nitrogen	NS	NS	NS
Extractable[¥] P	**	NS	NS
Extractable[¥] K	**	NS	NS
Soil pH	NS	NS	NS
Organic matter (% in topsoil)	NS	NS	NS

[δ] Extractable with 0.5 M K_2SO_4 solution
[¥] Extractable with modified Morgan's solution

Table 6-69 Effect of 3 factors on soil chemical analyses
(NS = not significant; ** = significant effect at $p \leq 0.05$ level)

Soil core nutrient data was analysed with Minitab statistical software (version 15.1) using the general linear model command. Factors included: column, row, amendment, rockdust and an amendment/rockdust interaction. The results of this statistical analysis are shown in Table 6-69. Significant effects of amendment on extractable P and K in field trial soils were further tested using Tukey's least significant differences test as shown in Table 6-70.

Amendment	Modified Morgan's solution extractable nutrients (mg kg^{-1})	
	Extractable P	Extractable K
Control	5.39 a	34.29 a
Manure	6.97 b	60.51 c
NPK	6.38 ab	40.05 ab
Compost	6.99 b	58.85 bc

Table 6-70 Effect of organic/inorganic amendment on extractable P and K in January 2005 soil samples. Concentrations in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

6.3.6.3 Nutrients in field trial soil in January 2005

There were no significant effects of organic/inorganic amendment, rockdust application or a significant interaction between the two on available nitrogen, soil pH, or organic matter content of the soil in January 2005 (Table 6-69). The analysis in Table 6-70 shows that the extractable P remaining in the soil after the first application of amendments and the first two harvests was highest in the manure and compost treated plots than in the control (no amendment) plots. The NPK treated plots were intermediate between the two (not significantly different to any other treatment). Extractable K was higher in manure and compost treated plots than in the control plots. Manure treated plots also had higher levels of extractable K than the NPK treated plots in January 2005 whereas compost treated plots were not significantly different to the NPK treatment.

6.3.6.4 January 2007 soil analysis

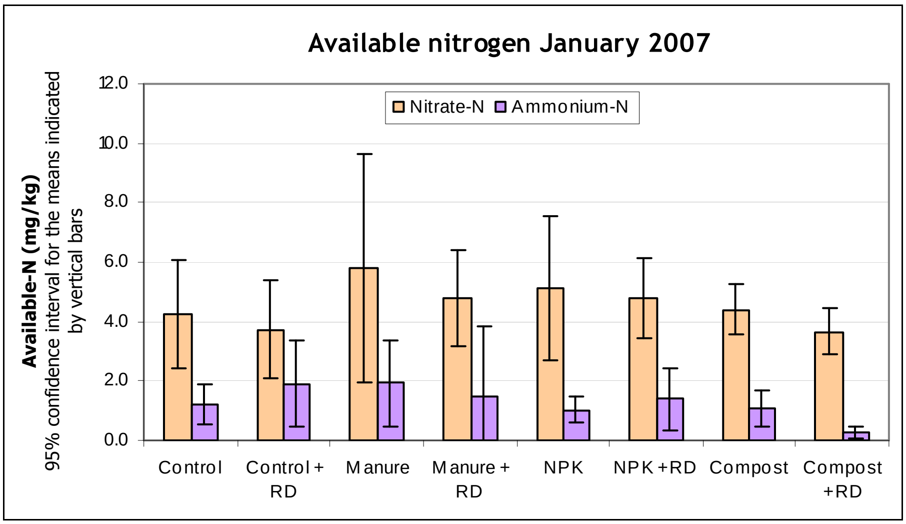


Figure 6-60 Available nitrogen in field trial soil samples at January 2007

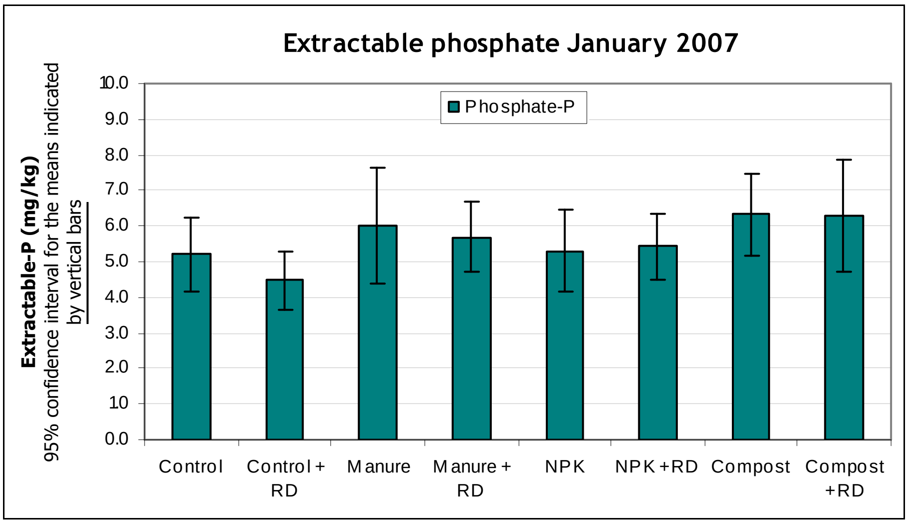


Figure 6-61 Extractable phosphate in field trial soil samples at January 2007

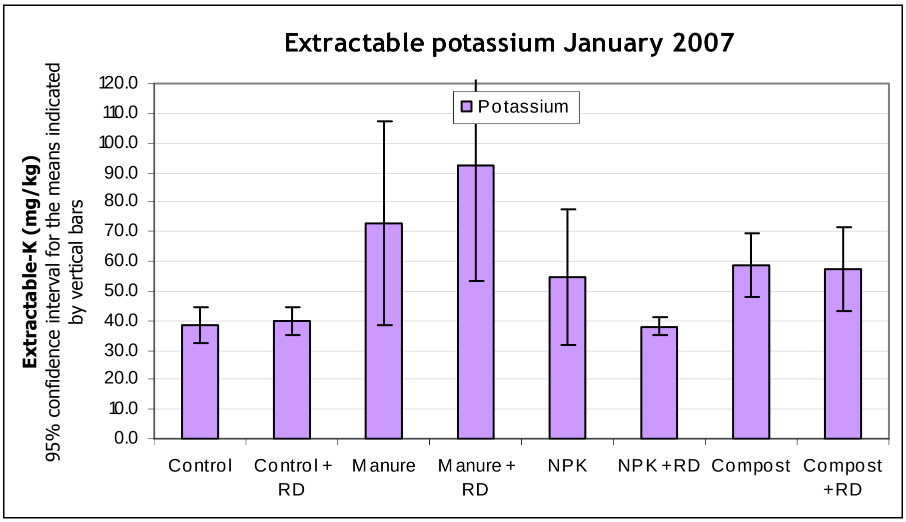


Figure 6-62 Extractable potassium in field trial soil samples at January 2007

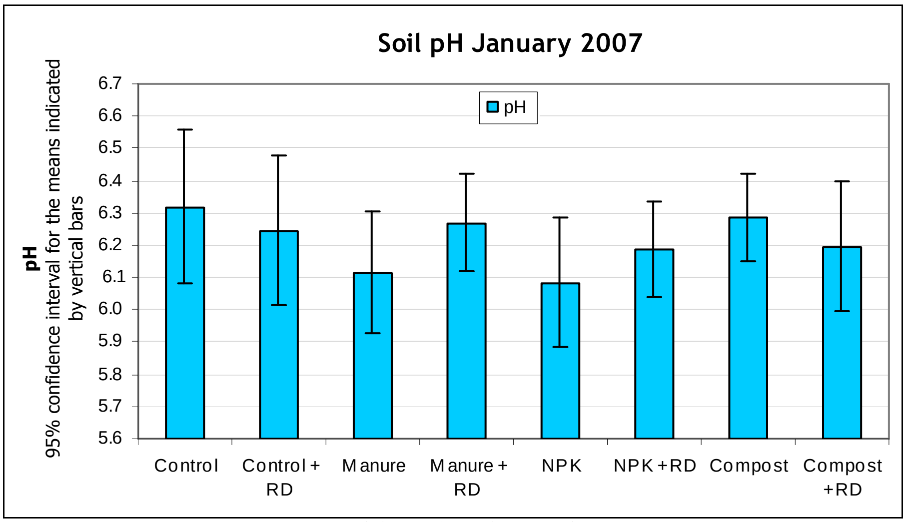


Figure 6-63 pH of field trial soil samples at January 2007

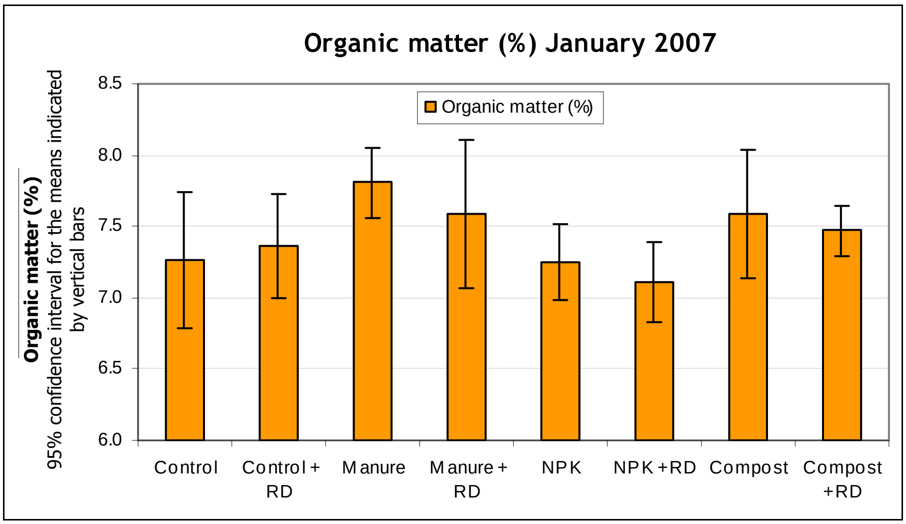


Figure 6-64 Organic matter content of topsoil in field trial soil samples at January 2007

6.3.6.5 January 2007 nutrient statistical analysis

	Effect		
	Amendment	Rockdust	Amendment/rockdust interaction
Available[δ] NO_3-N	NS	NS	NS
Available[δ] NH_4-N	NS	NS	NS
Available[δ] nitrogen	NS	NS	NS
Extractable[¥] P	**	NS	NS
Extractable[¥] K	**	NS	NS
Soil pH	NS	NS	NS
Organic matter (% in topsoil)	**	NS	NS

[δ] Extractable with 0.5 M K_2SO_4 solution
[¥] Extractable with modified Morgan's solution

Table 6-71 Effect of 3 factors on soil chemical analyses
(NS = not significant; ** = significant effect at p ≤ 0.05 level)

Soil core nutrient data was analysed with Minitab statistical software (version 15.1) using the general linear model command. Factors included: column, row, amendment, rockdust and an amendment/rockdust interaction. The results of this statistical analysis are shown in Table 6-71. Significant effects of amendment on extractable P and K and organic matter content in field trial soils were further tested using Tukey's least significant differences test as shown in Table 6-72.

Amendment	Modified Morgan's solution extractable nutrients (mg kg^{-1})		Organic matter (% in topsoil)
	Extractable P	Extractable K	
Control	4.84 a	39.16 a	7.31 ab
Manure	5.85 ab	82.60 c	7.70 b
NPK	5.40 ab	46.18 ab	7.18 a
Compost	6.31 b	57.98 bc	7.53 ab

Table 6-72 Effect of organic/inorganic amendment on extractable P and K and organic matter in January 2007 soil samples. Concentrations in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

6.3.6.6 Nutrients in field trial soil in January 2007

There were no significant effects of organic/inorganic amendment, rockdust application or a significant interaction between the two on available nitrogen or soil pH of the soil in January 2007 (Table 6-71). Table 6-72 shows that organic matter content was higher in the manure treated plots than in the NPK treated soils. The control and compost treatments had organic matter contents not significantly different to either the manure or the NPK treated soils. The analysis in Table 6-72 shows that the extractable P remaining in the soil after three applications of amendments and the after all 5 harvests was higher in the compost treated plots than in the control (no amendment) plots. The manure and NPK treated plots were intermediate between the two (not significantly different to each other or to compost or control plots). Extractable K was higher in manure and compost treated plots than in the control plots. Manure treated plots also had higher levels of extractable K than the NPK treated plots in January 2007 whereas compost treated plots were not significantly different to the NPK treatment.

6.3.7 Field trial soil trace metal analyses

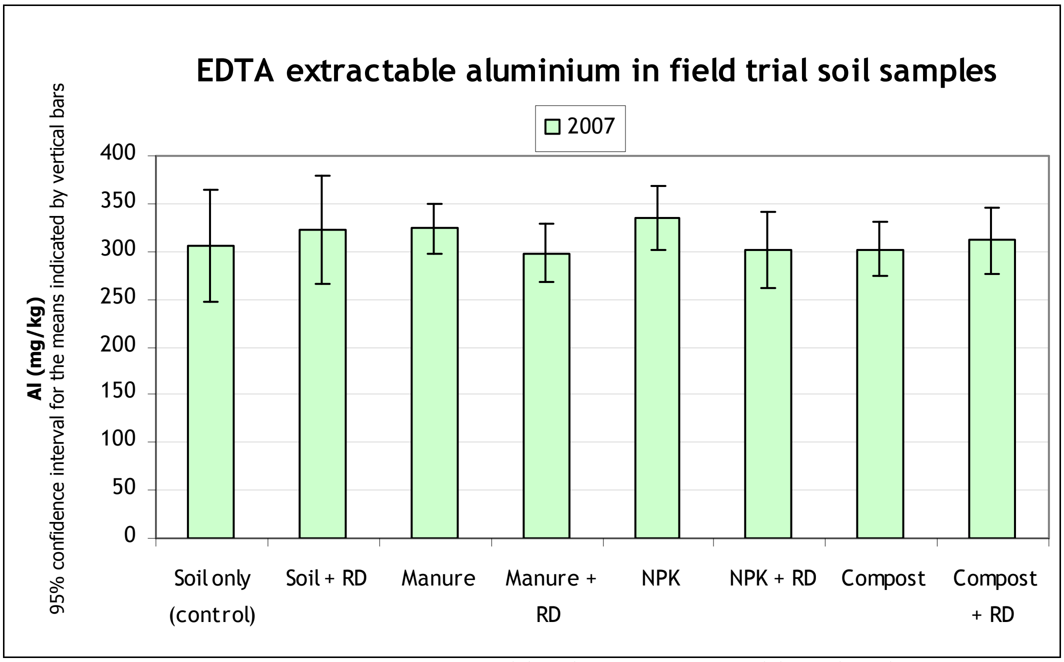


Figure 6-65 EDTA extractable aluminium in field trial soil

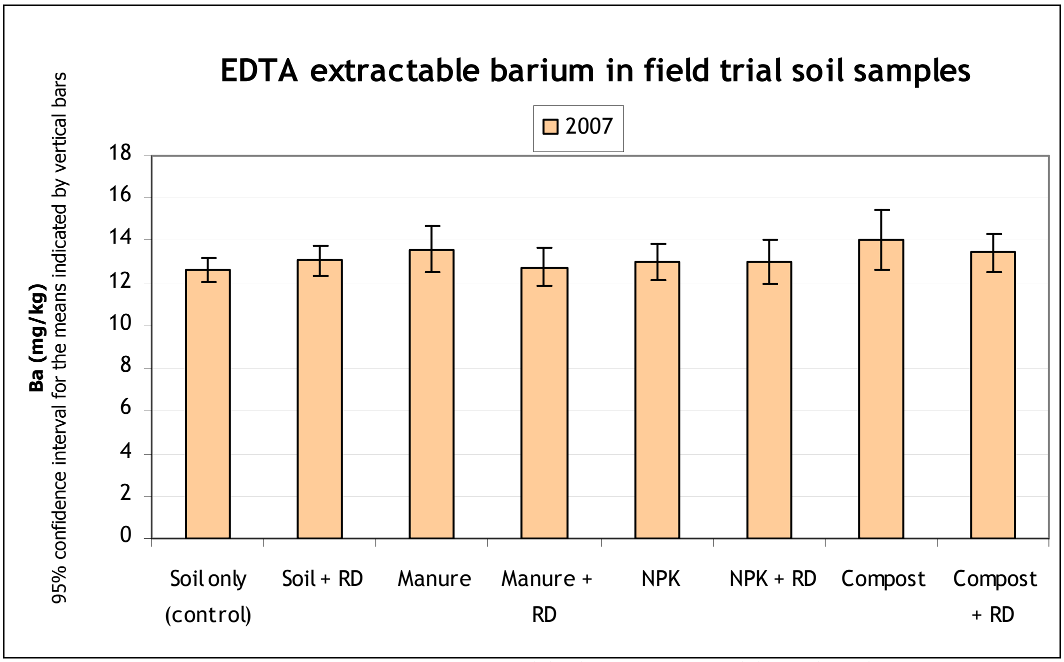


Figure 6-66 EDTA extractable barium in field trial soil

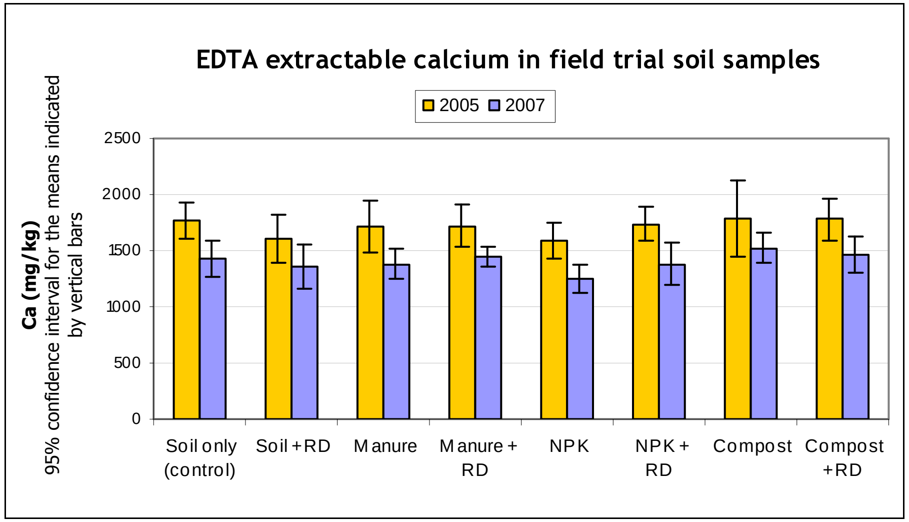


Figure 6-67 EDTA extractable calcium in field trial soil

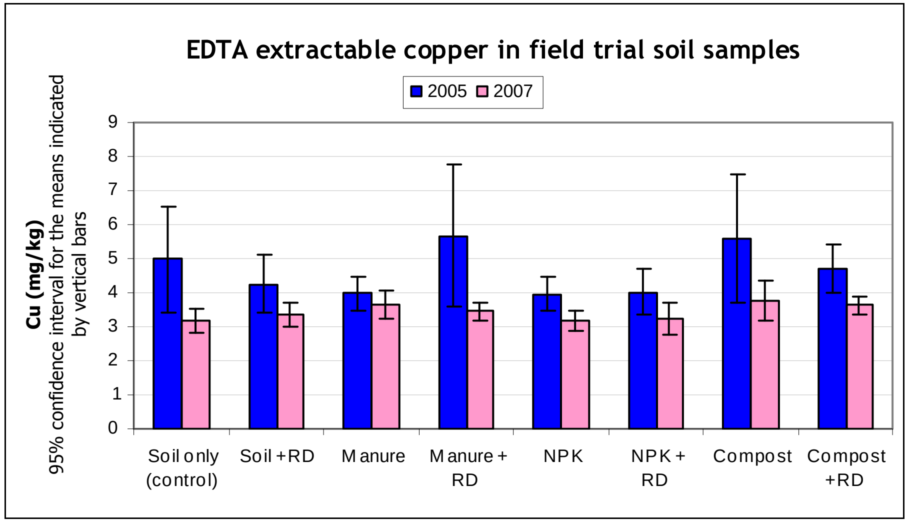


Figure 6-68 EDTA extractable copper in field trial soil

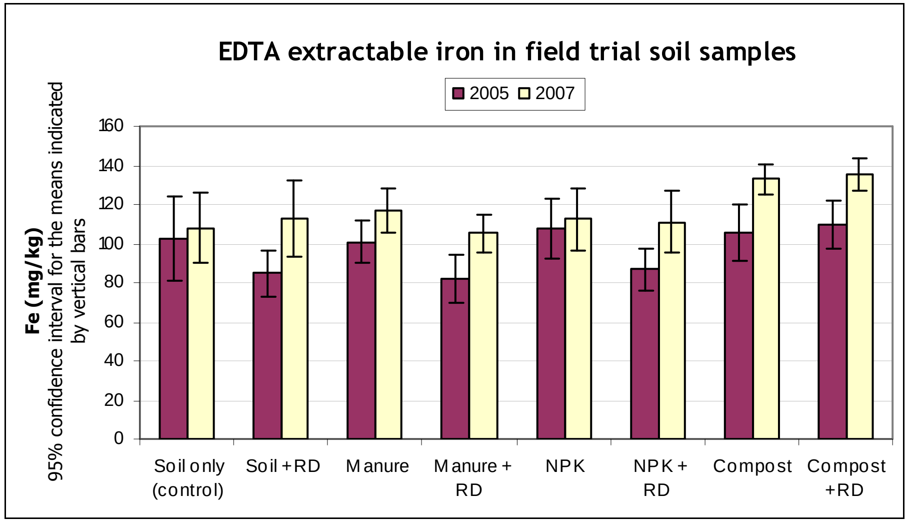


Figure 6-69 EDTA extractable iron in field trial soil

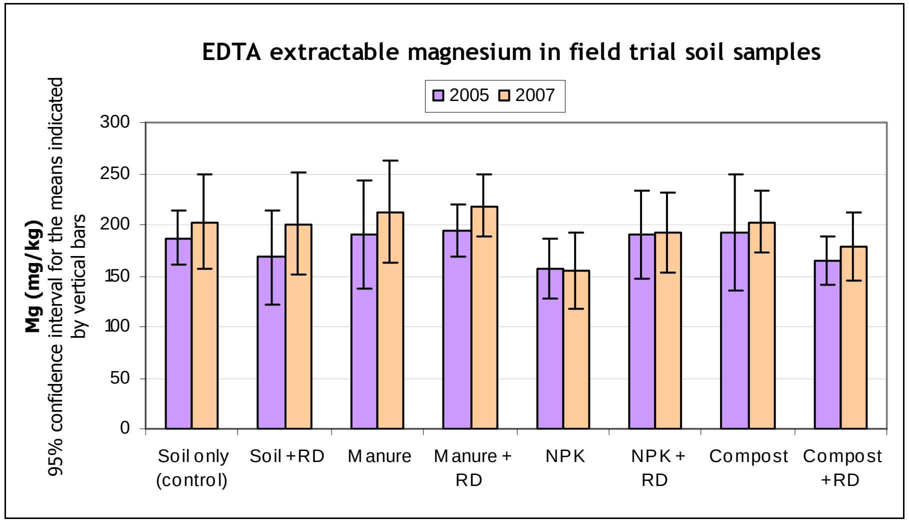


Figure 6-70 EDTA extractable magnesium in field trial soil

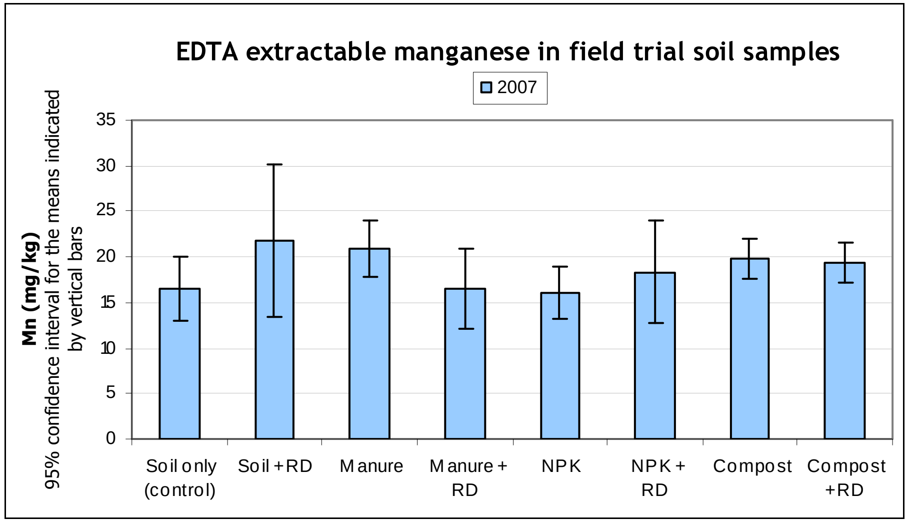


Figure 6-71 EDTA extractable manganese in field trial soil

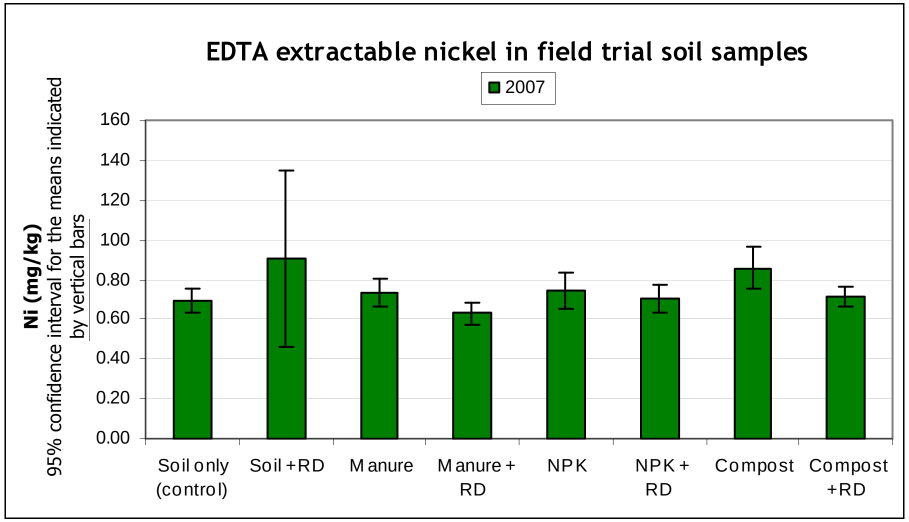


Figure 6-72 EDTA extractable nickel in field trial soil

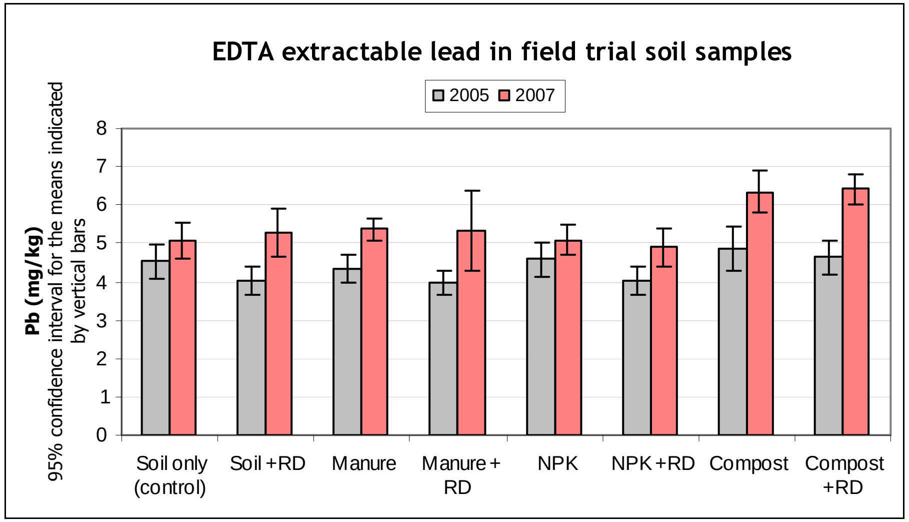


Figure 6-73 EDTA extractable lead in field trial soil

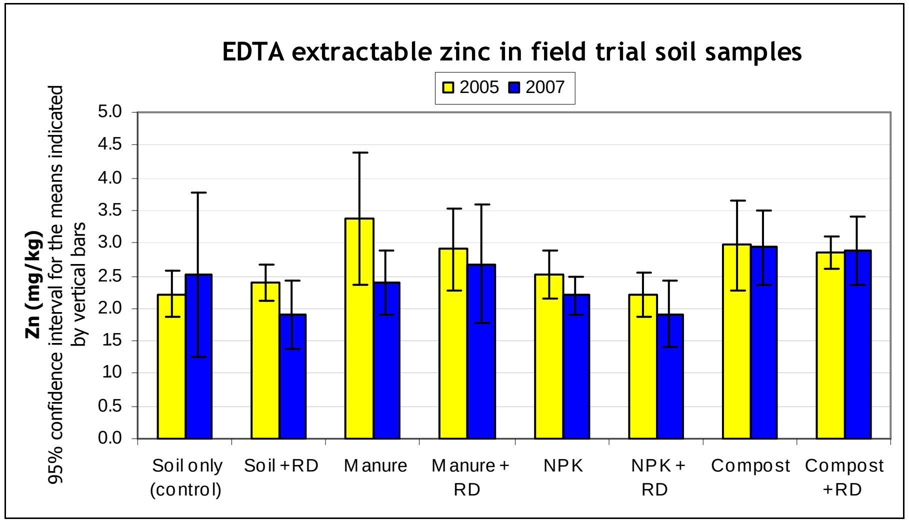


Figure 6-74 EDTA extractable zinc in field trial soil

6.3.7.1 January 2005 trace metal statistical analysis

EDTA extractable metals	Effect		
	Amendment	Rockdust	Amendment/rockdust interaction
Ca	NS	NS	NS
Cu	NS	NS	NS
Fe	**	***	NS
Mg	NS	NS	NS
Pb	**	***	NS
Zn	***	NS	NS

Table 6-73 Effect of 3 factors on EDTA extractable metals in January 2005 soil samples (NS = not significant; ** = significant effect at $p \le 0.05$ level; * = highly significant at $p \le 0.01$ level)**

The results of the statistical analysis of extractable metals in field trial cores are shown in Table 6-73. As this data was analysed by Atomic Absorption Spectroscopy and not Inductively Coupled Plasma Emission Spectroscopy, fewer elements could be analysed owing to the time required per analysis. The significant effects of amendment on extractable Fe, Pb and Zn; and significant effect of rockdust on Fe and Pb were further tested using Tukey's least significant differences test as shown in Table 6-74 and Table 6-75.

Amendment	EDTA extractable nutrients (mg kg^{-1})		
	Iron	Lead	Zinc
Control	93.85 ab	4.29 ab	2.31 a
Manure	91.38 a	4.15 a	3.14 b
NPK	97.33 ab	4.31 ab	2.37 a
Compost	107.71 b	4.74 b	2.91 ab

Table 6-74 Effect of organic/inorganic amendment on EDTA extractable Fe, Pb and Zn in January 2005 soil samples. Concentrations in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Rockdust addition	EDTA extractable nutrients (mg kg^{-1})	
	Iron	Lead
No rockdust	104.23 b	4.57 b
Rockdust	90.90 a	4.16 a

Table 6-75 Effect of rockdust addition on EDTA extractable Fe and Pb in January 2005 soil samples. Concentrations in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

6.3.7.2 Metals in field trial soil in January 2005

There were no significant effects of organic/inorganic amendment, rockdust application or a significant interaction between the two on Ca, Cu and Mg in the soil in January 2005 (Table 6-73). Amendment had a significant effect on extractable Fe, Pb and Zn. Rockdust had a significant effect on extractable Fe and Pb only. There was no significant interaction between amendment and rockdust on concentration of any extractable metal. The analysis in Table 6-74 shows the differences by amendment. Compost treated plots had higher extractable iron and lead levels than manure. The control and NPK treated soils were intermediate between manure and compost. Extractable zinc was higher in the manure treated soils than in the control and NPK treated soils. Table 6-75 shows that rockdust addition gave lower concentrations of iron and lead than in untreated plots.

6.3.7.3 January 2007 trace metal statistical analysis

EDTA extractable metals	Effect		
	Amendment	Rockdust	Amendment/rockdust interaction
Al	NS	NS	NS
Ba	NS	NS	NS
Ca	NS	NS	NS
Cu	**	NS	NS
Fe	***	NS	NS
Mg	NS	NS	NS
Mn	NS	NS	NS
Ni	NS	NS	NS
Pb	***	NS	NS
Zn	**	NS	NS

Table 6-76 Effect of 3 factors on EDTA extractable metals in January 2007 soil samples (NS = not significant; ** = significant effect at $p \leq 0.05$ level; * = highly significant at $p \leq 0.01$ level)**

The results of the statistical analysis of extractable metals in field trial cores are shown in Table 6-76. The significant effects of amendment on extractable Cu, Fe, Pb and Zn were further tested using Tukey's least significant differences test as shown in Table 6-77.

Amendment	EDTA extractable nutrients (mg kg^{-1})			
	Copper	Iron	Lead	Zinc
Control	3.28 a	110.53 a	5.19 a	2.20 a
Manure	3.55 ab	111.09 a	5.35 a	2.56 ab
NPK	3.21 a	111.71 a	4.99 a	2.07 a
Compost	3.69 b	134.32 b	6.38 b	2.91 b

Table 6-77 Effect of organic/inorganic amendment on EDTA extractable Cu, Fe, Pb and Zn in January 2007 soil samples. Concentrations in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

6.3.7.4 Metals in field trial soil in January 2007

There were no significant effects of organic/inorganic amendment, rockdust application or a significant interaction between the two on Al, Ba, Ca, Mg, Mn and Ni in the soil in January 2007 (Table 6-76). Amendment had a significant effect on extractable Fe, Pb and Zn. Rockdust did not have a significant effect on any extractable metal nor were there any significant interactions between rockdust and organic/inorganic amendment. The analysis in Table 6-77 shows the differences by amendment. Compost treated soil had a higher copper concentration than the control and NPK treated soil. Manure treated soil copper concentration was intermediate between the control/NPK and the compost treatment. Compost treated plots had higher extractable iron and lead levels than the control, manure and NPK treated soils. Extractable zinc was highest in the compost treated soils than in the control and NPK treated soils. Again manure treated soils had zinc concentrations were not significantly different to any of the other treatments.

6.4 Discussion

6.4.1 Field trial plant material yields

6.4.1.1 Effect of rockdust addition

The analysis of plant dry matter yield showed that there was no significant effect of rockdust addition on any individual harvest or on the overall combined yields. There were no significant amendment/rockdust interactions on plant yield in any of the harvests. This means that rockdust application to any of the organic/inorganic amendments did not increase the plant yield. In another field trial using ground feldspar, Sanz Scovino and Rowell (1988) showed that plant growth after feldspar application was not significantly increased. Bolland and Baker (2000) found that high applications of granite rockdust actually reduced yields of wheat grown in sandy soils compared to the control treatment.

6.4.1.2 Effect of organic/inorganic amendment addition

The field trial showed that organic additions to permanent grazing could give significant yield improvements compared to a no addition control. In the case of farmyard manure, these additions required 5 months to increase the yield compared to the control. The first harvest was not significantly different to the control while the yield at harvest 2 was significantly higher. The compost treatment took even longer to produce significantly higher yields than the control, requiring two applications until results were seen at the third harvest. After the third harvest, the two organic treatments did not produce statistically different plant yields to each other. The data from the field trial therefore display the residual effects of organic fertilizer application. With repeated applications, there is a build up of nutrients added that lead to increased yields. Erhart *et al.* (2005) used an agricultural trial of compost to show that there is long-term value to using this material. Yield responses due to compost application were low at the beginning of the trial but increased with time. Compost at an application rate of 23 t ha^{-1} y^{-1} was shown to increase yields 10 % on average over 10 years compared to the control.

There was an immediate effect on plant yield compared to the control due to inorganic fertilizer addition. This was shown at harvest 1 and continued to give statistically higher yields throughout the field trial. The organic treatments always gave significantly lower yields than the NPK treatment. This can be attributed to the nutrient analysis of these materials. The total N added by the organic amendments was always higher than that added by the inorganic fertilizer. However, the available nitrogen added by the NPK treatment was much higher than the compost and manure treatments. The available phosphorus added by the inorganic treatment was also higher than that added by the organic treatments each year. Available potassium was the exception to the trend where manure and compost treatments added far more available K than the NPK treatment each year. In the first two years, the available K added by the manure treatment was approximately double that added by compost.

These findings were similar to those of Chen *et al.* (1996) who showed that manure and biosolids composts were excellent sources of P while cow manure was an excellent source of K. They showed that cow manure compost did not provide sufficient N for ryegrass growth in a greenhouse study. The results from the field trial reported in this chapter agree somewhat with this finding although the manure treatment was able to sustain plant growth above that of a control despite lower available N contents than NPK fertilizer. However, the manure and compost treatments did not perform as effectively as the NPK treatment. Urban compost was also shown by Cabrera *et al.* (1989) to be high in plant available P but slightly lower in available K. Levels of K in composted urban refuse were shown to be low in terms of crop requirement by Guidi *et al.* (1983) who concluded that deficiencies might be seen in some crops with high requirements. In this case, manure would be a better K source than compost.

6.4.2 Field trial plant material quality

6.4.2.1 Effect of rockdust addition

Rockdust addition appeared to have little impact on plant material quality. The only significant effect of rockdust addition was on manganese content of plant material at harvests 2 and 4. The analysis showed that the manganese contents were significantly lower in rockdust treated plots in these harvests. In terms of nutrient uptake, rockdust addition only gave a significant effect at harvest 2. In this harvest, manganese uptake was shown to be higher in untreated plots compared to those rockdust had been applied to. These effects were unexpected, rockdust was expected to add nutrients to soil and hence increase plant uptake of those added nutrients. However, the overall effect on plant material quality was shown to be negligible. Bakken *et al*, (2000) concluded that "even the most soluble rocks weather too slowly to replenish the native pool of plant available K in a short time scale". This is probably the case for many other elements especially as many of the trace elements present in rockdust will be in accessory minerals or resistant structures.

He *et al*. (2005) discussed the fact that basaltic igneous rocks contained higher concentrations of metals than acid igneous rocks or sedimentary rocks. Cu, Zn, Co and Mn occur mainly in the easily weathered constituents of igneous rocks (augite, hornblende and olivine). These elements would be expected to be taken up by plants by application of rockdust to soil. However, rockdust application did not increase plant zinc levels, copper concentrations were below the method limit of quantification until harvest 5 where it was not affected by rockdust application. Cobalt was always below quantification limits in plant material despite the trace element digestion used in harvest 5. Manganese uptake was the only nutrient in plant material to be affected by rockdust application and the effect was not as expected. The field trial therefore was unable to prove that rockdust effectively adds trace elements to soil to improve plant nutrient content.

6.4.2.2 Effect of organic/inorganic amendment addition

There were many significant effects on plant material quality that were evident from the first harvest. Data from the Kjeldahl digestions showed that nitrogen content of plant material was affected by soil amendment type. The NPK treatment often gave lowest plant N contents while the control and organic treatments (especially manure) gave highest N contents. A similar pattern was shown in the phosphorus content data where the NPK treatment gave the lowest plant P contents. Grass grown on the compost and the control treatments were highest in P content and the manure treatment gave plant material with statistically the same P content as the compost. These results show that although the NPK treatment gave the highest plant material yields, the quality of the grass was lower than that grown in the control or organically amended plots after the third harvest.

In terms of nutrient uptake, at the first harvest the NPK gave statistically higher nitrogen and phosphorus uptakes than the control and the two organic treatments. By harvest 2, the uptake of these two nutrients was the same as the control in the compost treatment while the manure and NPK treatments gave statistically higher uptakes. It took until harvest 3 for the compost treatment to give N and P uptakes that were statistically higher than that of the control. By harvest 4, nitrogen and phosphorus uptake by plant material grown on the manure, NPK and compost treatments were statistically the same and higher than that of the control. This observation continued into harvest 5. The nutrient uptake data therefore shows that as the NPK produced an immediate effect on plant yield, the uptake of N and P rapidly increased. The uptake of N and P by the organic treatments was slower due to the time taken to produce a yield response. However, even though the plant yields were lower than the NPK treatment in harvests 4 and 5, the increased plant quality in the organic amended plots led to nutrient uptake that was not significantly different to that of the NPK treatment.

Analysis of the nitric acid data showed that addition of different organic and inorganic treatments to soil gave differences in plant nutrient content from the first harvest. At this harvest, the control treatment had the lowest potassium content while the manure treatment had the highest. The NPK and compost treatments also gave higher plant potassium contents than the control although the NPK treatment gave lower concentrations of K in plant material than the manure treatment. In further harvests, a similar pattern to this was shown although the NPK treatment gave low K contents that were statistically the same as the control. The compost and manure samples gave higher plant K contents than the control and NPK treatments from harvests 2 – 5. The compost treatment took until harvest 4 to 'catch-up' with the manure treatment, after which the two treatments continued to give statistically the same plant K contents. This shows that the two organic treatments were excellent sources of plant available K as was shown in the analysis of the material prior to application each year. Grey and Henry (1999) showed that highly humified compost had a greater capacity to hold and release nutrient cations (Ca, Mg and K) than less mature compost. In the field trial, release of potassium from the compost was shown to transfer to plant material.

Calcium and magnesium in plant material followed similar patterns from harvest 2 onwards. The statistical analysis often showed that the NPK treatment gave the lowest Ca and Mg contents (often lower than the control). The compost treatment produced statistically the same concentrations of these elements as the control until harvest 5 where it began to give lower concentrations. At this harvest, the calcium content of plant material continued to be statistically higher than material from the manure and NPK plots while the magnesium contents were similar. This shows the capacity for compost to supply plant available Ca as was shown by Grey and Henry (1999) although the release of Mg was not proven.

In harvests 4 and 5, manganese concentration in plant tissue was shown to be highest in the control treatment while the compost (and NPK in harvest 5) treatment gave lowest levels.

As the analysis of harvest 5 material was obtained from a more concentrated digest, trace elements could be determined. However, the only extra elements that were measurable were copper, lithium and lead. Further to this, significant differences in plant concentration of these nutrients were only shown in copper levels where the control gave higher levels than the compost treatment. In this harvest for all measurements, the NPK treatment was statistically lowest in nutrient concentration. Plants grown in the control were highest in every element except potassium and zinc. The manure treatment led to high levels of barium, potassium and zinc compared to the NPK treatment. The compost treatment gave high levels of calcium and potassium compared to the NPK treatment at this harvest.

When the nutrient uptake data were analysed, many more differences were seen in harvest 1 – 4 data. In these harvests, the NPK treatment led to higher uptake of nutrients in almost every case compared to the control and the two organic treatments. The main difference to this rule was that potassium uptake by plant tissue was statistically the same in NPK, compost and manure treatments in harvest 1 and 4. In harvest 2, both the manure and the NPK treatments gave higher uptakes than the control and compost treatments. In harvest 3, the manure gave the highest uptake, followed by the compost. At harvest 5, the NPK treatment gave lower uptake of K compared to the manure and compost treatments. This difference was due to the quality of the plant matter where the organic treatments gave better quality tissue (higher K content) than the NPK treatment.

The compost treatment did not give significantly different nutrient uptakes to the control in the first year of the field trial (harvests 1 and 2) with the exception of potassium in harvest 1. By harvests 3 – 5, the compost began to produce higher nutrient uptake of most nutrients compared to the control. The manure treatment, on the other hand, began to increase nutrient uptake at the second harvest (again with the exception of potassium which was higher at the first harvest). This was due to the time taken to produce a yield effect since a quality effect was evident from the first harvest.

By the final harvest, fewer nutrient uptake differences were evident with only 4 significant differences between treatments. These differences mainly separated out the control from the amendments with only potassium uptake varying between organic and inorganic amendments. This shows that by the final harvest, the differences in plant yield (highest in the NPK treatment) and plant quality (highest nutrient content in organic treatments) had effectively cancelled out. The benefit of using inorganic fertilizer is in the increased plant yield but the quality of the crop suffers. Organic fertilizers increase plant quality while the yield benefits are lower than those gained using NPK fertilizer (although statistically higher than the yield in the control).

The differences between organic and inorganic amendments were clear from the first harvest where the NPK treatment gave far greater nutrient uptake due to the enhanced rate of plant growth compared to the other three treatments. The compost treatment took longer than the manure treatment to produce an increase in plant nutrient uptake (harvest 3 compared with harvest 2 for manure). This could be attributed to the time taken to produce a yield effect.

The main differences between organic and inorganic treatments were shown by comparing nutrient content with the patterns in nutrient uptake. This was best demonstrated by the analysis of N, P and K in plant material. Although the application of inorganic NPK treatment led to a yield increase from the first harvest and therefore an increase in uptake of these nutrients, the nitrogen, phosphorus and potassium content of the collected herbage was lowest in this treatment from harvest 2 onwards. This therefore represents a decrease in the quality of the plant tissue from harvest 2 onwards with repeated application of inorganic fertilizer.

In contrast to this, the organic amendments required time to produce yield effects and therefore increases in plant nutrient uptake versus the control were delayed also. However, the N content of the plant tissue was higher than the NPK treatment in manure treatments in harvests 1, 2 and 4. The compost treatment gave higher N content than the NPK treatment in harvests 2 and 4. In agreement with these findings, Bernal *et al.* (1998b) showed that plants grown in soil treated with mature sewage sludge compost did not give a statistically higher yield than soil with inorganic fertilizer, while N uptake was highest in the compost treatment.

A similar pattern was seen in P content of plant material with the compost and manure treatments giving higher P content than the NPK treatment in harvests 4 and 5. Similarly the plant K concentration was higher in compost treatments than NPK treatments from harvest 2 onwards. The manure treated plots gave higher uptake of K than the NPK treatment from harvest 1 onwards. The organic treatments were also higher than the control treatment in K content which shows that while the NPK treatment was giving similar quality plant tissue to that of the control, the organic amendments were increasing the nutrient content and therefore quality of the tissue.

6.4.3 Field trial soil analysis

6.4.3.1 Effect of rockdust addition

Rockdust addition only had an effect on iron and lead concentrations in soil in the January 2005 soil extractions. The analysis of this data showed that the addition of rockdust actually lowered the concentration of these metals compared to no rockdust addition. This was unexpected since rockdust was expected to increase trace metal availability in soil following application. Sanz Scovino and Rowell (1988) focused on K uptake in a trial of ground feldspar but found little increase in crop uptake of K. Supanjani *et al.* (2006) showed that P and K rock-solubilising bacteria would need to be applied with P and K rich rock for the materials to compete with soluble fertilizer in terms of plant nutrient uptake. Bakken *et al.* (2000) showed that less than 30 % of K added by crushed rocks was taken up by plants compared to 70 % of fertilizer K. There were no effects due to rockdust addition in January 2007 and no amendment/rockdust interactions in either 2005 or 2007.

6.4.3.2 Effect of organic/inorganic amendment addition

The soil analyses in January 2005 and in 2007 showed that the organic amendment materials gave increased extractable P and K compared to the control. In agreement with this finding, soil available P was maintained at 'high' levels throughout a trial of urban compost application at a rate of 14 t ha^{-1} by Cabrera *et al.* (1989). Jakobsen (1995) showed that the water soluble P content of compost could have a similar fertilizing effect to superphosphate. Soil available K also slightly increased in compost applications. The field trial again shows that these materials were excellent sources of these two nutrients in agreement with Chen *et al.* (1996). Annual applications of composted municipal solid wastes were shown by Hadas *et al.* (2004) to replace the need for P fertilization. They also reported a continuous increase in soil organic matter each year in the top 5 cm of soil after surface applications of compost. In the January 2007 analysis, differences were seen in the organic matter content of topsoil of the field trial where the manure treatment gave higher levels than the NPK treatment. This shows that after 3 years of application, the organic matter content of topsoil treated with manure slowly increased although it was not yet statistically higher than the organic matter level in the control. Although the organic matter content of the NPK treated soil was not lower than that of the control, the analysis points towards a general decrease in organic matter in these plots.

In the 2005 soil analysis, the compost amended soil had higher extractable iron and lead than the manure treated soil. The manure treated soil had higher zinc levels than the control and NPK treated soil. In the 2007 soil analysis, the compost amended soil had the highest copper, iron, lead and zinc levels. The manure treated soil had statistically the same levels of copper and zinc as the compost treatment but less iron and lead. These findings are in line with the findings of He *et al.* (2005) who stated that as farm manures and compost contain higher concentrations of trace elements than most agricultural soil, application can lead to an increase in trace elements in soils. In the case of this field trial, the application of compost increased availability of some trace elements in soil. Cabrera *et al.* (1989) also showed that compost treatments at rates of 14 t ha^{-1} led to increases in total copper and zinc after 2 years of applications. They stated that this could be of concern at higher application rates. Svensson *et al.* (2004) also expressed concern that compost amended plots received high doses of heavy metals (especially lead) compared to those supplied with mineral fertilizer only. BSI PAS 100 (British Standards Institution, 2005b) introduces upper limits for 7 potentially toxic elements that limit the amount (including Cu, Pb and Zn that were shown to be highest in soil amended with compost) that will be added to soil. However, if high application rates of compost were to be applied over a long period of time, the heavy metal content of soil should also be periodically checked.

Agassi *et al.* (2004) showed that annual applications of composted municipal solid wastes eliminated the need to fertilize the crop. A rate of 100 m^3 ha^{-1} (40 t ha^{-1}) was recommended to provide these benefits without any negative effects increasing of soil salinity or heavy metal content.

Similarly to the results from the field trial, Soumaré *et al.* (2003) showed that compost addition could increase plant available K, Fe, Mn, Zn and Cu in the soil although, due to low dry matter yields, trace metal uptake by plants after compost application alone was not significantly affected. They recommended compost application in combination with NPK fertilizer.

6.5 Summary

The results reported in this chapter showed that rockdust did not produce any yield effects. Since the effect of rockdust application was investigated as an independent factor in the statistical analysis and as an interaction term with the amendment type, the results show that rockdust had no overall effect nor did it increase the yield on the basis of any individual amendment without rockdust.

The field trial clearly demonstrates the effectiveness of organic amendments (manure and compost) as soil fertility amendments. These materials increased plant yields compared to the control in by the second application and continued to increase plant yields throughout the trial. The time taken to produce yield effects was either due to a high residual effect in the untreated control or due to nutrient limitation in the organically amended plots. Nutrient analysis of the materials prior to application indicated that they were good sources of plant available P and K but poor sources of plant available N. Therefore the time required to produce yield effects could have been related to the mineralization rate of organic-N in these materials.

The high grass yields gained by inorganic fertilizer application affected the nutrient content of the plant matter whereby the nutrient content was lower than in the organically fertilized plots. This was especially true for N, P, K and Ca. Generally, the organic treatments produced better quality grass (in terms of nutrient content) than the NPK treatment while the NPK treatment produced higher yields.

Analysis of the field trial soil showed that manure and compost provided an excess of plant available P and K while the NPK treatment did not. Manure application was shown to increase plant available copper and zinc in the plots although differences in the plant matter were not apparent. Compost application increased extractable iron, lead, copper and zinc in the soil but again, these effects could not be measured in the harvested material.

Chapter 7: Microbial community analysis

7.1 Introduction

Since changes in relative abundance of individual organisms are less ecologically meaningful than changes in the functional profile of microbial communities; community level classification and characterisation was first developed to give a more useful measure of the metabolic ability of a given community (Garland and Mills, 1991).

This initial technique for classifying and characterising microbial communities, described by Garland and Mills (1991), was based on rapid assessment of sole carbon source utilization. The method (developed by Biolog, Inc) required reduction of a tetrazolium dye to indicate a respiration response but was limited due to the indirect nature of measuring substrate usage. The high substrate concentrations required in Biolog plates caused bacterial growth and were unlikely to show in situ community function (Smalla *et al.*, 1998). Rather, the Biolog assay could be regarded more as a measure of community structure after growth in the wells rather than original community function (Garland, 1997).

Respiration responses using the BD Biosciences Oxygen Biosensor System (BDOxy) were shown at substrate additions 10 – 100 times less concentrated than in Biolog plates by Garland *et al.* (2003) representing a more realistic substrate addition. This technique used a rapid direct method for assessing respiration by measuring oxygen depletion in 96-well micro-titre plates. Community level physiological profiling (CLPP) involves analysis of the pattern of respiration in these wells. The speed of substrate respiration and the extent to which they are respired can be compared between samples. This physiological profiling technique can therefore give information on the potential functional profile of the microbial communities existing in soil or water samples. The lower substrate concentrations employed in the method allow for easier analysis and interpretation of the data. BDOxy-CLPP analysis was able to detect the differences at a substrate concentration of 50 mg l^{-1} whereas Biolog-CLPP analysis was not (Garland, 2003).

The BDOxy-CLPP system was chosen to analyse differences in microbial communities in soil from the SEER Centre field trial. It was hypothesised that application of rockdust and organic or inorganic fertilizers to agricultural soil of the field trial could lead to significant long-term changes in microbial communities. This work was carried out at Dynamac Corporation, Kennedy Space Center, USA using soil samples from the field trial.

7.2 Methods

7.2.1 BD Oxy-CLPP system

The BD Oxygen Biosensor System (BDOxy) was used to investigate functional differences in microbial community physiological profile (CLPP) between soil samples from the field trial. The BDOxy system uses fluorescence of an oxygen-sensitive gel that is quenched in the presence of O_2 to indicate a respiration response in covered microplate wells (Wodnicka *et al.*, 2000). The O_2-sensitive fluorophore (4,7-diphenyl-1,10-phenathroline ruthenium (II) chloride) is absorbed onto a silicone matrix that is permeable to O_2 and sits below the sample. As O_2 in a well is consumed, the signal from the fluorophore-gel increases indicating an increase in respiration due to substrate utilization (Garland *et al.*, 2003). The reversible nature of the reaction of the ruthenium dye suggests that plates could be reused after decontamination with ethylene oxide (Birmele *et al.*, 2006).

7.2.1.1 Fluorometer settings

All plates in Experiments 1, 2 and 4 were read on a Dynex MFX microplate fluorometer while Experiment 3 plates were read on a Bio-tek Synergy HT fluorometer using the bottom reading mode. 485 nm excitation and 604 nm (590 nm in Experiment 3) emission wavelengths were used and incubation temperature was 30 °C. Each run was set up to last 48 hours with a reading every 15 minutes.

7.2.2 Samples for BD Oxy-CLPP analysis

Half of the field trial plots were chosen to be sampled on 25 July 2007 according to the method in Section 6.2.5.1. This was because too much time would be required to sample and process soil from all 64 plots and the samples had to be sent as close to sampling time as possible. Also the sample number was restricted since there was a weight limit on what could be sent to the Kennedy Space Center for analysis. The plots chosen were in columns 3, 4, 6 and 8 since these showed less variation than the others in the previous soil chemical analyses. These samples were to be used for soil microbial community analysis and were not dried. They were processed as in Section 6.2.5.2.

7.2.3 Experiment 1: Endogenous respiration

The first experiment using BD Oxy-CLPP analysis was designed to show endogenous respiration in the non-carbon supplemented soils along with utilization of a range of carbon sources.

11 carbon sources were chosen to represent 3 major groups of compounds: sugars, amino acids and carboxylates. The compounds chosen were:

Sugars	**Amino acids**	**Carboxylates**
Fructose	Alanine	Citric acid
Glucose	Arginine	Malic acid
Lactose	Glycine	Sodium acetate
Mannose	Leucine	

7.2.3.1 Carbon source preparation

- Carbon source stock solutions (1500 mg l^{-1})

0.15 g of each carbon source was weighed accurately to 4 decimal places and dissolved in 100ml deionised water.

- Carbon source solutions (150 mg l^{-1})

10 ml of the 1500 mg l^{-1} stock solution was diluted with 90 ml deionised water.

The 150 mg l^{-1} carbon source solutions were autoclaved at 120 °C for 1 hour to sterilize them of any microbial contaminants, sealed tightly and kept in the refrigerator at 4 °C until use.

7.2.3.2 Soil slurry preparation

10 g fresh soil was weighed to 1 decimal place into a centrifuge tube containing approximately 5 ml small glass beads. 25 ml sterile deionised water was pipetted into the tube. The tubes were capped and mixed thoroughly by shaking for 2 minutes.

7.2.3.3 BD Oxy-CLPP plate preparation

Working in a sterile laminar flow cabinet, 80 µl of sterile deionised water was pipetted into every well on the plate. 80 µl of 150 mg l^{-1} carbon substrate stock solution was added to the wells according to the plan (Figure 7-1). In the no carbon source wells (column 12), an additional 80 µl of sterile deionised water was added in order that the total well volume remained constant. 80 µl of the soil slurry was then pipetted into the wells (according to Figure 7-1). The carbon substrate concentration in each well was therefore 50 mg l^{-1}. Once all the soil slurries were added, the plate was covered with Titre-Tops™ non-breathable adhesive film to prevent air re-entering. The plate was then immediately taken to the plate reader and the run started.

		1	2	3	4	5	6	7	8	9	10	11	12
A	Soil	Citric acid	Malic acid	Sodium acetate	Alanine	Arginine	Glycine	Leucine	Fructose	Glucose	Lactose	Mannose	No carbon source
B	Soil + RD												
C	Manure												
D	Manure + RD												
E	NPK												
F	NPK + RD												
G	Compost												
H	Compost + RD												

Figure 7-1 BD Oxy-CLPP plate plan for Experiment 1

7.2.4 Experiment 2: Nutrient limitations

Experiment 2 was designed to show nutrient limitations in the field trial soils. By amending with N, P or N and P together versus a no amendment control; increases in respiration caused by increases in N or P concentration could show nutrient deficiencies in the samples. The amendments were also run with two carbon sources (mannose and sodium acetate) to show increases in respiration when adding nutrients along with carbon sources. Nutrient additions were set to a molar ratio of 100 C: 10 N: 1 P.

7.2.4.1 Carbon source preparation

- Mannose solution (150 mg carbon l^{-1})

375.4 mg of mannose was dissolved per litre deionised water to give a solution of 150 mg l^{-1} carbon.

- Sodium acetate solution (150 mg carbon l^{-1})

512.7 mg of sodium acetate was dissolved per litre deionised water to give a solution of 150 mg l^{-1} carbon.

The two carbon source solutions were autoclave sterilized, sealed tightly and kept in the refrigerator at 4 °C until use.

7.2.4.2 Nutrient solution preparation

- Nitrogen solution (15 mg l^{-1} N)

70.7 mg of ammonium sulphate was dissolved in 1 litre deionised water.

- Phosphorus stock solution (15 mg l^{-1} P)

66 mg of potassium dihydrogen phosphate was dissolved in 1 litre deionised water.

- Phosphorus solution (1.5 mg l^{-1} P)

10 ml of the 15 mg l^{-1} P stock solution was diluted to 100 ml with deionised water.

- Mixed N+P stock solution (150 mg l^{-1} N and 15 mg l^{-1} P)

707.1 mg ammonium sulphate and 66 mg potassium phosphate were dissolved per litre deionised water.

- Mixed N+P solution (15 mg l^{-1} N and 1.5 mg l^{-1} P)

10 ml of the mixed N+P (150 mg l^{-1} N and 15 mg l^{-1} P) stock solution was diluted to 100 ml with deionised water.

The 3 working concentration nutrient solutions were autoclaved at 120 °C for 1 hour to sterilize them of any microbial contaminants, sealed tightly and kept in the refrigerator at 4 °C until use.

7.2.4.3 Soil slurry preparation

10 g fresh soil was weighed to 1 decimal place into a centrifuge tube containing approximately 5 ml small glass beads. 25 ml sterile deionised water was pipetted into the tube. The tubes were capped and mixed thoroughly by shaking for 2 minutes.

7.2.4.4 BD Oxy-CLPP plate preparation

Working in a sterile laminar flow cabinet, 80 µl of sterile deionised water was pipetted the no carbon wells (9–12). 80 µl of 150 mg l^{-1} carbon substrate stock solution was added to the appropriate wells according to the plan (Figure 7-2). 80 µl of nutrient solution or sterile deionised water was the added to the wells as in Figure 7-2. Finally, 80 µl of the soil slurry was pipetted into the appropriate wells. The carbon substrate concentration in each well was therefore 50 mg C l^{-1}. Once all the soil slurries were added, the plate was covered with Titre-Tops™ non-breathable adhesive film to prevent air re-entering. The plate was then immediately taken to the plate reader and the run started.

The plate set-up is shown in Figure 7-2 below:

<table>
<tr><th></th><th></th><th>1
N</th><th>2
P</th><th>3
N+P</th><th>4
No</th><th>5
N</th><th>6
P</th><th>7
N+P</th><th>8
No</th><th>9
N</th><th>10
P</th><th>11
N+P</th><th>12
No</th></tr>
<tr><td>A</td><td>Soil</td><td colspan="4" rowspan="8">Sodium acetate</td><td colspan="4" rowspan="8">Mannose</td><td colspan="4" rowspan="8">No carbon</td></tr>
<tr><td>B</td><td>Soil + RD</td></tr>
<tr><td>C</td><td>Manure</td></tr>
<tr><td>D</td><td>Manure + RD</td></tr>
<tr><td>E</td><td>NPK</td></tr>
<tr><td>F</td><td>NPK + RD</td></tr>
<tr><td>G</td><td>Compost</td></tr>
<tr><td>H</td><td>Compost + RD</td></tr>
</table>

Figure 7-2 BD Oxy-CLPP plate plan for Experiment 2

Carbon sources	**Nutrient additions**
Mannose (50 mg l^{-1} C)	5 mg l^{-1} N
Sodium acetate (50 mg l^{-1} C)	0.5 mg l^{-1} P
	5 mg l^{-1} N + 0.5 mg l^{-1} P

7.2.5 Experiment 3: Bacterial vs. fungal communities

Experiment 3 was set up to show the different contribution to substrate respiration between the bacterial and the fungal communities in the soil samples. The addition of cycloheximide inhibits fungal activity so that only bacterial respiration is shown in treated wells. 5 carbon substrates were chosen (plus 1 no carbon treatment) per soil sample and there was a nitrogen addition in half of the wells.

7.2.5.1 Carbon source preparation

- Carbon source stock solution preparation (300 mg l^{-1})

0.3 g of carbon source was weighed accurately to 4 decimal places and dissolved in 1 litre deionised water. The solution was autoclave sterilized at 120 °C for 1 hour, sealed tightly and stored in the refrigerator at 4 °C.

7.2.5.2 Nitrogen solution preparation

- Nitrogen stock solution preparation (60 mg l^{-1} N)

0.283 g of ammonium sulphate was dissolved in 1 litre deionised water to give a nitrogen stock solution concentration of 60 mg N l^{-1}. The solution was autoclave sterilized at 120 °C for 1 hour, sealed tightly and stored in the refrigerator at 4 °C.

7.2.5.3 Cycloheximide preparation

- Cycloheximide (32 mg l^{-1})

1.6 g solid cycloheximide was dissolved in 50 ml sterile deionised water.

7.2.5.4 Soil slurry preparation

10 g fresh soil was weighed to 1 decimal place into a centrifuge tube containing approximately 5 ml small glass beads. 25 ml sterile deionised water was pipetted into the tube. The tubes were capped and mixed thoroughly by shaking for 2 minutes.

7.2.5.5 BD Oxy-CLPP plate preparation

Working in a sterile laminar flow cabinet, 40 µl of sterile deionised water was pipetted into the no carbon wells (columns 6 and 12). 40 µl of 300 mg l^{-1} carbon source stock solution was added to the appropriate wells according to the plan (Figure 7-3). 40 µl of nitrogen solution (or sterile deionised water in the - N wells) was the added to the +N wells. 80 µl of the soil slurry was pipetted into the wells (according to Figure 7-3). 80 µl of cycloheximide (or deionised water in the – cycloheximide wells) was pipetted into the appropriate wells (see Figure 7-3). The carbon substrate concentration in each well was 50 mg C l^{-1} due to the 6x dilution factor. Once all the soil slurries were added, the plate was covered with Titre-Tops™ non-breathable adhesive film to prevent air re-entering. The plate was then immediately taken to the plate reader and the run started.

The plate plan is shown in Figure 7-3 below:

<table>
<tr><th></th><th></th><th>1
C1</th><th>2
C2</th><th>3
C3</th><th>4
C4</th><th>5
C5</th><th>6
C6</th><th>7
C1</th><th>8
C2</th><th>9
C3</th><th>10
C4</th><th>11
C5</th><th>12
C6</th></tr>
<tr><td>A</td><td>Soil</td><td colspan="6" rowspan="4">+ N
+ cycloheximide</td><td colspan="6" rowspan="4">- N
+ cycloheximide</td></tr>
<tr><td>B</td><td>Manure</td></tr>
<tr><td>C</td><td>NPK</td></tr>
<tr><td>D</td><td>Compost</td></tr>
<tr><td>E</td><td>Soil</td><td colspan="6" rowspan="4">+ N
- cycloheximide</td><td colspan="6" rowspan="4">- N
- cycloheximide</td></tr>
<tr><td>F</td><td>Manure</td></tr>
<tr><td>G</td><td>NPK</td></tr>
<tr><td>H</td><td>Compost</td></tr>
</table>

Figure 7-3 BD Oxy-CLPP plate plan for Experiment 3

	Carbon sources	**Nitrogen addition**	**Cycloheximide addition**
C1	Sodium acetate (50 mg l^{-1})	10 mg N l^{-1}	10.7 mg ml^{-1}
C2	Coumaric acid (50 mg l^{-1})		
C3	Casein (50 mg l^{-1})		
C4	Mannose (50 mg l^{-1})		
C5	Asparagine (50 mg l^{-1})		
C6	No carbon		

7.2.6 Experiment 4: Micronutrient limitations

Experiment 4 was designed to show the effect of micronutrient additions (with and without additional N+P) on respiration in soil samples with 4 different carbon sources. Due to time constraints, this could only be carried out on 3 replicates from the field trial soils as an extra plate had to be read with no carbon source and micronutrients (with and without N+P).

7.2.6.1 Carbon source preparation

- Sodium acetate solution (150 mg carbon l^{-1})

512.7 mg of sodium acetate was dissolved per litre deionised water to give a solution of 150 mg l^{-1} carbon.

- Mannose solution (150 mg carbon l^{-1})

375.4 mg of mannose was dissolved per litre deionised water to give a solution of 150 mg l^{-1} carbon.

- Malic acid solution (150 mg carbon l^{-1})

419.0 mg of malic acid was dissolved per litre deionised water to give a solution of 150 mg l^{-1} carbon.

- Glucose solution (150 mg carbon l^{-1})

375.3 mg of glucose was dissolved per litre deionised water to give a solution of 150 mg l^{-1} carbon.

The 4 carbon source solutions were autoclaved at 120 °C in order to sterilize them of any microbial contaminants, sealed tightly and kept in the refrigerator at 4 °C until use.

7.2.6.2 Nutrient solution preparation

- Mixed N+P stock solution (150 mg l^{-1} N and 15 mg l^{-1} P)

707.1 mg ammonium sulphate and 66 mg potassium phosphate were dissolved in 1 litre deionised water.

- Mixed N+P solution (15 mg l^{-1} N and 1.5 mg l^{-1} P)

10 ml of the mixed N+P stock solution (150 mg l^{-1} N and 15 mg l^{-1} P) was diluted to 100 ml with deionised water.

- Micronutrient stock solution

A micronutrient solution was devised using a trace mineral solution for microbiological media preparation in Atlas (1997) as the basis. The following weights of salts were added to 1 litre deionised water:

Salt	**Weight added (g l^{-1})**
$ZnSO_4.7H_2O$	0.1
$MnCl_2.H_2O$	0.03
H_3BO_3	0.3
$CoCl_2.6H_2O$	0.2
$CuCl_2.2H_2O$	0.01
$NiCl_2.6H_2O$	0.02
$Na_2MoO_4.2H_2O$	0.03

- Micronutrient solution

15 ml of micronutrient stock solution and 5 mg $FeSO_4.7H_2O$ were diluted in 1 litre deionised water so that the micronutrient concentrations were:

Salt	**Concentration (mg l^{-1})**
$ZnSO_4.7H_2O$	1.50
$MnCl_2.H_2O$	0.45
H_3BO_3	4.50
$CoCl_2.6H_2O$	3.00
$CuCl_2.2H_2O$	0.15
$NiCl_2.6H_2O$	0.30
$Na_2MoO_4.2H_2O$	0.45
$FeSO_4.7H_2O$	5.00

- Mixed N+P+micronutrient solution (15 mg l^{-1} N and 1.5 mg l^{-1} P plus micronutrients)

100 ml of the mixed 150 mg l^{-1} N and 15 mg l^{-1} P stock solution plus 15 ml of micronutrient stock solution and 5 mg $FeSO_4.7H_2O$ were diluted in 1 litre deionised water. The nutrient concentration of this solution was therefore:

Nutrient	**Concentration (mg l^{-1})**
Nitrogen	15.00
Phosphorus	1.50
$ZnSO_4.7H_2O$	1.50
$MnCl_2.H_2O$	0.45
H_3BO_3	4.50
$CoCl_2.6H_2O$	3.00
$CuCl_2.2H_2O$	0.15
$NiCl_2.6H_2O$	0.30
$Na_2MoO_4.2H_2O$	0.45
$FeSO_4.7H_2O$	5.00

The 3 working concentration nutrient solutions were autoclaved at 120 °C for one hour to sterilize them of any microbial contaminants, sealed tightly and kept in the refrigerator at 4 °C until use.

7.2.6.3 Soil slurry preparation

10 g fresh soil was weighed to 1 decimal place into a centrifuge tube containing approximately 5 ml small glass beads. 25 ml sterile deionised water was pipetted into the tube. The tubes were capped and mixed thoroughly by shaking for 2 minutes.

7.2.6.4 BD Oxy-CLPP plate preparation

Working in a sterile laminar flow cabinet, 80 µl of the 150 mg l^{-1} carbon source solutions were added to the wells according to the Figure 7-4 and 7-5. 80 µl of nutrient solution was the added to the wells followed by 80 µl of soil slurry (Figure 7-4 and 7-5). The carbon substrate concentration in each well was therefore 50 mg C l^{-1} and the nutrient solutions were 3 times diluted in the wells. Once all the soil slurries were added, the plate was covered with Titre-Tops™ non-breathable adhesive film to prevent air re-entering and the run started.

Sodium acetate and mannose with no nutrient; no carbon with N+P; and no carbon with no nutrient data from Experiment 2 was combined with data from Experiment 4 to give a complete dataset. The plate plans for Experiment 4 are shown in Figure 7-4 and 7-5 below:

<table>
<tr><th></th><th></th><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th>7</th><th>8</th><th>9</th><th>10</th><th>11</th><th>12</th></tr>
<tr><th></th><th></th><th>N1</th><th>N2</th><th>N3</th><th>N1</th><th>N2</th><th>N3</th><th>N1</th><th>N2</th><th>N3</th><th>N1</th><th>N2</th><th>N3</th></tr>
<tr><td>A</td><td>Soil</td><td colspan="3" rowspan="8">Na Acetate</td><td colspan="3" rowspan="8">Mannose</td><td colspan="3" rowspan="8">Malic acid</td><td colspan="3" rowspan="8">Glucose</td></tr>
<tr><td>B</td><td>Soil + RD</td></tr>
<tr><td>C</td><td>Manure</td></tr>
<tr><td>D</td><td>Manure + RD</td></tr>
<tr><td>E</td><td>NPK</td></tr>
<tr><td>F</td><td>NPK + RD</td></tr>
<tr><td>G</td><td>Compost</td></tr>
<tr><td>H</td><td>Compost + RD</td></tr>
</table>

Figure 7-4 BD Oxy-CLPP plate plan for Experiment 4 (Part A)

<table>
<tr><th></th><th></th><th>1</th><th>2</th><th>3</th><th>4</th><th>5</th><th>6</th><th>7</th><th>8</th><th>9</th><th>10</th><th>11</th><th>12</th></tr>
<tr><th></th><th></th><th>N1</th><th>N1</th><th>N1</th><th>N3</th><th>N3</th><th>N3</th><th>No</th><th>No</th><th>No</th><th>No</th><th>No</th><th>No</th></tr>
<tr><td>A</td><td>Soil</td><td colspan="6" rowspan="8">No Carbon</td><td colspan="3" rowspan="8">Malic Acid</td><td colspan="3" rowspan="8">Glucose</td></tr>
<tr><td>B</td><td>Soil + RD</td></tr>
<tr><td>C</td><td>Manure</td></tr>
<tr><td>D</td><td>Manure + RD</td></tr>
<tr><td>E</td><td>NPK</td></tr>
<tr><td>F</td><td>NPK + RD</td></tr>
<tr><td>G</td><td>Compost</td></tr>
<tr><td>H</td><td>Compost + RD</td></tr>
</table>

Figure 7-5 BD Oxy-CLPP plate plan for Experiment 4 (Part B)

Carbon sources

sodium acetate (50 mg C l^{-1})
mannose (50 mg C l^{-1})
malic acid (50 mg C l^{-1})
glucose (50 mg C l^{-1})
no carbon

Nutrient additions

N1	micronutrients
N2	N (5 mg l^{-1}) + P (0.5 mg l^{-1})
N3	N (5 mg l^{-1}) + P (0.5 mg l^{-1}) + micronutrients
No	no nutrients, sterile deionised water only

Micronutrient addition (N1 and N3)

$ZnSO_4.7H_2O$	0.50 mg l^{-1}
$MnCl_2.H_2O$	0.15 mg l^{-1}
H_3BO_3	1.50 mg l^{-1}
$CoCl_2.6H_2O$	1.00 mg l^{-1}
$CuCl_2.2H_2O$	0.05 mg l^{-1}
$NiCl_2.6H_2O$	0.10 mg l^{-1}
$Na_2MoO_4.2H_2O$	0.15 mg l^{-1}
$FeSO_4.7H_2O$	1.67 mg l^{-1}

7.2.7 Data analysis

After 48 hours, the run was stopped and the data was normalized to the $t_{1\ \text{hour}}$ reading. Previous work at Dynamac Corporation (Garland, personal communication) had shown that any anomalous readings that could occur due to temperature effects had stabilized by 1 hour into the run. The $t_{1\ \text{hour}}$ normalized data (Normalized Relative Fluorescent Units: NRFU) was used in statistical analysis using Minitab Version 15 software.

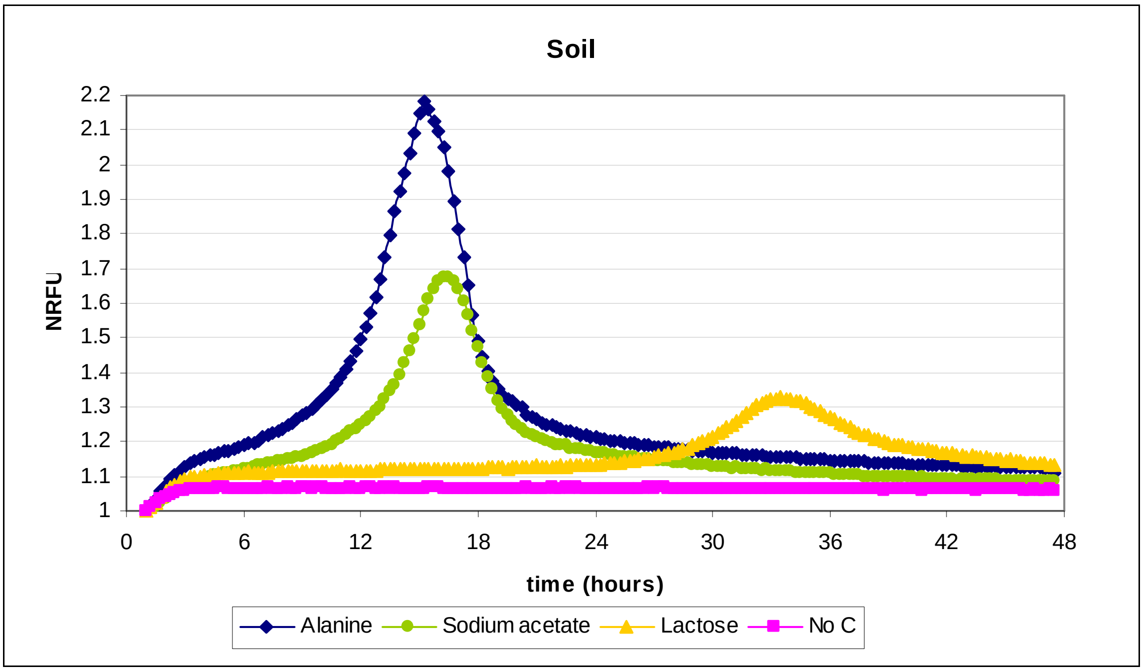


Figure 7-6 Example oxygen consumption trace: Experiment 1 - soil microbial community respiration of 3 carbon substrates vs. a no carbon control over 48 hours

The normalized data was a measure of oxygen consumption in the micro-titre plates and also an indirect measure of substrate use. An example of some normalized data from Experiment 1 is shown in Figure 7-6. A clear increase in oxygen consumption was seen in micro-titre plate wells containing each of the 3 carbon substrates compared to the no carbon control well. However, the respiration peak in the alanine treatment was much higher than those in the sodium acetate and lactose treatements. The lactose treated soil reached maximum peak height much later than the alanine and sodium acetate treated soil. Respiration in the no C addition well reached a plateau very early.

7.2.7.1 Measured parameters

The following parameters of the oxygen consumption trace were analysed using plate reading software and a Microsoft Excel spreadsheet:

- Maximum peak height

This was the maximum respiration response shown in the well. This shows the extent to which the substrates were utilized by the microbial communities.

- Time at maximum peak

This was the time that corresponded to the maximum response. It showed the speed at which the community could reach the maximum utilization of the substrates.

- Time to minimum response (10 %)

A 10 % increase on the $t_{1\ \mathrm{hour}}$ reading was deemed as the minimum response that could be distinguished from background noise. This shows the speed at which the microbial community could begin to utilize the substrates.

These 3 parameters are shown graphically in Figure 7-7 below:

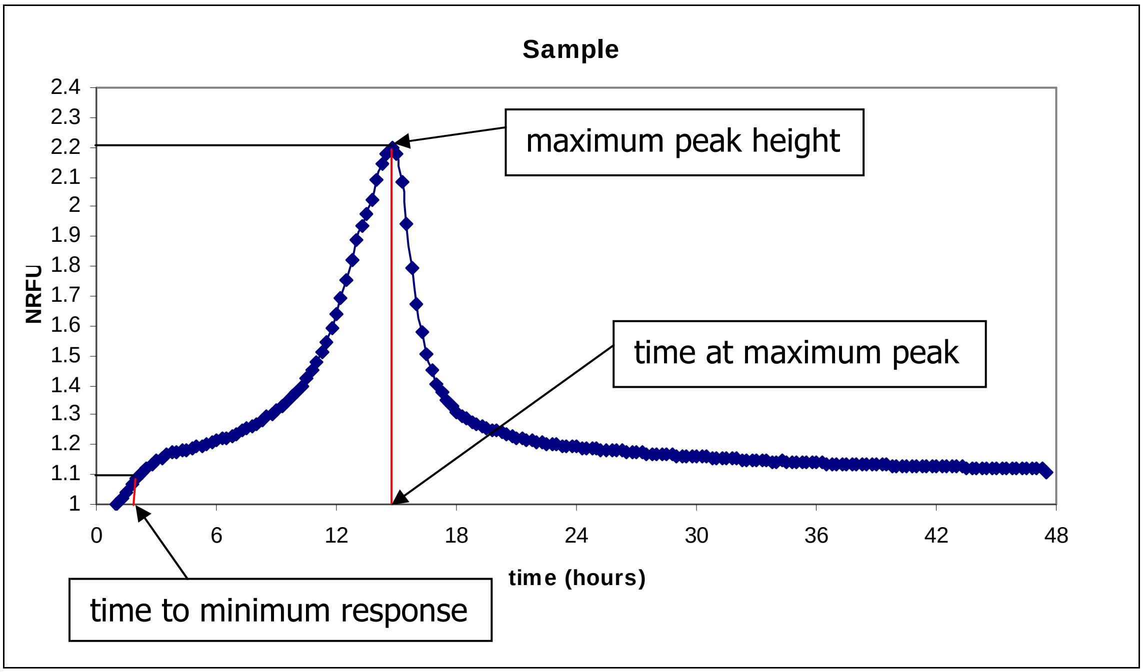


Figure 7-7 Example showing the 3 parameters used to describe substrate use

- Peak area

Peak area was calculated as the difference between the carbon source treated well and the corresponding control treatment (no carbon) for a given soil. In the nutrient addition experiment, peak area was calculated as the difference between the nutrient addition well and the non-treated well within a given carbon source treatment. The difference at each data point was summed and used as peak area (Figure 7-8). This gave a measure of the total extra respiration in the C source treated wells above that in the no C control.

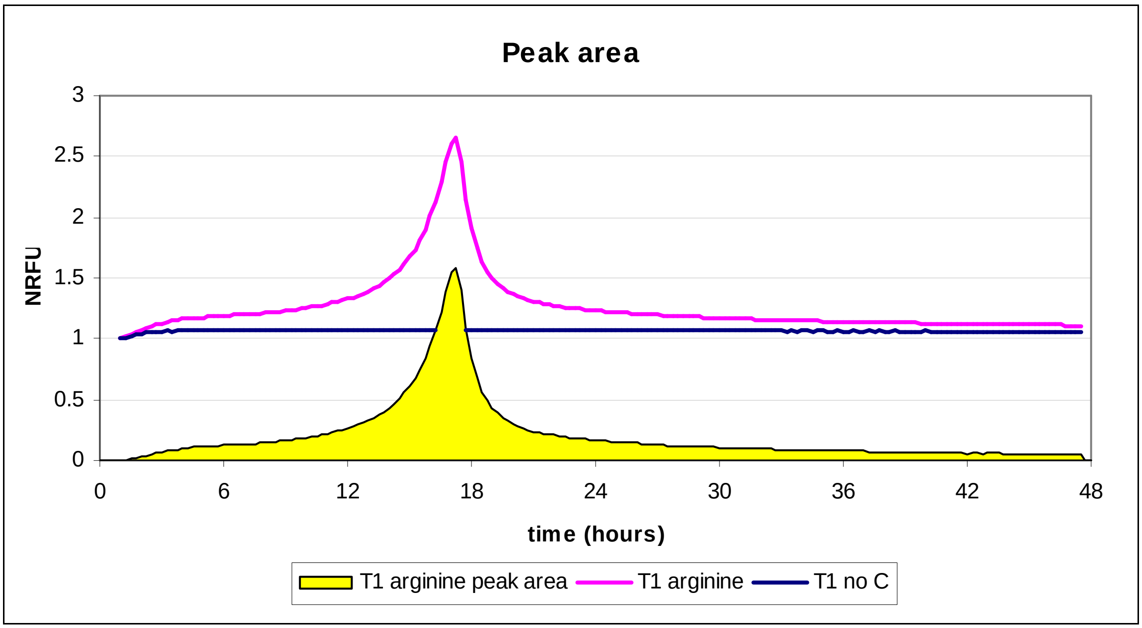


Figure 7-8 Example showing peak area calculation: no carbon (control) well subtracted from carbon source treated well

7.2.7.2 Statistical analysis of data

Maximum peak, time at maximum peak, time to minimum response and peak area data were analysed using Minitab statistical software (Version 15) using the general linear model (GLM) command. Some data were required to be log transformed to give a normal distribution before analysis. Factors describing sample location (column of field trial) and carbon source addition along with interactions of these terms with those being investigated were used in the GLM analyses but are not reported here as they were not being investigated. The factors investigated in each experiment are listed in Table 7-1.

Experiment 1	Experiment 2
Carbon source Amendment Rockdust Amendment*rockdust	Amendment Rockdust Nutrients Amendment*rockdust Amendment*nutrient Nutrients*rockdust

Experiment 3	Experiment 4
Amendment	Amendment
Nitrogen	Rockdust
Cycloheximide	Amendment*rockdust
Amendment*nitrogen	Nutrients
Amendment*cycloheximide	Nutrients*amendment
Nitrogen*cycloheximide	Nutrients*rockdust

Table 7-1 Minitab GLM factors investigated in BDOxy-CLPP analysis

7.3 Results

7.3.1 Experiment 1: Endogenous respiration

7.3.1.1 Example data

Some example oxygen consumption data from Experiment 1 are shown in Figure 7-9 – 7-12.

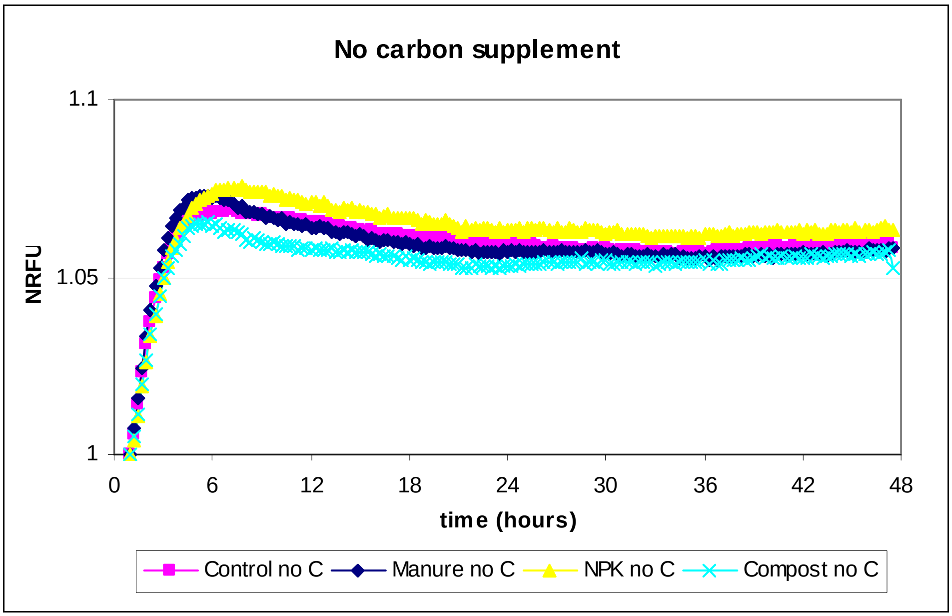


Figure 7-9 Respiration in no carbon supplemented wells (no rockdust plots)

The unsupplemented wells show the endogenous respiration in these samples and indicate that there were few differences in microbial respiration rate between treatments (Figure 7-9). This showed that BDOxy-CLPP analysis rather than traditional respirometric techniques could be more useful for determining functional differences between the field trial treatments.

The greatest responses to carbon substrates (for all soil treatments) were seen in amino acid supplemented wells (Figure 7-10) compared to sugar and carboxylate substrates (Figure 7-11 and 7-12). This enhanced response was likely to have been caused by the increased nitrogen in treated wells. This effect was tested further in Experiment 2 where nutrient limitations were investigated.

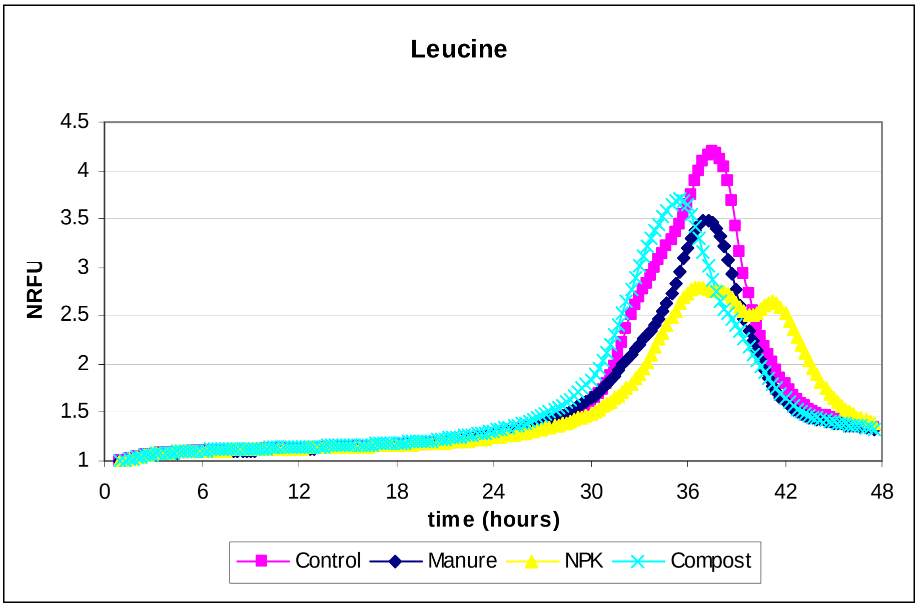


Figure 7-10 Respiration in leucine supplemented wells (no rockdust plots)

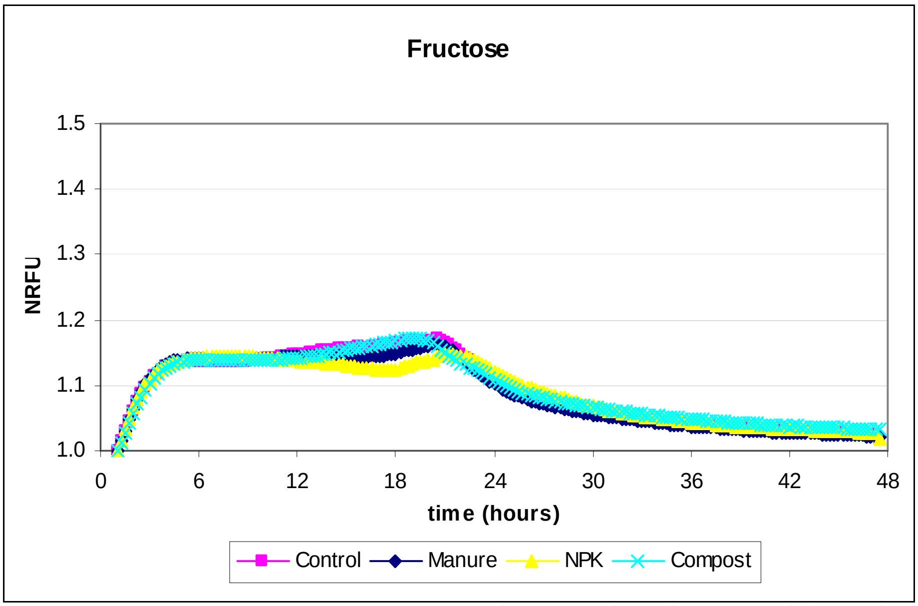


Figure 7-11 Respiration in fructose supplemented wells (no rockdust plots)

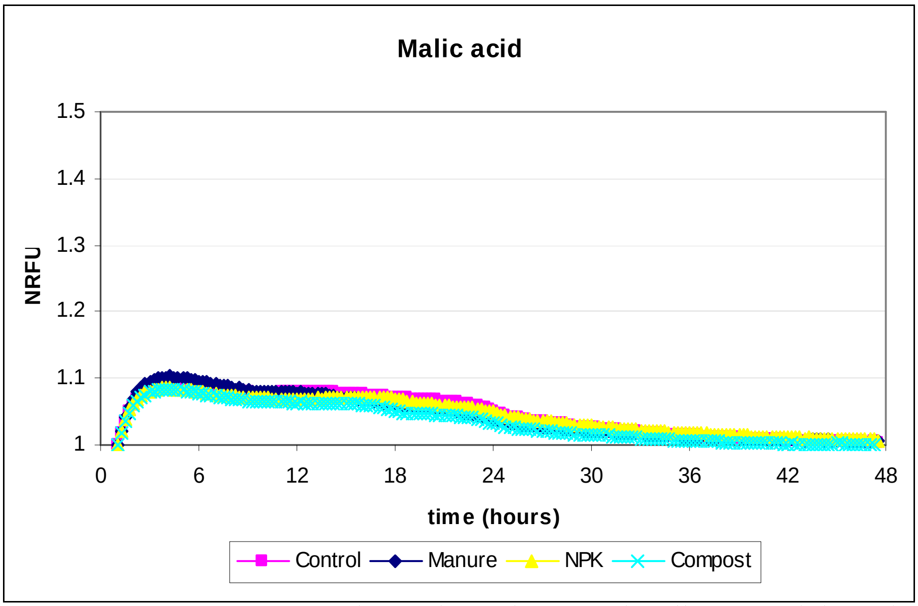


Figure 7-12 Respiration in malic acid supplemented wells (no rockdust plots)

7.3.1.2 Statistical analysis

Results for the statistical analysis of Experiment 1 data are shown in Table 7-2:

Effect	Response			
	Maximum peak	Time at maximum peak	Time to minimum response	Peak area
Carbon source	***	***	***	***
Amendment	NS	NS	**	NS
Rockdust	NS	**	NS	***
Amendment*rockdust	NS	**	**	NS

Table 7-2 Effect of 4 factors on BDOxy-CLPP analyses (NS = not significant; ** = significant effect at $p \leq 0.05$ level; * = significant effect at $p \leq 0.01$ level)**

Statistical significance was tested using Tukey's LSD test, the results of which are shown in Table 7-3 – Table 7-6.

Carbon source	Response			
	Maximum peak	Time at maximum peak	Time to minimum response	Peak area
Citric acid	1.126 b	13.42 bc	N/A	5.05 a
Malic acid	1.113 b	7.70 a	N/A	2.81 a
Sodium acetate	1.347 d	13.13 bc	3.62 ab	11.69 b
Alanine	2.451 f	15.80 c	4.13 ab	41.27 d
Arginine	2.619 f	14.88 c	3.18 a	42.15 d
Glycine	1.455 e	45.94 h	4.67 ab	26.86 cd
Leucine	4.803 g	37.32 g	9.63 de	99.85 e
Fructose	1.237 c	16.23 c	7.25 bcd	9.04 b
Glucose	1.223 c	15.49 f	5.65 abc	8.12 b
Lactose	1.259 cd	31.95 e	15.24 e	13.72 bc
Mannose	1.265 cd	22.92 d	8.70 cd	13.66 bc
No C	1.075 a	10.56 ab	N/A	N/A

Table 7-3 Effect of carbon source on maximum peak, time at maximum peak, time to minimum response and peak area. Values followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 7-3 shows the differences in respiration response due to the different C sources. It shows that the amino acids gave the highest maximum peaks and peak areas. Citric acid, malic acid and the no carbon treatments did not give a clear respiration response (the 10 % increase in respiration was not attained). There were some significant differences in time at maximum peak and time to minimum response where the sugars and the amino acids took longer to reach maximum peak. Time to minimum response showed that leucine and lactose took the longest to show an initial response compared to the other C sources. This data analysis is in agreement with the example data shown in Figure 7-9 – 7-12 whereby the greatest respiration response is always in the amino acid treated wells. There were no significant interactions of carbon source with amendment or rockdust, therefore the differences due to C source addition did not depend on soil treatment.

Amendment	Time to minimum response (hours)
Control	5.82 a
Manure	6.30 ab
NPK	7.19 ab
Compost	8.17 b

Table 7-4 Effect of organic/inorganic amendment on time to minimum response
Values followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

The analysis in Table 7-4 shows that the compost treated soil took longer to reach the minimum response threshold than the control treatment. The manure and NPK treatments were not significantly different to either the control or the compost treatment.

Rockdust application	Response	
	Time at maximum peak (hours)	Peak area
No rockdust applied	18.31 a	26.00 b
Rockdust applied	19.69 b	23.86 a

Table 7-5 Effect of rockdust on time at maximum peak and peak area
Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 7-5 shows that overall, rockdust addition to field trial soil increased the time taken to reach maximum peak height. Rockdust addition also significantly reduced the peak area.

Amendment	Rockdust application	Response	
		Time at maximum peak (hours)	Time to minimum response (hours)
Control	No rockdust applied	18.98 ab	5.12 a
	Rockdust applied	20.39 ab	6.55 ab
Manure	No rockdust applied	17.08 a	6.58 ab
	Rockdust applied	18.47 ab	6.01 ab
NPK	No rockdust applied	17.82 a	6.14 ab
	Rockdust applied	21.44 b	8.20 ab
Compost	No rockdust applied	19.37 ab	9.18 b
	Rockdust applied	18.47 ab	7.09 ab

Table 7-6 Effect of amendment/rockdust interaction on time at maximum peak and time to minimum response. Values in the same column followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test

The significant amendment/rockdust interactions were investigated in Table 7-6; this shows that rockdust had a significant effect on time at maximum peak in the NPK treated soil where it significantly increased the time to maximum peak. The increase in time to minimum response found in Table 7-4 was also tested further in Table 7-6 and showed that this was significant in the control and compost only when no rockdust was applied.

7.3.1.3 Further statistical analysis

As the amino acid treatments gave the greatest respiration responses in Experiment 1, the data were re-analysed by omitting all treatments other than alanine, arginine, glycine and leucine. The results are summarized in Table 7-7:

Effect	Response			
	Maximum peak	Time at maximum peak	Time to minimum response	Peak area
C source	***	***	***	***
Amendment	NS	***	NS	NS
Rockdust	NS	***	NS	NS
Amendment*rockdust	NS	NS	NS	***

Table 7-7 Effect of 3 factors on BDOxy-CLPP analyses (NS = not significant; ** = significant effect at $p \leq 0.05$ level; * = significant effect at $p \leq 0.01$ level)**

Statistical significance was tested using Tukey's LSD test, the results of which are shown in Table 7-8 – 7-10. The significant effects due to C source were not investigated since differences had already been shown (Table 7-3) but were not of further interest once the other carbon sources had been omitted from the data.

Amendment	Time at maximum peak (hours)
Control	24.72 b
Manure	23.29 a
NPK	25.02 b
Compost	23.55 ab

Table 7-8 Effect of organic/inorganic amendment on time to maximum peak Values followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test

Table 7-8 shows that there were some differences in time at maximum peak due to amendment when the amino acid data was analysed. These differences were not shown in the initial analysis (Table 7-2). Manure was shown to reach maximum respiration response faster than the control and NPK treatments.

Rockdust application	Time at maximum peak (hours)
No rockdust applied	23.68 a
Rockdust applied	24.62 b

Table 7-9 Effect of rockdust on time at maximum peak Values followed by the same letter are not significantly different at $p = 0.05$ according to Tukey's LSD test

Table 7-9 shows that the response shown in Table 7-5 whereby rockdust application increased the time taken to reach maximum response was significant in the amino acid treatments.

Amendment	Rockdust application	Peak area
Control	No rockdust applied	63.60 ab
	Rockdust applied	44.88 a
Manure	No rockdust applied	47.50 ab
	Rockdust applied	49.78 ab
NPK	No rockdust applied	54.08 ab
	Rockdust applied	46.84 ab
Compost	No rockdust applied	48.02 ab
	Rockdust applied	65.60 b

Table 7-10 Effect of amendment/rockdust interaction on peak area
Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 7-10 shows that the significant interaction of amendment and rockdust where the control with rockdust gave a smaller peak area than the compost with rockdust. This interaction did not show up in the initial analysis of the whole dataset (Table 7-2).

This further data analysis showed some significant effects that did not appear in the initial analysis due to the poor response in some C source treated wells. The conclusions from this further analysis can be compared with the data from the Experiment 2 which looks at N limitations in the samples.

7.3.2 Experiment 2: Nutrient limitations

7.3.2.1 Example data

Nitrogen addition (with and without P) could increase the maximum peak height compared to the no nutrient control and P addition only. An example of nutrient addition in the manure treated soil (with mannose as the C source) is shown in Figure 7-13 below:

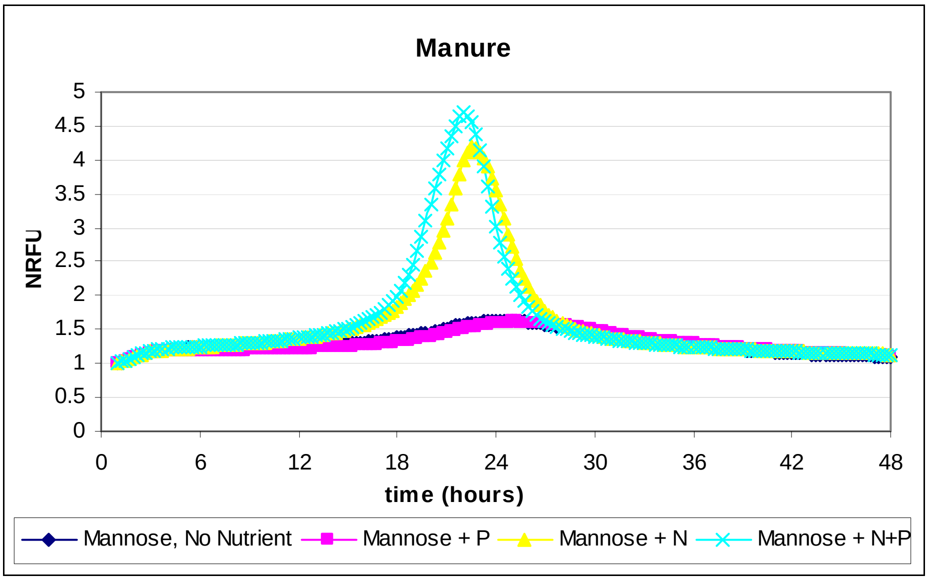


Figure 7-13 Effect of nutrient additions with mannose as the carbon source in manure treated plots

Figure 7-14 shows an example of the differences in time at maximum peak between the 4 amendments.

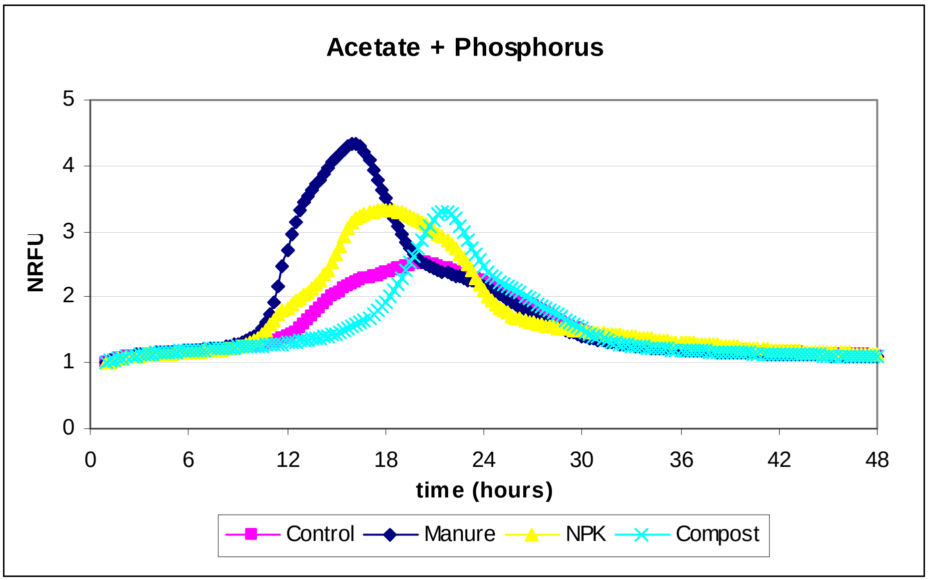


Figure 7-14 Effect of acetate plus phosphorus addition to 4 soil amendment treatments

7.3.2.2 Statistical analysis

Effect	Response			
	Maximum peak	Time at maximum peak	Time to minimum response	Peak area
Amendment	NS	***	***	NS
Rockdust	NS	NS	***	NS
Nutrients	***	***	NS	***
Amendment*rockdust	NS	NS	NS	NS
Amendment*nutrient	NS	NS	NS	NS
Nutrients*rockdust	NS	NS	NS	NS

Table 7-11 Effect of 6 factors on BDOxy-CLPP analyses (NS = not significant; * = significant effect at p ≤ 0.01 level)**

Statistical significance was tested using Tukey's LSD test, the results of which are shown in Table 7-12 – Table 7-14:

Amendment	Response	
	Time at maximum peak (hours)	Time to minimum response (hours)
Control	21.88 ab	4.85 ab
Manure	19.23 a	3.61 a
NPK	23.22 ab	4.68 ab
Compost	24.94 b	5.38 b

Table 7-12 Effect of organic/inorganic amendment on time at maximum peak and time to minimum response. Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 7-12 shows that compost treated soil took significantly longer than manure treated soil to reach the minimum response and maximum peak. The control and NPK treated soils were not significantly different to manure or compost treated soil in either case.

Rockdust application	Time to minimum response (hours)
Rockdust applied	5.27 b
No rockdust applied	4.02 a

Table 7-13 Effect of rockdust on time to minimum response Values followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Rockdust application was shown to increase the time to minimum response in Table 7-13.

Nutrient addition	Maximum peak	Time at maximum peak (hours)	Peak area
no nutrient	2.29 a	20.60 a	N/A
N only	4.76 b	22.22 ab	53.80 b
P only	2.00 a	21.29 a	5.60 a
N + P	5.10 b	25.17 b	59.39 b

Table 7-14 Effect of nutrient addition on maximum peak and time at maximum peak Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

There was a significant effect of N addition (with and without P) across all treatments. This effect did not depend on which treatment had been applied to soil (i.e. it was independent of organic/inorganic amendment). Table 7-14 shows N (both with and without P) addition significantly increased the maximum peak height and peak area compared to no nutrient addition and P addition only. N+P addition significantly increased the time taken to reach maximum peak compared to no nutrient addition and P addition only. For time at maximum peak, N addition alone was not significantly different to any of the other 3 treatments.

7.3.3 Experiment 3: Bacterial vs. fungal communities

7.3.3.1 Example data

The addition of N and cycloheximide was shown to increase the maximum peak height. An example of the effect of cycloheximide addition with and without nitrogen is shown in Figure 7-15.

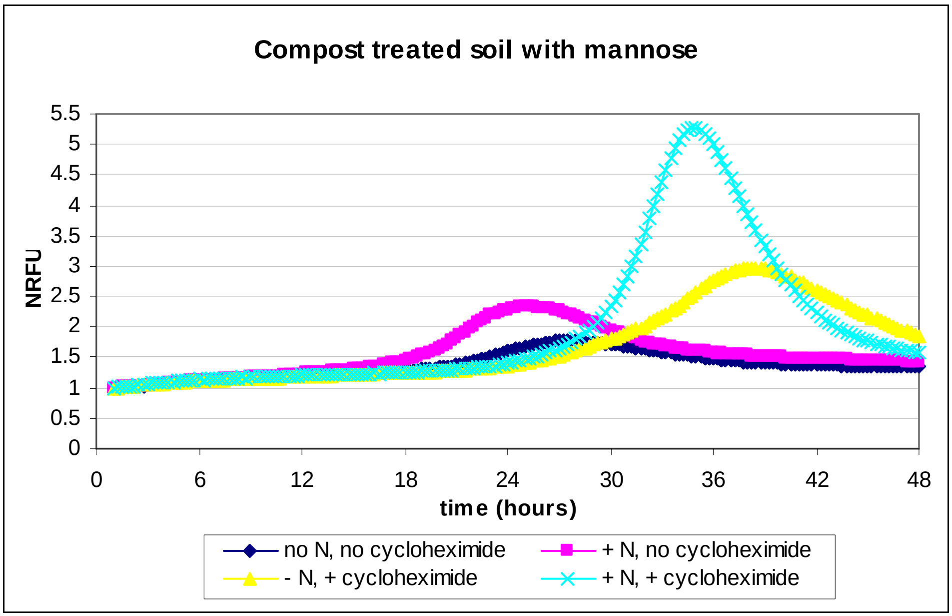


Figure 7-15 Effect of nitrogen and cycloheximide addition (separately or together) on peak height, time to peak, and peak area in compost treated soils

An example of the differences between soil amendments on the time at maximum peak is shown in Figure 7-16.

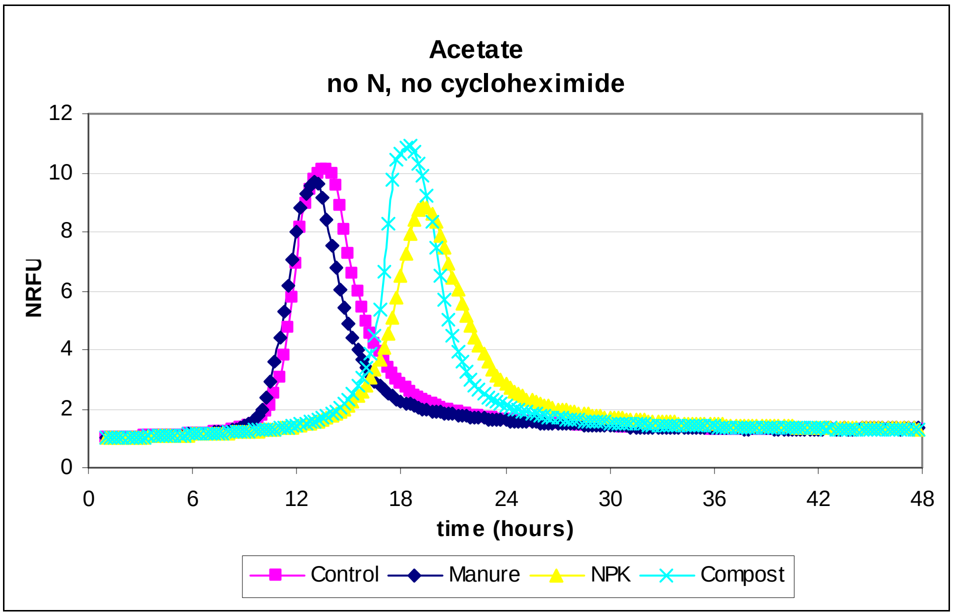


Figure 7-16 Effect of different organic/inorganic soil amendments on time at maximum peak in acetate, no nitrogen, no cycloheximide treatments

7.3.3.2 Statistical analysis

Effect	Response			
	Maximum peak	Time at maximum peak	Time to minimum response	Peak area
Amendment	NS	**	**	NS
Nitrogen	***	***	***	***
cycloheximide	***	***	***	***
amendment*nitrogen	NS	NS	NS	NS
amendment*cycloheximide	NS	NS	***	NS
Nitrogen*cycloheximide	NS	NS	NS	NS

Table 7-15 Effect of 6 factors on BDOxy-CLPP analyses (NS = not significant; ** = significant effect at p ≤ 0.05 level; * = significant effect at p ≤ 0.01 level)**

Statistical significance was tested using Tukey's LSD test, the results of which are shown in Table 7-16 – 7-19.

Amendment	Time at maximum peak (hours)	Time to minimum response (hours)
Control	22.76 ab	4.08 ab
Manure	21.80 a	3.95 a
NPK	23.96 b	4.46 b
Compost	23.19 ab	4.09 ab

Table 7-16 Effect of organic/inorganic amendment on time at maximum peak and time to minimum response. Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

In this experiment, the significant overall effect of amendment showed that manure treated soil reached maximum peak height faster than NPK treated soil while the control and compost treatments were intermediate between these two extremes. The pattern of significant differences in time taken to reach minimum response was the same – manure treated soil responded earlier than NPK treated soil.

Nutrient addition	Maximum peak	Time at maximum peak (hours)	Time to minimum response (hours)	Peak area
Nitrogen	4.74 b	21.97 a	3.90 a	152.0 b
No addition	4.16 a	23.89 b	4.39 b	145.3 a

Table 7-17 Effect of nitrogen addition on maximum peak, time at maximum peak, time to minimum response and peak area. Values followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Addition of nitrogen to the samples gave highly significant responses on all measurements overall. The time taken to give a minimum response was faster, maximum peak height was higher, and earlier and the peak area was larger compared to no nitrogen additions (Table 7-17). The significant effects of nitrogen addition did not depend on organic/inorganic amendment treatment (no significant interaction in Table 7-16).

Cycloheximide addition	Maximum peak	Time at maximum peak (hours)	Time to minimum response (hours)	Peak area
Cycloheximide	5.12 b	23.88 b	3.49 a	168.3 b
No addition	3.78 a	21.98 a	4.80 b	129.0 a

Table 7-18 Effect of cycloheximide addition on maximum peak, time at maximum peak, time to minimum response and peak area. Values followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Table 7-18 shows that cycloheximide addition significantly increased maximum peak height and lead to a later time at maximum peak. Peak area was shown to be increased by cycloheximide addition. The minimum response was reached faster in cycloheximide wells. The significant interaction between amendment and cycloheximide addition was tested further in Table 7-19.

Amendment	Cycloheximide addition	Time to minimum response (hours)
Control	Cycloheximide	3.43 a
	No addition	4.73 b
Manure	Cycloheximide	3.01 a
	No addition	4.90 b
NPK	Cycloheximide	4.20 b
	No addition	4.73 b
Compost	Cycloheximide	3.33 a
	No addition	4.86 b

Table 7-19 Effect of amendment/cycloheximide interaction on time to minimum response Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

This shows that in the control, manure and compost samples cycloheximide addition led to shorter time to minimum responses. However, in NPK treated plots cycloheximide did not significantly affect time to minimum response.

7.3.4 Experiment 4: Micronutrient limitations

7.3.4.1 Example data

Figure 7-17 shows an example of the effects of N+P and micronutrient addition (separately or together) to soil samples.

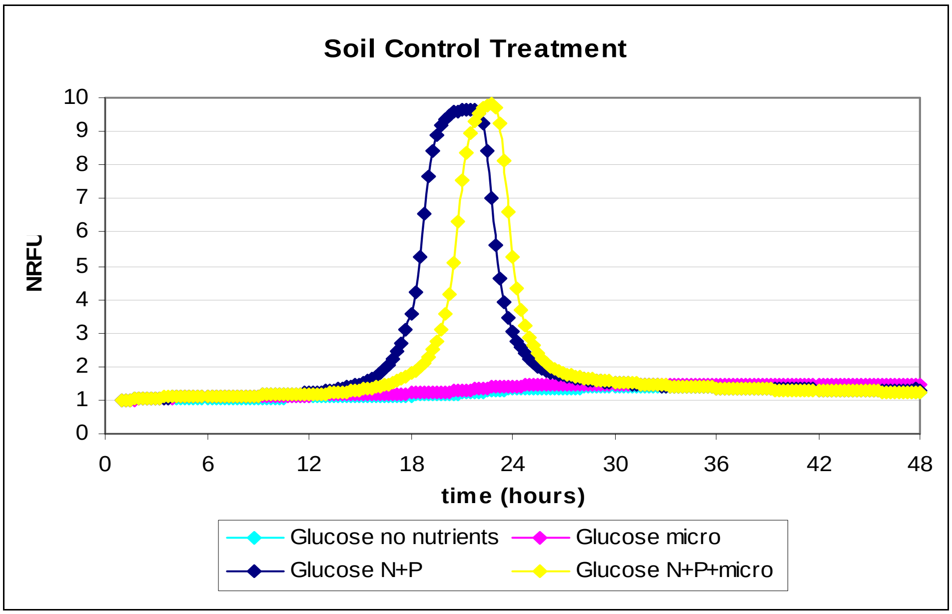


Figure 7-17 Effect of nutrient addition with glucose carbon source on maximum peak in field trial control soil

Figure 7-18 shows an example of differences in time at maximum peak between soil amendments.

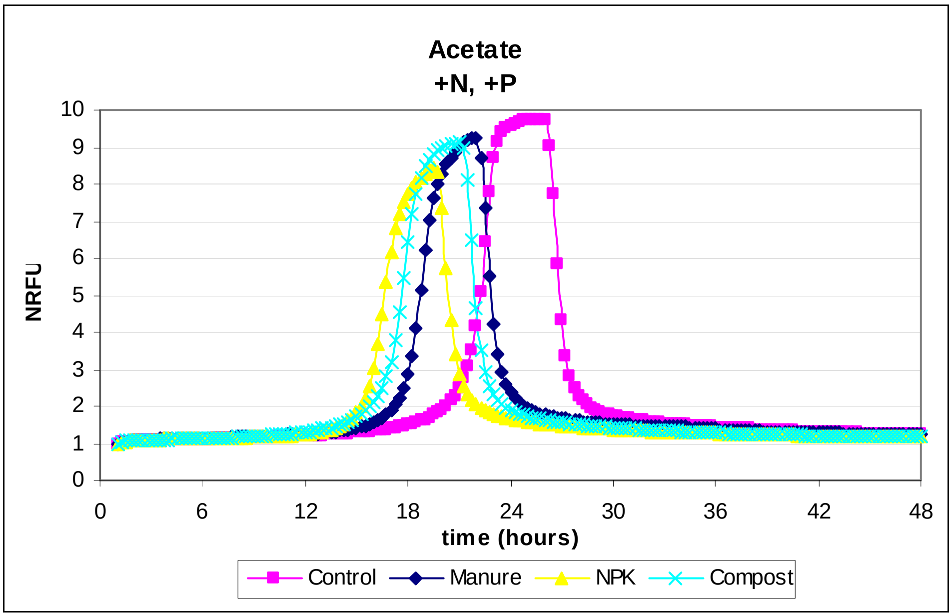


Figure 7-18 Effect of different soil organic/inorganic amendments on time to maximum peak in acetate with N and P treatments

7.3.4.2 Statistical analysis

Effect	Response			
	Maximum peak	Time at maximum peak	Time to minimum response	Peak area
Amendment	NS	***	***	NS
Rockdust	NS	NS	NS	NS
Amendment*rockdust	NS	NS	***	***
Nutrients	***	NS	NS	***
Nutrients*amendment	NS	NS	***	NS
Nutrients*rockdust	NS	NS	NS	NS

Table 7-20 Effect of 6 factors on BDOxy-CLPP analyses (NS = not significant; ** = significant effect at p ≤ 0.05 level; * = significant effect at p ≤ 0.01 level)**

Statistical significance shown in Table 7-20 was tested using Tukey's LSD test, the results of which are shown in Table 7-21 – 7-24.

Amendment	Time at maximum peak (hours)	Time to minimum response (hours)
Control	24.68 b	6.16 b
Manure	22.06 ab	5.11 ab
NPK	21.50 a	4.35 a
Compost	23.90 ab	4.64 a

Table 7-21 Effect of organic/inorganic amendment on time at maximum peak and time to minimum response. Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

The significant amendment effects showed that the control took longer than the NPK treated soil to reach the minimum response or to reach maximum peak height (Table 7-21). For time to minimum response, the control was also shown to take longer than the compost treatment to respond.

The significant interaction between amendment and rockdust shown in Table 7-20 for time to minimum response and peak area was tested in Table 7-22. This analysis showed that when rockdust was not applied, the control took longer than the other 3 organic/inorganic amendments to reach the minimum response. When rockdust was applied, the differences between treatments were not significant. Rockdust addition within each amendment type did not lead to any significant differences in time to minimum response compared to those that had no rockdust added. The significant interaction between rockdust and amendment on peak area was tested in Table 7-22. This analysis shows that the only difference was that manure with rockdust applied gave significantly lower peak areas than NPK without rockdust applied. Therefore this significant interaction was not an important one.

Amendment	Rockdust application	Response	
		Time to minimum response (hours)	Peak area
Control	Rockdust applied	6.16 ab	53.39 b
	No rockdust applied	6.17 b	65.28 b
Manure	Rockdust applied	5.45 ab	39.03 a
	No rockdust applied	4.79 a	48.07 b
NPK	Rockdust applied	4.71 a	58.57 b
	No rockdust applied	3.99 a	51.50 b
Compost	Rockdust applied	5.22 ab	55.25 b
	No rockdust applied	4.13 a	54.46 b

Table 7-22 Effect of amendment/rockdust interaction on time to minimum response and peak area. Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

Nutrient addition	Maximum peak	Peak area
no nutrients	2.03 a	N/A
Micronutrients	1.82 a	14.06 a
N + P	5.18 b	71.96 b
N + P + micronutrients	5.05 b	73.56 b

Table 7-23 Effect of nutrient addition on maximum peak and peak area Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

As was shown in Figure 7-17, micronutrients did not significantly increase maximum peak compared to no nutrient addition wells. Again, N and P addition increased maximum peak height and peak area and addition of micronutrients with N and P did not increase maximum peak or peak area further (Table 7-23).

Amendment	Nutrients	Time to minimum response (hours)
Control	none	5.88 ab
Manure	none	2.65 a
NPK	none	2.96 ab
Compost	none	6.50 b

Table 7-24 Effect of organic/inorganic amendment with no nutrients on time to minimum response. Values in the same column followed by the same letter are not significantly different at p = 0.05 according to Tukey's LSD test

The significant interaction of amendment/nutrients on time to minimum response was tested in Table 7-24 and showed that manure responded faster than compost only when no additional nutrients were supplied.

7.4 Discussion

7.4.1 Choice of carbon substrates

8 of the carbon sources chosen in Experiment 1 were included in CLPP tests by Campbell *et al.* (2003) and described as 'ecologically relevant to soil'. 3 were included from the 31 C sources on Biolog Ecoplates described as 'useful for soil community analysis' (Biolog Inc., 2007) and two were used by Väisänen *et al.* (2005) who used a range of molecules from simple sugars to complex molecules like cellulose and starch. Complex molecules were not used in these experiments due to their low solubilities although if further testing on CLPP was to be undertaken, either complex, long-chain molecules or intermediate molecules formed in their degradation could be used.

7.4.2 Whole soil vs. soil extract

One of the major drawbacks to this method is that it uses a soil water extract rather than the whole soil. This means that the activities measured may not accurately represent what is occurring in the soil as a whole. A whole soil method was developed by Campbell *et al.* (2003) who used a pH indicator gel to measure CO_2 evolution from deep-well plates. This technique showed differences in the 'metabolic fingerprint' between soils treated with different wastewater sludges while the Biolog technique did not. These authors showed that the use of the whole soil could have advantages over soil extracts used in traditional CLPP methods; specifically where Biolog plates produced a lag phase corresponding to microbial growth whereas the whole soil method reflected immediate microbial activity. This is not a problem in BDOxy analysis as nutrient addition is at lower levels therefore there is less opportunity for microbial growth and immediate microbial activity is more easily determined.

7.4.3 Variability within treatments

One reason for the lack of significant effects of amendment and rockdust on respiration in treated soils was that there was a large amount of variation between replicate plots and that any differences between the treatments was masked by large standard deviations between samples. This could be investigated further by conducting laboratory experiments under more controlled conditions (e.g. soil incubations) although the field trial was much more useful for investigating the effects in a 'real-life' setting.

7.4.4 Effect of rockdust on microbiological community

The only significant effects of rockdust were shown in Experiments 1 and 2 (Sections 7.3.1 and 7.3.2). In Experiment 1, rockdust was shown to give overall, smaller peak areas compared to soil with no rockdust applied. This indicates that the microbial community utilised carbon sources to a lesser degree in rockdust treated plots. Rockdust also led to an overall delay in time at maximum peak that was especially significant in NPK treated soil. This shows that the microbes in rockdust and NPK treated soil were less equipped to utilize added carbon sources than those treated with NPK alone. In the statistical analysis of the amino acid data from Experiment 1, rockdust was shown to increase the time at maximum peak, while in Experiment 2 rockdust gave longer time to minimum response overall (independently of amendment type and nutrient addition). This shows that the microbial community took longer to begin respiring the added C sources and to reach the maximum respiration rate.

These significant effects of rockdust are quite contradictory to the initial hypothesis that expected rockdust to increase microbial activities in treated soils. Rather, if there was an effect of rockdust, it was shown that its application led to slower responses and smaller peaks. In many of the statistical analyses there were no effects of rockdust on any of the measured parameters.

Overall, these experiments conclude that almost 4 years after rockdust addition to agricultural soil there were few effects to be seen on the microbial population's ability to utilize added or endogenous carbon that could be attributed to rockdust application.

7.4.5 Effect of soil amendment on microbiological community

7.4.5.1 Ability to respire added carbon substrates

Some differences between organic/inorganic amendments were shown in these experiments. Often compost treated soil was shown to respond slowest to added nutrients (i.e. longest time to minimum response and time at maximum peak). This indicates that the microbial community in compost treated soil was less ready to begin respiring new substrates. Manure often responded fasted to added nutrients showing that the microbial community was more dynamic and able to quickly begin utilizing newly added substrates.

Amendment type did not increase maximum peak or peak area in any of the experiments whether in nutrient treated wells or control wells. This indicates that the microbial communities were no more able to respire added nutrients to a greater extent in any of the amendment treatments.

These results show that there were little long-term effects on the physiological profile of the soil microbial community when the plots were treated with organic and inorganic amendments over the three years of the field trial. There had been over 1 year since the last application of amendment materials at the time of sampling although residual effects due to the fertilization history were expected. Garland (personal communication) had shown that differences in microbial community could be seen between organic and inorganic soil fertilizer treatments immediately after application. Metabolic diversity in soil treated with crop residues was shown to decline over time when analysed with Biolog GN plates (Bending *et al.*, 2002). In addition to this, under certain conditions it was shown that the enzymatic and Biolog profiles obtained 112 days after certain crop residue additions to soil could be the same as those obtained in the untreated control. However, this depended on soil type and crop residue type as most additions did show differences in microbial profiles at this time.

Sharma *et al.* (1998) showed the effects on microbial communities during decomposition of maize litter that was either mulched or incorporated into the soil. The treated soils were clearly different to untreated controls after 2 and 52 weeks incubation. Degens (1998) also showed changes in the functional diversity (after 20 weeks) of an arable soil following simple C substrate addition. These differences in pattern of catabolic potential versus the non-treated soil occurred despite similar biomass carbon.

Therefore, these other researchers show that there could have been differences between the microbial communities up to 1 year after application these soil amendments (i.e. in the short term) compared with the control. However, the results from these experiments show that if there were any short-term effects they mostly did not last into the long-term.

7.4.5.2 Inorganic nutrient requirements

There were no significant interactions of amendment with inorganic nutrients in Experiments 2, 3 and 4. This shows that microbes in soil amended with different treatments did not respond any differently to nutrient addition compared with the other treatments or the control. Therefore the microbial N, P and micronutrient limitations in all of the soil samples amended with different materials were the same and no different to the limitation present in the control.

As was discussed earlier, the best nutrient response was seen in wells treated with nitrogen-containing molecules (Experiment 1) or those that had N added (Experiments 2, 3 and 4). This effect was also reported by Garland *et al.* (2003) who showed that the removal of N from leaf-litter samples eliminated the BDOxy response in non-N containing carbon source substrates. The results from the field trial (Chapter 6) show that there were clear plant growth differences due to the effect of different amendment addition. It was expected that given the fertilization history (3 years of additions had occurred), a clear difference in the microbial communities in these plots would be seen. However, these differences were not seen in this microbial community analysis as all samples responded similarly to N addition. It seems that nitrogen limitation in these samples was more severe than carbon limitation for microbial respiration. This conclusion is confirmed by the data from Experiment 1 that showed the best responses were shown in amino acid treated wells compared to non-N containing carbon substrates.

In Experiment 3, the effect of nitrogen response occurred independently of amendment type and rockdust. However the significant effect of cycloheximide addition depended on amendment type where, in every treatment but NPK, cycloheximide reduced the time to minimum response. As cycloheximide is a fungicide, this faster response is attributed to the bacterial community. Cycloheximide addition always led to increased peak area and height and faster response times although the time to maximum peak was delayed. Hence, in the absence of the fungal community, the bacterial community is able to quickly adapt to the change in conditions and respire substrates to a greater extent. Nitrogen addition in Experiment 3 was shown to increase maximum peak and peak area and decrease the response time (time to minimum response) and time at maximum peak. This effect was independent of cycloheximide addition indicating that in all of the field trial soils, nitrogen addition led to stronger responses of the microbial population whether the fungal population was present or not indicating that the bulk of this respiration was carried out by bacteria.

To the contrary, Väisänen *et al*. (2005) did not show a significant effect of N addition on the physiological response of the microbial community as a whole. However, mineral N addition was shown to have a stronger effect on the bacterial community composition although the response was not significant due to variation within replicates.

7.5 Summary

BDOxy-CLPP analysis proved a useful tool for assessing the microbial community of a soil as a whole. Statistical analysis of the data produced using this technique can be used to determine differences in the catabolic potential between different soil treatments.

This analysis was unable to show any lasting effects of rockdust application on microbial community function. Further testing would be required to determine if there were any immediate effects after applying rockdust to soil. This could be carried out on soil/rockdust incubations and measured over a period of months in a similar way to experiments carried out by Sharma *et al.* (1998) who used maize litter as a treatment to soil.

There were some effects that could be seen due to amendment type using this analysis. These effects showed that compost treated soil was less readily able to utilize added nutrients while manure treated soil was most readily able. Amendment type was never shown to increase the extent to which a carbon substrate could be utilized. Any differences that were significant were on time to respond or time to maximum, corresponding to rate of utilization differences rather than extent of respiration of the substrates. Differences between organic/inorganic amendments were less pronounced than they might have been if BDOxy-CLPP analysis had been carried out on soil closer to last application time. However, there had been 3 years of amendment additions prior to sampling and a long-lasting residual effect of fertilizer addition was expected. These results show that any differences that might occur in the short-term do not last into the long-term.

Chapter 8: Greenhouse Pot Trials

8.1 Introduction

The SEER Centre uses a deep-bed system consisting of a mixture of greenwaste compost and rockdust to demonstrate the effects on plant growth. They market a commercial product (SEER Rocksoil™) based on the 4:1 compost/rockdust mixture that is sold as a plant growth medium. They also produce a soil improver called SEER Rockmix™ that consists of a lower ratio of 1:1. Rockmix is sold to be used as a soil top dressing.

Pot trials were designed to investigate the effects of combining greenwaste compost with various rockdust samples. This was chosen to replicate the original deep-bed system at the SEER Centre. Soil was not used as they applied compost/rockdust mixture over native soil without incorporating the soil. These pot trials were also set up to broaden the information gained from the SEER Centre field trial. While the field trial tested one rock type and one test crop, pot trials were used to investigate the effects of various rocks on a range of crops.

Pot trials of various rockdust types have been carried out by other researchers to investigate macronutrient supply to plants. These have mainly focused on addition of rockdust to low nutrient status native soil and many of these primarily focused on potassium supply from the added rockdust compared with that supplied by soluble salts. Pot trials with rocks and minerals were used to assess their potential as slow releasing K fertilizers for Italian ryegrass (*Lolium multiflorum*) by Bakken *et al*. (1997b). Rocks and minerals were also assessed by Bakken *et al*. (1997a) as K fertilizers for growth of barley (*Hordeum vulgare*). Peat moss, loamy sand or silt loam were used as a growing base with nutrient solutions and rockdust added to support plant growth.

Coroneos *et al*. (1996) used sandy, nutrient deficient soil to assess the effect of granite powder application as a potassium fertilizer. Ryegrass (*Lolium rigidum*) and subterranean clover (*Trifolium subterraneum*) growth were measured in pot trials lasting 20 weeks. Plant dry weight, K content of plant tissue and exchangeable cations in soil were measured to assess the effect of granite application compared with a KCl treatment and a control treatment with no K added. Similarly, Bolland and Baker (2000) carried out greenhouse pot trials using K deficient sandy soils and added powdered granite to determine nutrient supply (especially K) to wheat (*Triticum aestivum*) and clover (*Trifolium subterraneum*) plants. In these pot trials, response was determined as plant dry matter yield.

Applications of granite and diorite (at a variety of levels) to highly weathered soil from Western Australia were tested by Hinsinger *et al*. (1996). Yield and nutrient content of wheat plants (*Triticum aestivum*) were used to assess effectiveness of the ground rocks. Five different rock types (basalt, sandstone, diorite, limestone and volcanic porphyry) were added to sandy or clay soil in pot experiments by Kahnt *et al*. (1986). Response was measured as increase in shoot yield of 5 different plants and grain yield of spring barley.

Guillou and Davies (2004) carried out work to formulate growing media using composts and quarry fines. The two pot trials detailed involved combination of rockdust (basalt, felsite and dolerite) with various compost types (food, anaerobically digested, greenwaste and kerbside collection). In the first experiment, tomato plant growth, fruit yield and consumer acceptability of the fruit were measured compared to 'Grow Bag' compost. In the second experiment, grass yield and compost/rockdust blend nutrient analysis were used to compare the novel growth media with a good agricultural soil control. Mitchell *et al*. (2004) also combined greenwaste compost and quarry fines in the manufacture of growing media for grass. They combined the materials on a volume basis and used grass as the test crop. Fresh grass yield was used as a measure of response to added fines. O'Brien *et al*. (1999) used vegetable by-product compost, perlite and basalt mineral fines or glacial moraine fines at two application rates to assess growth of tomato plants. They analysed extractable nutrients at the start and the end of the experiment, elemental composition of leaf tissue, tomato stem diameter and fruit yield to assess the effect compared to a no mineral fine control.

The pot trials detailed in this chapter used a similar formulation to those described by Guillou and Davies (2004). One compost type was used, (greenwaste compost) and this was mixed as in Mitchell *et al*. (2004) on a volume basis. The results gained by carrying out these pot trials could give an indication on the effectiveness of greenwaste compost and rockdust as plant growth media for use in agriculture, professional horticulture or amateur gardening as an alternative to peat based media. Plant dry yield and nutrient content are used to measure effectiveness compared to plants grown in a commercial peat medium.

8.2 Methods

8.2.1 8 week pot trials

8.2.1.1 Crops

There were three greenhouse pot trials carried out over 8 week growing periods. The chosen crops were:

- Ryegrass *Lolium perenne* var. Kent Indigenous
- Forage rape *Brassica napus* var. Broad Leaf Essex
- White clover *Trifolium repens* var. Aberconcord

The crops were chosen to represent monocotyledons, dicotyledons and legumes which may show different responses to rockdust addition. The plants were also chosen due to the short timescale to produce sufficient growth for analysis. The plants were also agriculturally significant and could provide a tie-in with the field trial.

8.2.1.2 Seeds

Ryegrass was obtained from Emorsgate Seeds, Norfolk, UK and forage rape and white clover were obtained from Cotswold Seeds Ltd, Gloucestershire, UK. All seeds were Certified Seed of 1st Generation according to EC rules and Standards. The weight of seed used in each pot trial was:

Ryegrass	1 g seed per pot
Forage rape	1.5 g seed per pot
White clover	0.5 g seed per pot

8.2.1.3 Growing media preparation

Bulk samples of Dundee compost were collected in August 2005 and 2006 for use in the three pot trials. Compost was used in the state that it was collected in (i.e. no additional sieving of the material was carried out prior to use in the pot trials). Growing media were prepared by mixing compost and rockdust in a 4 compost: 1

rockdust (v/v) ratio. Mixing by volume was preferred to take into account the differences in bulk density between rockdust samples. This was achieved by filling a 1 litre pot (12.6 cm diameter) with a rockdust sample (being careful not to over-compact) and recording the weight. 1/5 of this weight was equal to 1/5 of the volume of the pot. This was repeated with compost to determine the weight for 4/5 of the volume of the pot.

Three control treatments were prepared: Dundee compost alone (1 litre); compost and acid-washed sand {4:1 (v/v)}; and a commercial peat based compost obtained from B&Q. Comparing the rockdust treated pots with each of these control pots would give different information on the impact of rockdust on compost growing media quality. Comparisons within the controls themselves give information on Dundee compost quality and suitability as a growing medium.

8.2.1.4 Pot trial treatments

The rockdust samples used in the treatments are described in Table 8-1. Further information on the rockdust can be found in Chapter 4. There were 5 replicates of each of the 11 treatments in each trial.

Treatment	Rockdust	Rock type	Compost
T1	SEER field trial certified quarry	Basaltic/andesitic	Dundee
T2	SEER field trial bulk delivery	Basaltic/andesitic	Dundee
T3	SEER 20 kg bag April 2005	Basaltic/andesitic	Dundee
T4	SEER 20 kg bag July 2005	Basaltic/andesitic	Dundee
T5	Clatchard quarry	Basaltic/andesitic	Dundee
T6	Orrock quarry	Basaltic	Dundee
T7	Furnace quarry	Granitic	Dundee
T8	Duntilland quarry fines	Quartz dolerite	Dundee
T9	None	N/A	Dundee
T10	Acid-washed sand	N/A	Dundee
T11	None	N/A	B&Q peat based

Table 8-1 Pot trial treatments

8.2.1.5 Block layout

The pots were laid out in randomized block designs as shown in Table 8-2 – Table 8-4. The sodium lamp was positioned above the centre of the blocks.

The ryegrass pot trial was carried out between 28 November 2006 and 26 January 2007. The block layout is shown in Table 8-2:

T10	T6	T3	T2	T1	T7	T5	T11	T4	T8	T9
T3	T7	T11	T8	T4	T10	T9	T2	T6	T1	T5
T5	T4	T10	T7	T11	T6	T8	T9	T1	T3	T2
T8	T2	T1	T9	T7	T11	T4	T3	T5	T10	T6
T6	T9	T5	T3	T10	T2	T1	T7	T8	T11	T4

Table 8-2 Pot layout in greenhouse during ryegrass pot trial

The forage rape pot trial was carried out between 14 September 2006 and 9 November 2006. The block layout is shown in Table 8-3:

T3	T9	T2	T5	T6	T1	T10	T4	T7	T8	T11
T5	T1	T11	T3	T7	T9	T6	T2	T8	T10	T4
T1	T3	T8	T9	T4	T5	T11	T10	T6	T2	T7
T10	T7	T4	T11	T5	T2	T1	T8	T3	T6	T9
T4	T2	T6	T7	T8	T11	T3	T9	T10	T5	T1

Table 8-3 Pot layout in greenhouse during forage rape pot trial

The white clover pot trial was carried out between 14 September 2006 and 9 November 2006. The block layout is shown in Table 8-4:

T7	T2	T10	T11	T3	T4	T8	T6	T1	T9	T5
T11	T5	T7	T2	T6	T10	T9	T4	T8	T1	T3
T10	T9	T8	T4	T1	T7	T5	T3	T11	T2	T6
T3	T1	T5	T8	T9	T6	T11	T10	T2	T4	T7
T9	T4	T3	T6	T2	T8	T1	T5	T7	T10	T11

Table 8-4 Pot layout in greenhouse during white clover pot trial

8.2.1.6 Greenhouse conditions

The greenhouse was maintained at approximately 20 °C with 16 hours of light supplied by two sodium lamps. The pots were watered regularly throughout the trials with deionised water. No additional nutrients were added to any treatment.

8.2.1.7 Pot trial harvests

The plants were harvested after 8 weeks of growth at the epicotyl-hypocotyl boundary and fresh yields weighed. The harvested material was dried at 70 °C for at least 24 hours then reweighed for dry yield determination. The dried shoots and leaves were then ground in a small mill for chemical analysis.

8.2.1.8 Harvested material analysis

Kjeldahl-N and P was determined on the dried, ground plant shoot and leaf tissue following the method detailed in Section 2.9 for digesting plant tissue.

8.2.2 21 week pot trial

To investigate the potential for greenwaste compost/rockdust growth media for longer term plant growth, a 21 week pot trial with 3 harvests was set-up.

8.2.2.1 Crop

The chosen crop for the 21 week pot trial was ryegrass *Lolium perenne* var. Kent Indigenous. Ryegrass was suitable for this trial since it could go through many crop/re-growth cycles in an exhaustive cropping experiment.

8.2.2.2 Seeds

Ryegrass was obtained from Emorsgate Seeds, Norfolk, UK. 1 g seed per pot was used in the trial.

8.2.2.3 Growing media preparation

Bulk samples of Dundee compost were collected in August 2005 for use in the pot trial. No additional sieving of the compost material was carried out prior to use in the pot trial. As in Section 8.2.1.3, growing media were prepared by mixing compost and rockdust in a 4 compost: 1 rockdust (v/v) ratio. Dundee compost alone and a peat free compost obtained from B&Q were used as controls.

8.2.2.4 Pot trial treatments

The rockdust samples used in the treatments are described in Table 8-5. There were 5 replicates of each of the 10 treatments.

Treatment	Rockdust	Rock type	Compost
T1	SEER field trial certified quarry	Basaltic/andesitic	Dundee
T2	SEER field trial bulk delivery	Basaltic/andesitic	Dundee
T3	SEER 20 kg bag April 2005	Basaltic/andesitic	Dundee
T4	SEER 20 kg bag July 2005	Basaltic/andesitic	Dundee
T5	Clatchard quarry	Basaltic/andesitic	Dundee
T6	Orrock quarry	Basaltic	Dundee
T7	Furnace quarry	Granitic	Dundee
T8	Duntilland quarry fines	Quartz dolerite	Dundee
T9	None	N/A	Dundee
T10	None	N/A	Peat free

Table 8-5 21 week pot trial treatments

8.2.2.5 Block layout

The pots were laid out in randomized block designs as shown in. The sodium lamp was positioned above the centre of the block. The 21 week ryegrass pot trial was carried out between 13 September 2005 and 16 February 2006. The block layout is shown in Table 8-6:

T1	T4	T8	T6	T2	T7	T3	T5	T10	T9
T7	T10	T6	T3	T8	T1	T9	T4	T5	T2
T4	T9	T2	T1	T5	T3	T10	T8	T7	T6
T5	T7	T4	T8	T6	T10	T2	T9	T1	T3
T9	T3	T10	T7	T1	T5	T6	T2	T8	T4

Table 8-6 Pot layout in greenhouse during 21 week ryegrass pot trial

8.2.2.6 Greenhouse conditions

The greenhouse was maintained at approximately 20 °C with 16 hours of light supplied by two sodium lamps. The pots were watered regularly throughout the trials with deionised water. No additional nutrients were added to any treatment.

8.2.2.7 Pot trial harvests

The plants were harvested at 3 points in the trial (every 7 weeks) at the epicotyl-hypocotyl boundary and fresh yields weighed. The harvested material was dried at 70 °C for at least 24 hours then reweighed for dry yield determination.

8.3 Results

8.3.1 Ryegrass pot trial

8.3.1.1 Dry yield analysis

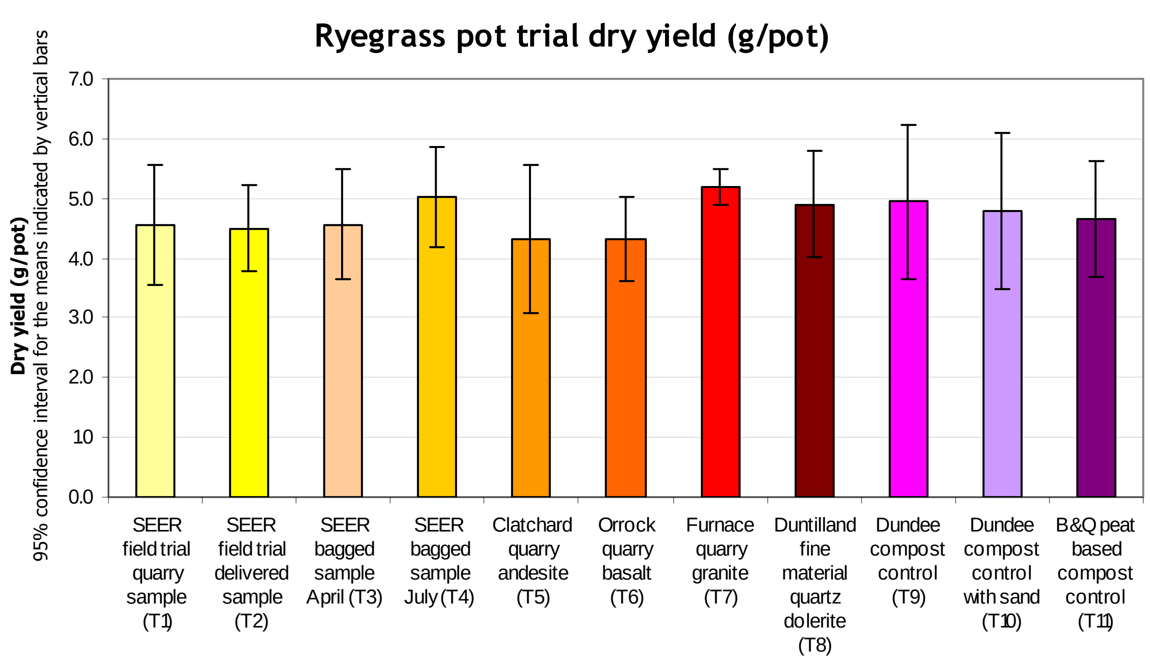


Figure 8-1 Dry yield analysis of ryegrass pot trial

Figure 8-1 shows the mean dry yields in the ryegrass pot trial along with 95 % confidence intervals to show variability within the replicates. It can be seen that addition of any rockdust sample to Dundee compost did not increase dry yield of ryegrass compared to the two controls (T9 and T10). The peat based compost control (T11) did not produce better growth than the Dundee compost (either alone or with sand).

8.3.1.2 Statistical analysis of dry yields

Data from the pot trial was analysed using Minitab statistical software (version 15.1) using the one-way analysis of variance command. No significant yield differences were found due to treatment (p = 0.746).

8.3.1.3 Visual comparisons with control

Figure 8-2 – Figure 8-10 show ryegrass growth prior to harvesting after 8 weeks growth. Rockdust treatments (T1 – T8) were compared to the two Dundee compost controls (T9 and T10). The growth in these two Dundee compost controls were also compared to the growth in the peat based compost control in Figure 8-10

Figure 8-2 Ryegrass growth in Dundee compost treated with SEER field trial quarry sample (T1) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-3 Ryegrass growth in Dundee compost treated with SEER field trial delivered sample (T2) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-4 Ryegrass growth in Dundee compost treated with SEER bagged sample April (T3) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-6 Ryegrass growth in Dundee compost treated with Clatchard quarry andesitic rockdust (T5) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-5 Ryegrass growth in Dundee compost treated with SEER bagged sample July (T4) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-7 Ryegrass growth in Dundee compost treated with Orrock quarry basaltic rockdust (T6) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-8 Ryegrass growth in Dundee compost treated with Furnace quarry granitic rockdust (T7) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-9 Ryegrass growth in Dundee compost treated with Duntilland quarry quartz dolerite fine rockdust (T8) compared to Dundee compost control (T9) and Dundee compost with acid-washed sand (T10)

Figure 8-10 Ryegrass growth in Dundee compost control (T9) compared to Dundee compost treated with acid-washed sand (T10) and B&Q peat based compost (T11)

8.3.1.4 Plant material analysis

The results of the Kjeldahl digestion analysis of dried ryegrass are shown in Table 8-7 below:

Treatment			Kjeldahl-N (%)	Kjeldahl-P (%)
	Rockdust	Compost		
T1	SEER field trial certified quarry	Dundee	2.514 a	0.330 a
T2	SEER field trial bulk delivery	Dundee	2.539 a	0.314 a
T3	SEER 20 kg bag April 2005	Dundee	2.622 a	0.345 a
T4	SEER 20 kg bag July 2005	Dundee	2.490 a	0.347 a
T5	Clatchard quarry	Dundee	2.692 a	0.307 a
T6	Orrock quarry	Dundee	2.667 a	0.314 a
T7	Furnace quarry	Dundee	2.015 a	0.335 a
T8	Duntilland quarry fines	Dundee	2.354 a	0.324 a
T9	None	Dundee	2.802 a	0.308 a
T10	Acid-washed sand	Dundee	2.424 a	0.344 a
T11	None	B&Q peat based	2.449 a	0.609 b

Table 8-7 Kjeldahl-N and P content of ryegrass after 8 week pot trial
Values followed by the same letter in the same column are not significantly different at p = 0.05 according to Tukey's LSD test

This information is shown graphically in the form of boxplots in Figure 8-11 and Figure 8-12. The length of the box shows the variability of the values around the mean.

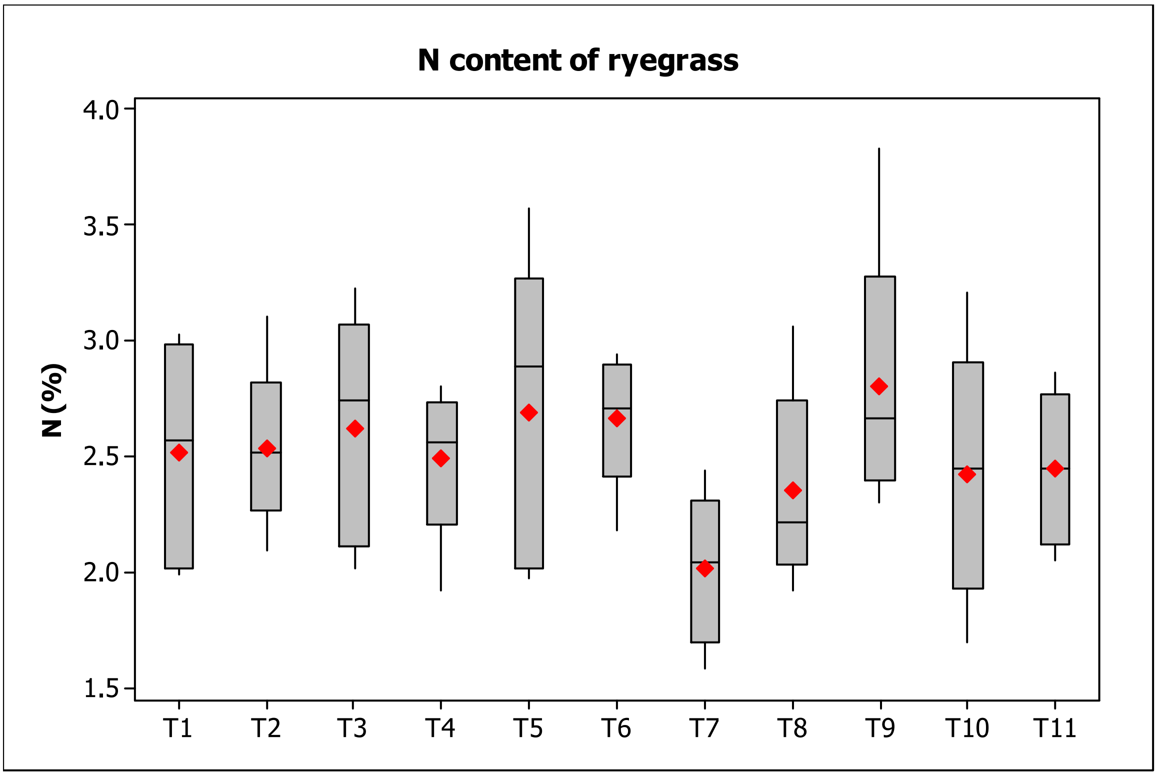


Figure 8-11 Boxplots of Kjeldahl-N content of ryegrass pot trial samples
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

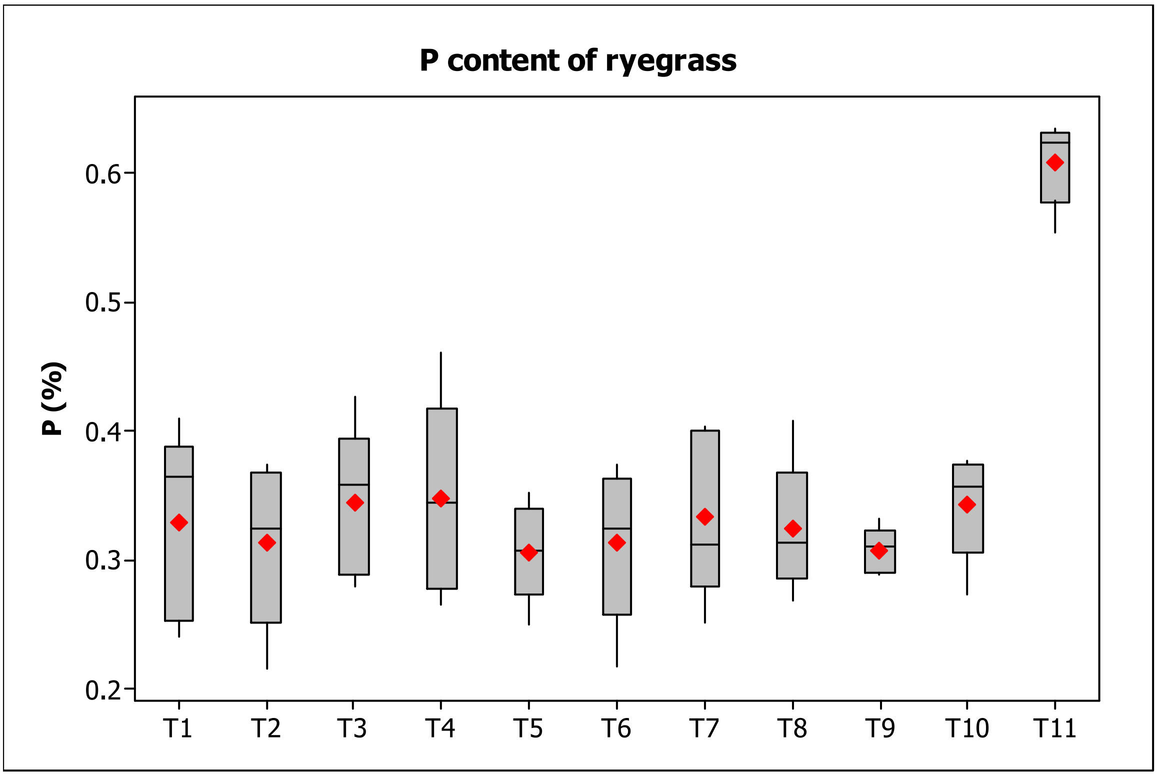


Figure 8-12 Boxplots of Kjeldahl-P content of ryegrass pot trial samples
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

Table 8-7 and Figure 8-11 show that nitrogen content of shoot material was not significantly different in any of the treatments. Table 8-7 and Figure 8-12 show that phosphorus content of ryegrass grown in the peat based growing medium was higher than that of plants grown in greenwaste compost.

8.3.1.5 Nutrient uptake by plants

Nutrient uptake in the shoot material was calculated from the weight of shoot material and the nutrient content of the shoot and is shown in Table 8-8 below:

Treatment			N uptake (mg pot^{-1})	P uptake (mg pot^{-1})
	Rockdust	Compost		
T1	SEER field trial certified quarry	Dundee	111.10 ab	14.94 a
T2	SEER field trial bulk delivery	Dundee	112.48 ab	14.04 a
T3	SEER 20 kg bag April 2005	Dundee	116.77 ab	15.65 a
T4	SEER 20 kg bag July 2005	Dundee	123.24 bc	17.13 a
T5	Clatchard quarry	Dundee	111.38 ab	13.52 a
T6	Orrock quarry	Dundee	114.15 ab	13.64 a
T7	Furnace quarry	Dundee	104.07 a	17.33 a
T8	Duntilland quarry fines	Dundee	112.94 ab	15.59 a
T9	None	Dundee	133.51 c	15.28 a
T10	Acid-washed sand	Dundee	111.39 ab	16.71 a
T11	None	B&Q peat based	111.78 ab	28.22 b

Table 8-8 Nutrient uptake by ryegrass (mg pot^{-1})
Values followed by the same letter in the same column are not significantly different at $p = 0.05$ according to Tukey's LSD test

These results show that despite there being no difference in the nitrogen content of ryegrass grown in these different media, there were significant differences in the N uptake by plants grown in different mixtures. The highest uptake was seen in T9 (Dundee compost alone) and this was significantly higher than every treatment but T4 (Dundee compost with SEER bagged rockdust). The lowest uptake was by plants grown in Dundee compost and Furnace quarry rockdust (T7). The P uptake followed the same pattern as the P content in shoot material whereby the commercial peat based medium produced ryegrass with the highest content of P and that had the highest uptake of P also.

8.3.2 Forage rape pot trial

8.3.2.1 Dry yield analysis

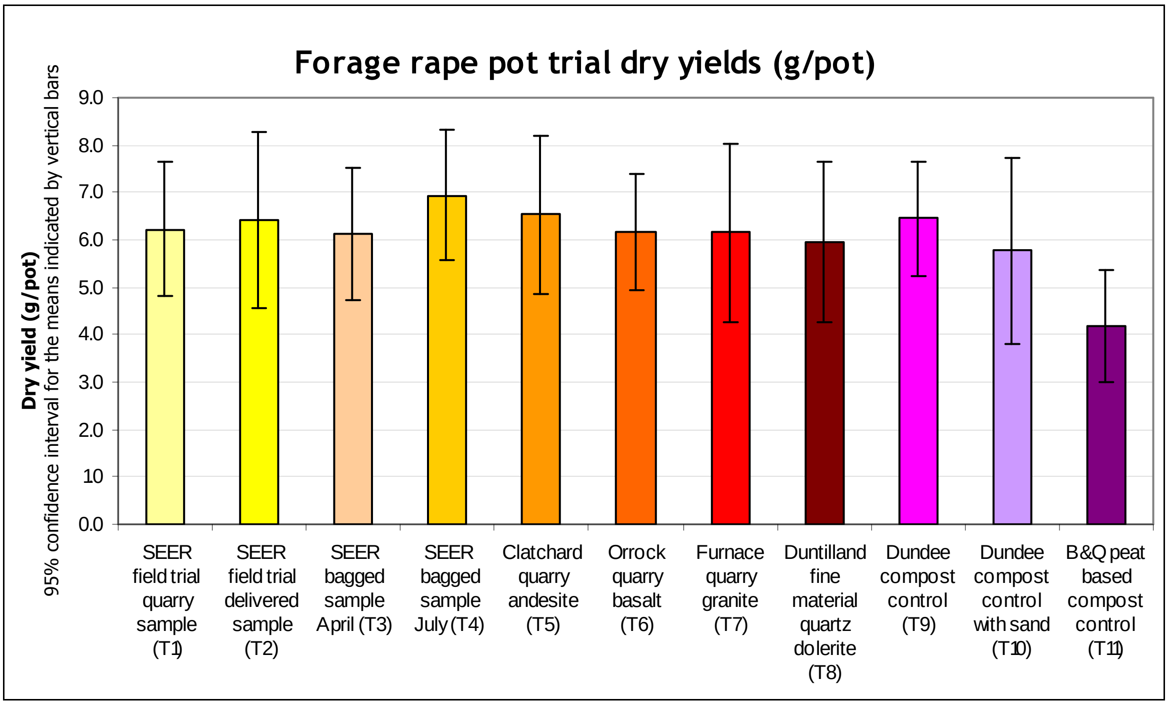


Figure 8-13 Dry yield analysis of forage rape pot trial

Figure 8-13 shows the mean dry yields in the forage rape pot trial along with 95 % confidence intervals show variability within the replicates. It can be seen that addition of any rockdust sample to Dundee compost did not increase dry yield of forage rape compared to the two controls (T9 and T10). The peat based compost control (T11) did not produce better growth than the Dundee compost (either alone or with sand).

8.3.2.2 Statistical analysis of dry yields

Data from the pot trial was analysed using Minitab statistical software (version 15.1) using the one-way analysis of variance command. No significant yield differences were found due to treatment ($p = 0.149$)

8.3.2.3 Visual comparisons with control

Figure 8-14 – Figure 8-22 show forage rape growth prior to harvesting after 8 weeks growth. Rockdust treatments (T1 – T8) were compared to the Dundee compost control (T9). The growth in the two Dundee compost controls were also compared to the growth in the peat based compost control in Figure 8-22.

Figure 8-14 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with SEER field trial quarry sample (T1)

Figure 8-15 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with SEER field trial delivered sample (T2)

Figure 8-16 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with SEER bagged sample April (T3)

Figure 8-17 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with SEER bagged sample July (T4)

Figure 8-18 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with Clatchard quarry andesitic rockdust (T5)

Figure 8-19 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with Orrock quarry basaltic rockdust (T6)

Figure 8-20 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with Furnace quarry granitic rockdust (T7)

Figure 8-21 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with Duntilland quarry quartz dolerite fine rockdust (T8)

Figure 8-22 Forage rape growth in Dundee compost control (T9) compared to Dundee compost treated with acid-washed sand (T10) and B&Q peat based compost (T11)

8.3.2.4 Plant material analysis

The results of the Kjeldahl digestion analysis of dried forage rape are shown in Table 8-9 below:

Treatment			Kjeldahl-N (%)	Kjeldahl-P (%)
	Rockdust	Compost		
T1	SEER field trial certified quarry	Dundee	1.843 a	0.582 a
T2	SEER field trial bulk delivery	Dundee	1.770 a	0.595 ab
T3	SEER 20 kg bag April 2005	Dundee	1.833 a	0.600 ab
T4	SEER 20 kg bag July 2005	Dundee	1.703 a	0.557 a
T5	Clatchard quarry	Dundee	1.734 a	0.572 a
T6	Orrock quarry	Dundee	1.808 a	0.584 a
T7	Furnace quarry	Dundee	1.754 a	0.589 a
T8	Duntilland quarry fines	Dundee	1.738 a	0.600 ab
T9	None	Dundee	1.940 a	0.623 ab
T10	Acid-washed sand	Dundee	1.783 a	0.603 ab
T11	None	B&Q peat based	1.997 a	0.775 b

Table 8-9 Kjeldahl-N and P content of forage rape after 8 week pot trial
Values followed by the same letter in the same column are not significantly different at p = 0.05 according to Tukey's LSD test

This information is shown graphically in the form of boxplots in Figure 8-23 and Figure 8-24. The length of the box shows the variability of the values around the mean.

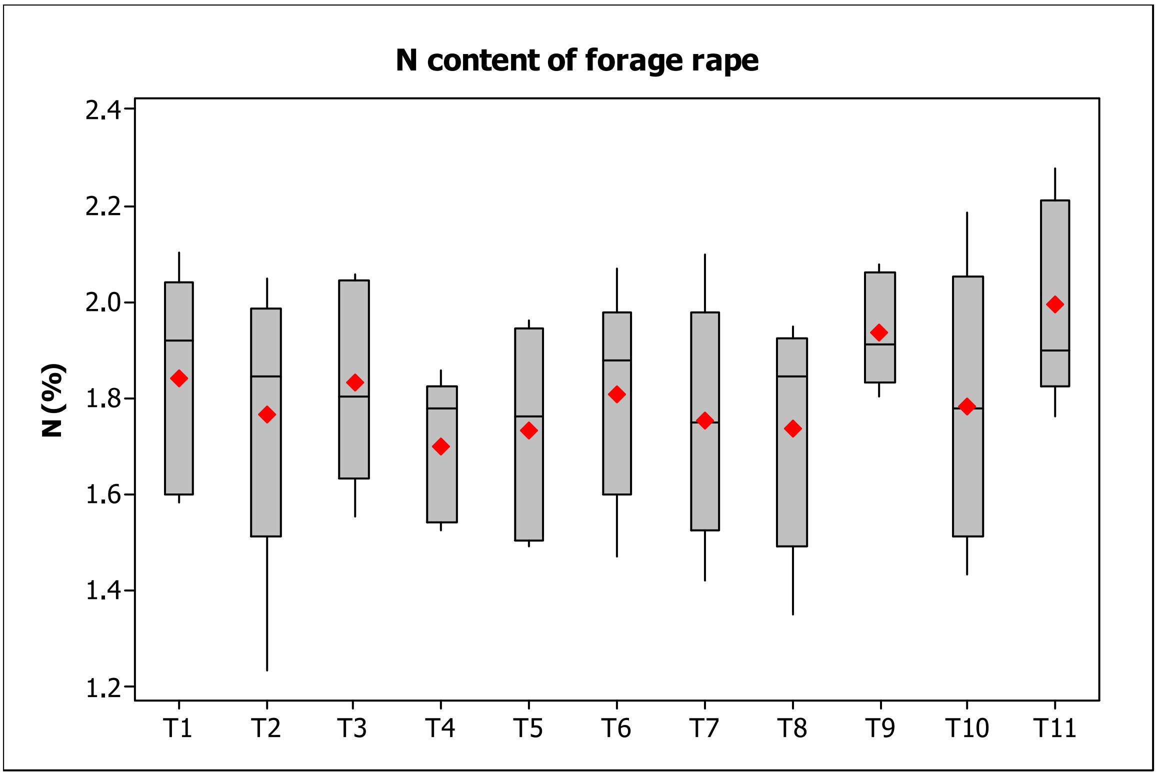


Figure 8-23 Boxplots of Kjeldahl-N content of forage rape pot trial samples
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

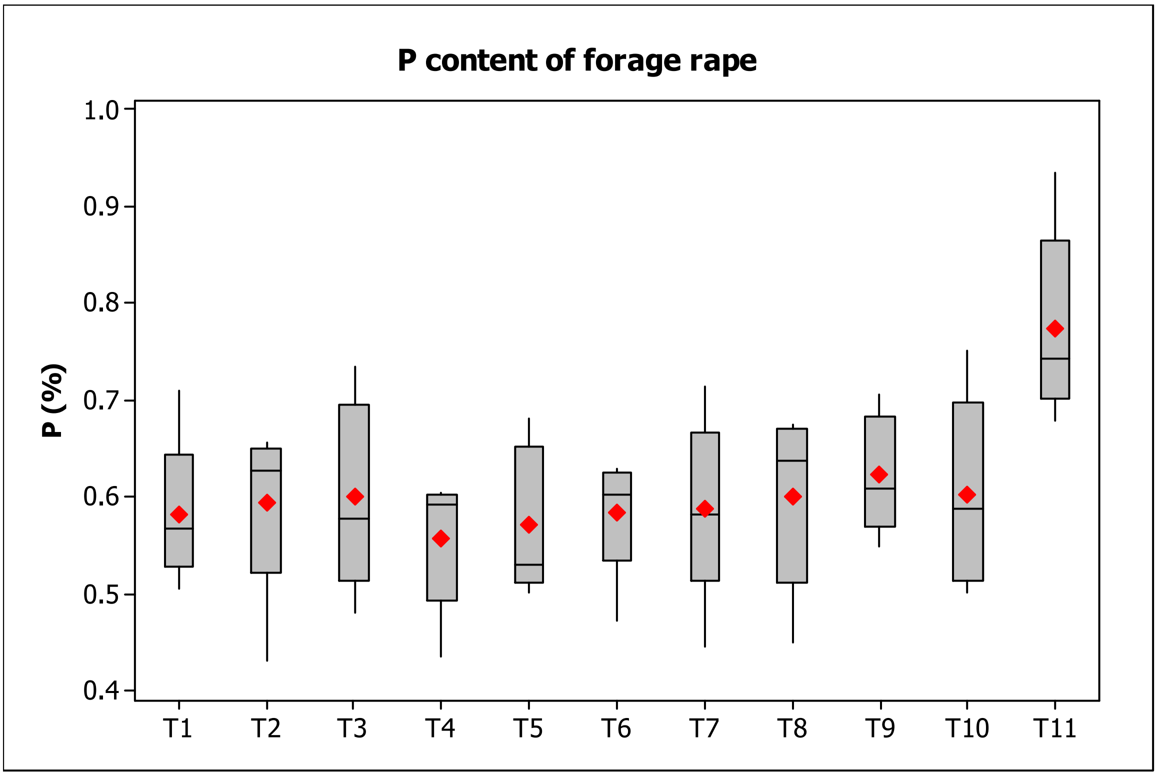


Figure 8-24 Boxplots of Kjeldahl-P content of forage rape pot trial samples
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

Table 8-9 and Figure 8-23 show that nitrogen content of shoot material was not significantly different in any of the treatments. Table 8-9 and Figure 8-24 show that phosphorus content of forage rape grown in the peat based growing medium was higher than that of some plants grown in greenwaste compost/rockdust mixtures.

8.3.2.5 Nutrient uptake by plants

Nutrient uptake in the shoot material was calculated from the weight of shoot material and the nutrient content of the shoot and is shown in Table 8-10 below:

Treatment			N uptake (mg pot^{-1})	P uptake (mg pot^{-1})
	Rockdust	Compost		
T1	SEER field trial certified quarry	Dundee	113.00 b	35.69 a
T2	SEER field trial bulk delivery	Dundee	110.62 ab	37.19 a
T3	SEER 20 kg bag April 2005	Dundee	110.71 ab	36.12 a
T4	SEER 20 kg bag July 2005	Dundee	117.21 b	38.10 a
T5	Clatchard quarry	Dundee	111.15 ab	36.69 a
T6	Orrock quarry	Dundee	110.03 ab	35.64 a
T7	Furnace quarry	Dundee	104.96ab	35.08 a
T8	Duntilland quarry fines	Dundee	100.97 ab	34.80 a
T9	None	Dundee	124.60 b	39.94 a
T10	Acid-washed sand	Dundee	99.34 ab	33.60 a
T11	None	B&Q peat based	83.66 a	32.32 a

Table 8-10 Nutrient uptake by forage rape (mg pot^{-1})
Values followed by the same letter in the same column are not significantly different at $p = 0.05$ according to Tukey's LSD test

These results show that despite there being no difference in the nitrogen content of forage rape grown in these different media, there were significant differences in the N uptake by plants grown in different mixtures. The lowest uptake was seen in T11 (B&Q peat based growing media) which was significantly lower than Dundee compost with SEER field trial rockdust (T1), SEER bagged rockdust (T4) and Dundee compost alone (T9). Despite higher P contents in forage rape grown in B&Q growing medium, there were no significant differences in P uptake across all of the treatments.

8.3.3 White clover pot trial

8.3.3.1 Dry yield analysis

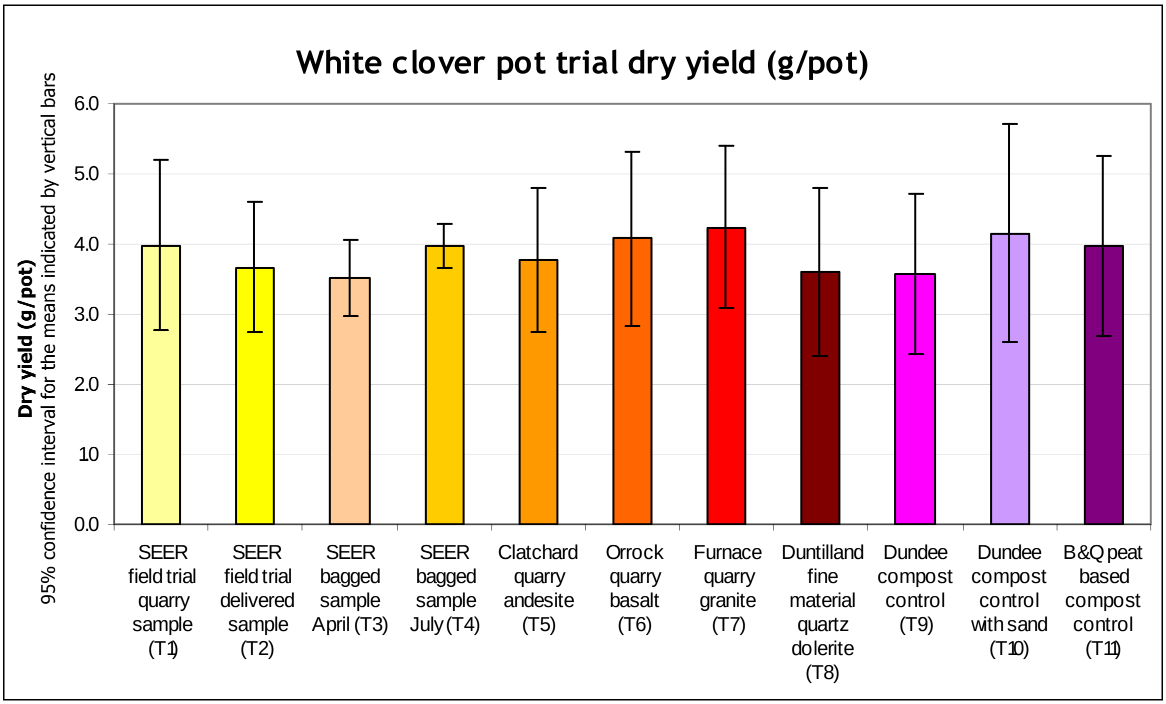


Figure 8-25 Dry yield analysis of white clover pot trial

Figure 8-25 shows the mean dry yields in the white clover pot trial along with 95 % confidence intervals to show variability within the replicates. It can be seen that addition of any rockdust sample to Dundee compost did not increase dry yield of white clover compared to the two controls (T9 and T10). The peat based compost control (T11) did not produce better growth than the Dundee compost (either alone or with sand).

8.3.3.2 Statistical analysis of dry yields

Data from the pot trial was analysed using Minitab statistical software (version 15.1) using the one-way analysis of variance command. No significant yield differences were found due to treatment (p = 0.942).

8.3.3.3 Visual comparisons with control

Figure 8-26 – Figure 8-34 show white clover growth prior to harvesting after 8 weeks growth. Rockdust treatments (T1 – T8) were compared to the Dundee compost control (T9). The growth in the two Dundee compost controls were also compared to the growth in the peat based compost control in Figure 8-34.

Figure 8-26 White clover growth in Dundee compost treated with SEER field trial quarry sample (T1) compared to Dundee compost control (T9)

Figure 8-27 White clover growth in Dundee compost treated with SEER field trial delivered sample (T2) compared to Dundee compost control (T9)

Figure 8-28 White clover growth in Dundee compost treated with SEER bagged sample April (T3) compared to Dundee compost control (T9)

Figure 8-29 White clover growth in Dundee compost treated with SEER bagged sample July (T4) compared to Dundee compost control (T9)

Figure 8-30 White clover growth in Dundee compost treated with Clatchard quarry andesitic rockdust (T5) compared to Dundee compost control (T9)

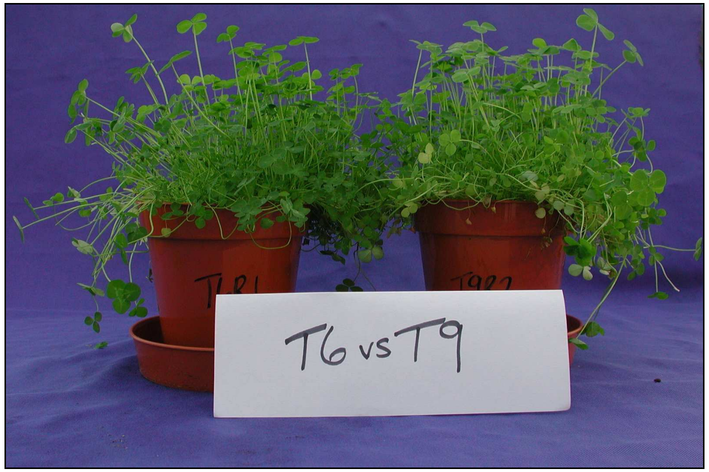


Figure 8-31 White clover growth in Dundee compost treated with Orrock quarry basaltic rockdust (T6) compared to Dundee compost control (T9)

Figure 8-32 White clover growth in Dundee compost treated with Furnace quarry granitic rockdust (T7) compared to Dundee compost control (T9)

Figure 8-33 White clover growth in Dundee compost treated with Duntilland quarry quartz dolerite fine rockdust (T8) compared to Dundee compost control (T9)

Figure 8-34 White clover growth in Dundee compost control (T9) compared to Dundee compost treated with acid-washed sand (T10) and B&Q peat based compost (T11)

8.3.3.4 Plant material analysis

The results of the Kjeldahl digestion analysis of dried white clover are shown in Table 8-11 below:

Treatment			Kjeldahl-N (%)	Kjeldahl-P (%)
	Rockdust	Compost		
T1	SEER field trial certified quarry	Dundee	2.516 a	0.378 ab
T2	SEER field trial bulk delivery	Dundee	2.701 a	0.373 ab
T3	SEER 20 kg bag April 2005	Dundee	2.735 a	0.355 a
T4	SEER 20 kg bag July 2005	Dundee	2.518 a	0.390 ab
T5	Clatchard quarry	Dundee	2.609 a	0.367 ab
T6	Orrock quarry	Dundee	2.644 a	0.312 a
T7	Furnace quarry	Dundee	2.613 a	0.327 a
T8	Duntilland quarry fines	Dundee	2.572 a	0.327 a
T9	None	Dundee	3.002 a	0.337 a
T10	Acid-washed sand	Dundee	2.834 a	0.342 a
T11	None	B&Q peat based	2.731 a	0.521 b

Table 8-11 Kjeldahl-N and P content of white clover after 8 week pot trial
Values followed by the same letter in the same column are not significantly different at p = 0.05 according to Tukey's LSD test

This information is shown graphically in the form of boxplots in Figure 8-35 and Figure 8-36. The length of the box shows the variability of the values around the mean.

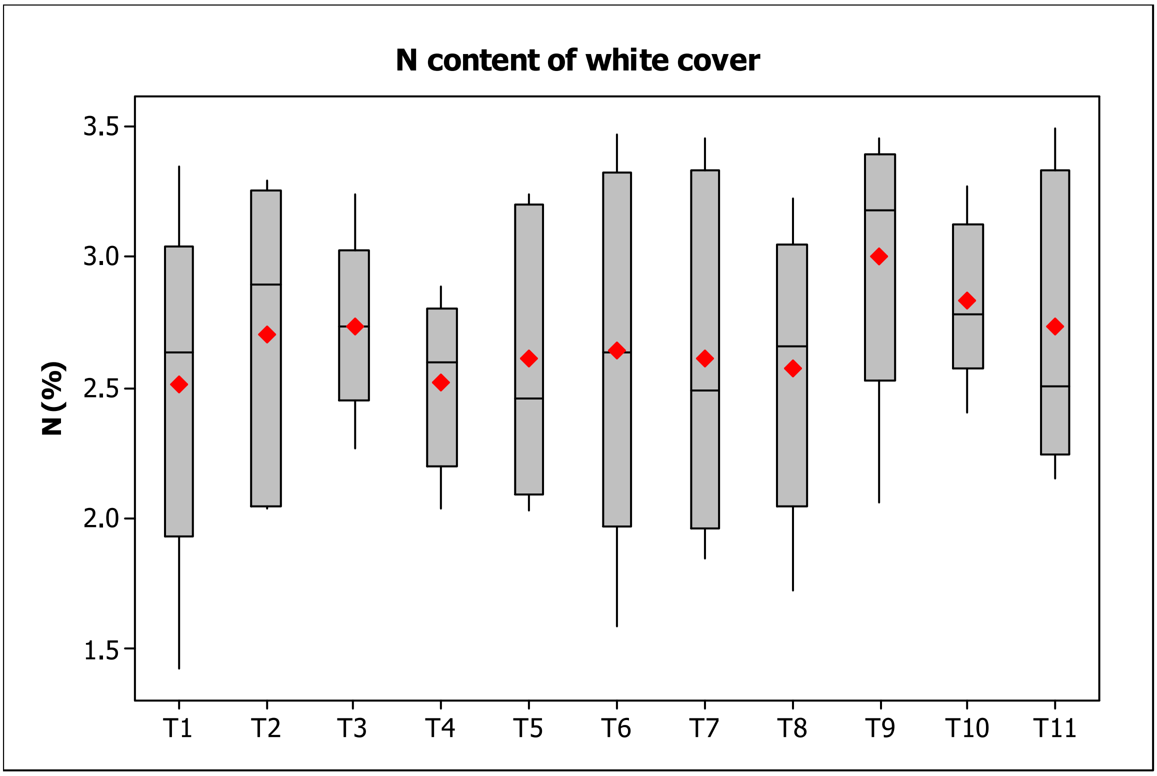


Figure 8-35 Boxplots of Kjeldahl-N content of white clover pot trial samples
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

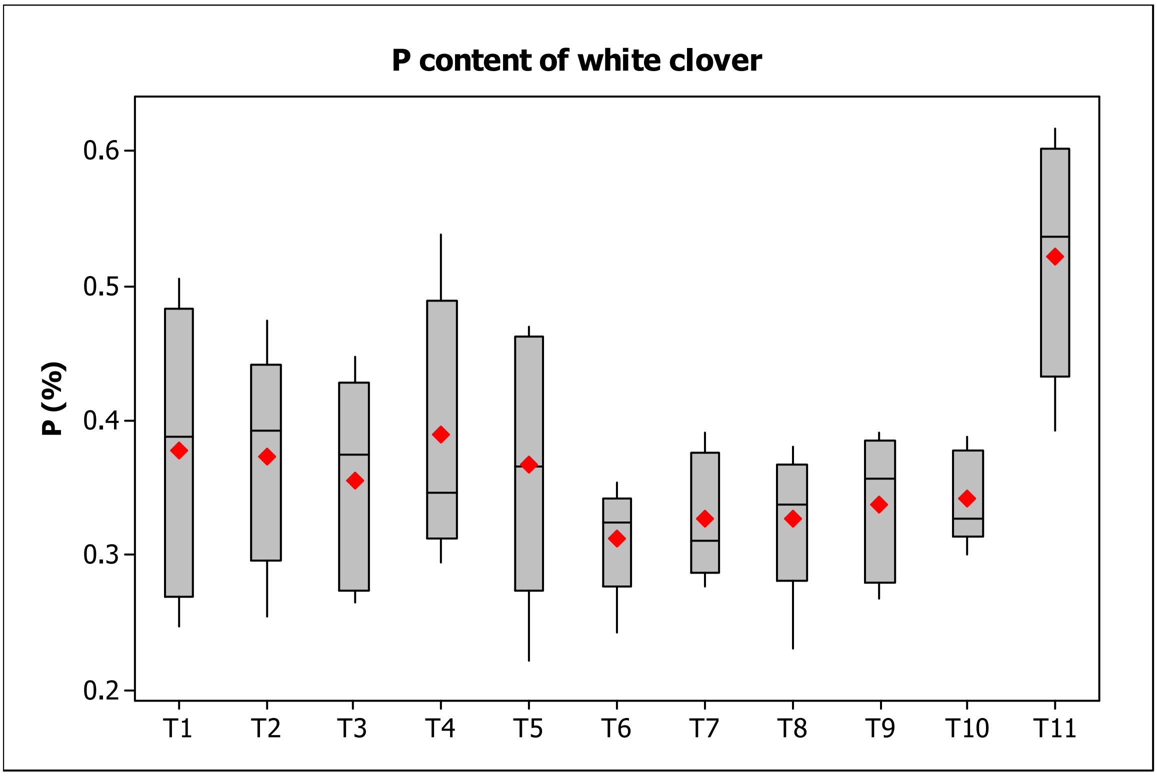


Figure 8-36 Boxplots of Kjeldahl-P content of white clover pot trial samples
Boxes indicate the inter quartile range (middle 50 % of the data), whiskers indicate upper and lower quartiles, red diamonds show mean values, horizontal lines show median values

Table 8-11 and Figure 8-35 show that nitrogen content of shoot material was not significantly different in any of the treatments. Table 8-11 and Figure 8-36 show that phosphorus content of clover grown in the peat based growing medium was higher than that of most plants grown in greenwaste compost/rockdust mixtures.

8.3.3.5 Nutrient uptake by plants

Nutrient uptake in the shoot material was calculated from the weight of shoot material and the nutrient content of the shoot and is shown in Table 8-12 below:

Treatment			N uptake (mg pot^{-1})	P uptake (mg pot^{-1})
	Rockdust	Compost		
T1	SEER field trial certified quarry	Dundee	94.54 a	14.53 ab
T2	SEER field trial bulk delivery	Dundee	95.50 a	13.35 ab
T3	SEER 20 kg bag April 2005	Dundee	94.85 a	12.48 a
T4	SEER 20 kg bag July 2005	Dundee	99.62 a	15.55 ab
T5	Clatchard quarry	Dundee	95.26 a	13.78 ab
T6	Orrock quarry	Dundee	102.39 a	12.69 ab
T7	Furnace quarry	Dundee	106.80 a	13.95 ab
T8	Duntilland quarry fines	Dundee	88.03 a	11.34 a
T9	None	Dundee	103.35 a	11.82 a
T10	Acid-washed sand	Dundee	114.92 a	14.04 ab
T11	None	B&Q peat based	105.12 a	20.46 b

Table 8-12 Nutrient uptake by white clover (mg pot^{-1})
Values followed by the same letter in the same column are not significantly different at $p = 0.05$ according to Tukey's LSD test

These results show that there were no significant differences in the N uptake by plants grown in different mixtures. Like the P content data, P uptake was highest in the peat based media although this was only significantly higher than the uptake in Dundee compost alone (T9), Dundee compost with Duntilland fines (T8) and Dundee compost with SEER bagged rockdust (T3).

8.3.4 21 week pot trial

The results from the 21 week pot trial (with harvests every 7 weeks) using ryegrass as the test crop are shown in Figure 8-37:

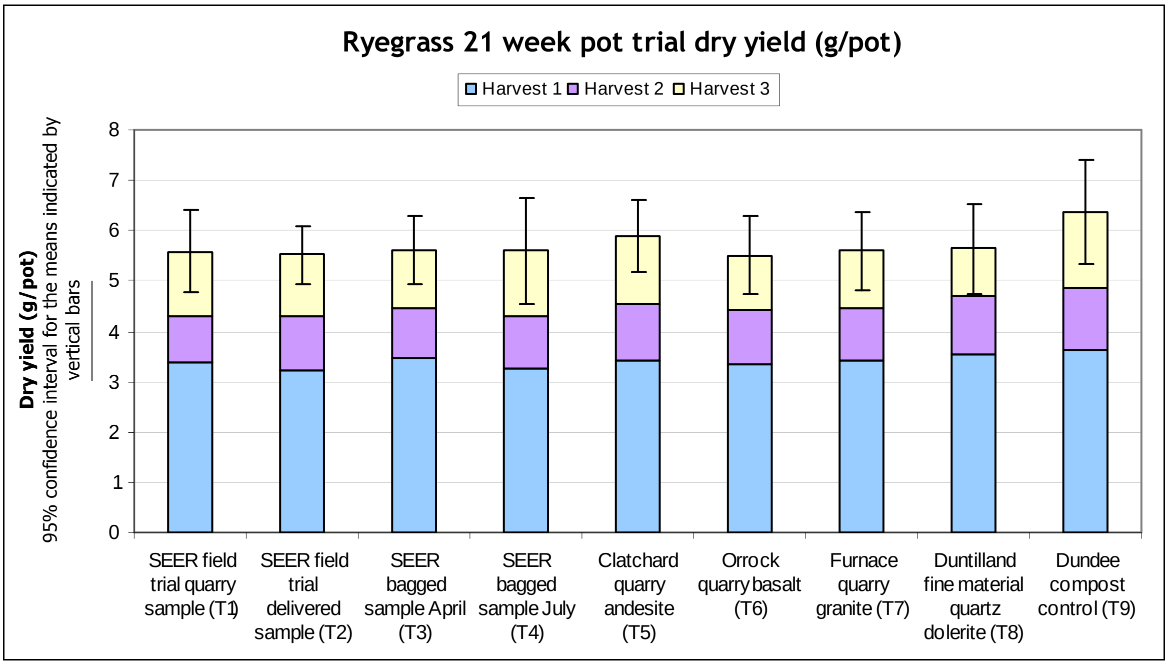


Figure 8-37 Long term dry yield analysis of ryegrass pot trial with greenwaste compost

The peat free commercial compost that was tested in this trial was omitted from the results due to very poor performance. The results from the rest of the treatments prove that the media could support plant growth beyond the 8 week growth period used in the earlier pot trials. Rockdust addition to greenwaste compost did not enhance this effect. The rate of growth in all treatments decreased with time showing that the available nutrients in the compost were depleted during the course of the trial.

8.3.5 Growing media physical properties

Growing media composition		Bulk density ($g\ cm^{-3}$)
Rockdust (vol. %)	Compost (vol. %)	
SEER field trial certified quarry (20 %)	Dundee (80 %)	0.885
SEER field trial bulk delivery (20 %)	Dundee (80 %)	0.836
SEER 20 kg bag April 2005 (20 %)	Dundee (80 %)	0.895
SEER 20 kg bag July 2005 (20 %)	Dundee (80 %)	0.881
Clatchard quarry (20 %)	Dundee (80 %)	0.862
Orrock quarry (20 %)	Dundee (80 %)	0.867
Furnace quarry (20 %)	Dundee (80 %)	0.857
Duntilland quarry fines (20 %)	Dundee (80 %)	0.777
None	Dundee (100 %)	0.681
Acid-washed sand (20 %)	Dundee (80 %)	0.828
None	B&Q peat based (100 %)	0.312

Table 8-13 Bulk density of the growing media used in the pot trials

Table 8-13 shows that growing media composed of 80 % compost and 20 % rockdust are significantly more dense than 100 % compost or peat based alternatives. The 100 % Dundee greenwaste compost was also much denser than the 100 % peat based compost. Duntilland quarry fines with Dundee compost was the least dense compost/rockdust combination while the other compost/rockdust media were quite similar. The bulk density calculations also show that rockdust addition to compost increased the density similarly to that of sand addition.

8.4 Discussion

8.4.1 Plant growth

Over the 8 week growth period used in these experiments, rockdust addition to greenwaste compost did not significantly increase plant growth in any of the crops tested compared to the compost controls (alone or with sand) or the peat based commercial compost. Similarly, Guillou and Davies (2004) showed that tomato plant growth was not influenced by rockdust type. They found rather that tomato plant growth was most influenced by compost C: N and electrical conductivity. However, similarly to the results shown in this chapter, they found that rockdust/compost blends produced similar results to no rockdust controls and that blends of compost with rockdust had no detrimental effect on consumer acceptability of the fruit.

The results from the pot trials described in this chapter show that greenwaste compost alone or with any of the rockdust samples tested could be as suitable for plant growth in the short term as peat based growing media. However, as the addition of nutrients by rockdust requires a degree of rock weathering, rockdust may not provide many plant available nutrients in the short term. Bakker *et al.* (2004) showed that weathering of plagioclase was firstly a pH effect but biological weathering could also contribute (to a lesser extent). pH conditions present in greenwaste compost would probably not facilitate rapid rock weathering although biological weathering could be important. Vetterlein (2004) explained that since most nutrients in quarry fines are not readily available, synthetic topsoil derived from compost and quarry fines would require supplementation with plant available nutrients. Mitchell *et al.* (2004) also concluded that soils manufactured from compost and quarry fines would need fertilizer supplementation to achieve good establishment and growth of plants.

In the longer term, some nutrient deficiencies might be seen since much of the nitrogen content of greenwaste compost is in the organic form and therefore unavailable for plant uptake. Nitrogen release from greenwaste compost is reliant upon mineralization rates which can be slow in this stable product. O'Brien *et al.* (1999) showed that vegetable by-product compost alone or with mineral fines did not supply sufficient N for plant growth and signs of deficiency in tomato plants were visible during pot trials of the materials.

The most promising results were gained in the forage rape trial where, although there were no significant effects on plant growth, plants grown in the peat based medium appeared less healthy than those grown on Dundee compost based media (Figure 8-13 to Figure 8-22). Therefore, there could be some instances where greenwaste compost (with or without rockdust) produces better plant growth than peat based growing media. In many previous experiments with rockdust, the only positive results could be gained using poor nutrient deficient soil e.g. Kahnt *et al*. (1986) showed yield increase of spring barley when basalt rock powder was added to sandy soil at a rate of 10 % (w/w). Hinsinger *et al*. (1996) used a nutrient poor soil and showed that granite application increased wheat yield compared to the no rock control. The K concentration of plant tissue also increased with granite application.

8.4.2 Nutrient content and uptake

As rockdust did not increase plant growth in these short-term growth experiments, micronutrient uptakes were not measured in the harvested material. Micronutrient supply was fully investigated in the field trial (Chapter 6) since the micronutrient addition by rockdust in the long-term was more likely to show positive results. Nitrogen and phosphorus content and uptake were fully investigated as these are likely to be the most important nutrient inputs supplied by greenwaste compost.

Nitrogen content of shoot material was not significantly different between the different treatments in any of the crops analysed. This means that nitrogen supply in the greenwaste compost was as good as in the peat based compost for short term plant growth. Garcia *et al*. (1991) showed that application (at high rates) of mature compost to soil could increase ryegrass yield above that of a control. N content of grass did not differ to that of the control whereas Fe, Mn and Zn were greater.

There were differences in the P content of shoot material at the end of the pot trials; this difference was most marked in the ryegrass trial where the peat based compost produced a higher shoot P content compared to all greenwaste compost treatments. The P content in greenwaste compost treatments was within the normal range for ryegrass (Spedding, 1976). However, P content of ryegrass grown in the peat based medium was much higher than the normal range (0.61 % compared to 0.26 – 0.42 %). In the white clover trial, the plants grown in peat based growing media again exhibited abnormally high P contents (0.52 % compared to a normal range of 0.25 – 0.40 % (Spedding, 1971). In this trial, plants grown on greenwaste compost were again the normal range (0.31 – 0.39 %).

The P content data from these pot trials show that the peat based media contained an excessive amount of plant available P that the plants took up in abnormally high concentrations. Plants grown on greenwaste compost mixtures were within the normal range showing that there was an adequate supply of P. O'Brien *et al*. (1999) also showed that compost and mineral fines could provide adequate P for plant growth. In the rockdust treated compost mixtures some phosphorus could be supplied at a maximum of 2 g P kg^{-1} rockdust applied (see Chapter 4).

Previous work on using rockdust in pot trials has focused on the supply of potassium to plants. For example Bolland and Baker (2000) showed that granite rockdust did not increase yields of clover or wheat in K-deficient soil as effectively as KCl in glasshouse experiments. Coroneos *et al*. (1996) agreed that granite rockdust was not as effective as KCl at supplying K to glasshouse crops. They did, however, report a positive growth response in clover after granite application compared to the control which was attributed to supply of K. The pot trials described in this chapter did not focus on potassium supply from rockdust since there were few positive results in this area reported in the literature. Potassium supply was investigated fully in the field trial since effects were more likely to occur in the long-term rather than in these short-term trials.

8.4.3 Greenwaste compost

The pot trials shown in this chapter show that greenwaste compost is a promising alternative to commercial peat based composts. In these short-term trials, plant yield was as good in greenwaste compost treated pots as in the peat based treatment. Bugbee (2002) reported that higher proportions of biosolids compost in growing media generally increased plant available nutrients with no adverse effects on aeration, moisture retention or bulk density. Chen *et al*. (1996) also showed that composts could provide an adequate supply of major and minor (trace) elements to plants.

Mathur and Voisin (1996) showed that plant growth media composed of composted materials were less depleted than the peat equivalent after plant growth. This shows that greenwaste compost might even support plant growth for longer periods than peat based products despite lower initial plant available nutrients. The 21 week pot trial experiment utilizing ryegrass as the test crop investigated the extent to which Dundee City Council compost with and without the various rockdust additions could be useful for longer-term plant growth.

The results from the 21 week pot trial showed that there was a residual effect beyond the 8 week growth period used in the earlier pot trials. Rockdust addition to greenwaste compost did not enhance this effect. This is somewhat in agreement with Mathur and Voisin (1996) although long-term N mineralization rates in the compost would be of concern for plants with high N requirements. Indeed, there was a clear decrease in harvested yield from the first to the second and third harvests that might be attributed to a reduction in available-N.

The major drawback to the use of greenwaste compost as an alternative to peat based growing media is the differences in bulk density between the products. Even without rockdust addition, greenwaste compost had a significantly higher bulk density than the peat based medium. Bugbee (2002) also showed a higher bulk density in composted biosolids compared with a peat based growing media. Because these products are normally sold by volume, greenwaste compost would have to be sold in smaller bags than peat based products to make them light enough to carry. Hence, the most appropriate way of selling greenwaste compost may be direct from the producer as already occurs in many cases (i.e. Dundee City Council and Forth Resource Management Ltd). The addition of rockdust or acid-washed sand further increased the density of the growing media. If greenwaste compost had to be diluted (to reduce the supply of macronutrients to plants) perhaps rockdust would be a suitable alternative to sand with the added benefit of possible micronutrient supply. However, with no increased plant growth occurring in these pots compared to the greenwaste compost alone, it is difficult to justify the increased density of the final product.

8.5 Summary

Rockdust addition to greenwaste compost did not increase plant growth in any of the three pot trials described in this chapter. Also, a commercial peat based growing media did not increase plant growth compared to any of the greenwaste compost/rockdust mixtures in any of the pot trials.

The nitrogen supplied by greenwaste compost as the growing medium was as good as the supply from a peat based medium in the short-term. This was contrasted by a significant difference in the phosphorus supply between the peat based compost and greenwaste compost. The P content of plants grown in peat based compost was much higher that that of plants grown in greenwaste compost based media. However, the plants grown in the peat based media were shown to be overly high in P compared to the normal expected range suggesting that this material was over-fertilized with respect to available-P. The P supplied by greenwaste compost was shown to be sufficient to match plant demands and levels were within the normal range.

Overall, these trials showed that peat based growing media could be substituted with greenwaste compost either wholly or in part without significantly affecting plant growth. However, the choice of crop would need to reflect the supply of nutrients from this material and short growing periods would be required to minimise nutrient depletion. Preliminary trials showed that greenwaste compost could sustain plant growth for longer periods than those used in the three pot trials described.

Rockdust addition to greenwaste did not significantly change the plant yields obtained but did increase the bulk density of the growing media. Hence, horticulture is an unsuitable use for this material where there is insufficient time to allow weathering of the rockdust to release plant nutrients. The best utilization of rockdust seems to be in combination with greenwaste compost in deep-bed systems as used by the SEER Centre. These long-term plant growth experiments have been shown to produce excellent plant growth for several years which could be attributed to nutrient turnover within the compost and weathering of rockdust over the long term.

Chapter 9: General Discussion

9.1 Use of rockdust

One of the main aims of this thesis was to quantify the effects of adding rockdust to soil or compost. These effects were measured by analysis of plant yield, plant nutrient content, soil chemistry and by carrying out extraction experiments on rockdust samples. The results from these various analyses can be compared to give a fuller understanding of the benefits of rockdust use.

9.1.1 Rockdust in horticulture

The effect of rockdust addition to greenwaste compost in the manufacture of plant growth media was examined in Chapter 8. Four different rock types were used to investigate differences across a range of possible rockdust sources. No increase in plant growth was shown in any of the compost/rockdust combinations tested over an 8 week growing period. In fact, the effect of rockdust addition on plant yield was similar to the greenwaste compost with and without acid washed sand. The lack of significant effects on plant yield can be explained by the results of nutrient extraction experiments as shown in Chapter 4. In this chapter, it was shown that all of the rockdust samples were low in water extractable nutrients. In the short growing period used in the pot trials, there was shown to be insufficient extractable elements added from rock weathering to increase plant growth. Therefore, at most only a portion of the extractable elements in the rockdust samples would be available in this short timescale. The extraction experiments show that the nutrients available in this short term would be limited to calcium, sodium, magnesium and potassium. As these nutrients are available in greenwaste compost (Chapter 5), the lack of significant effects on plant growth in the short term experiment was explained. The pot trials reached a similar conclusion as O'Brien *et al.* (1999) who showed that there were no detrimental effects of addition of mineral fines and only minor effects on Ca and Mn addition to the plant growth medium.

9.1.2 Rockdust in agriculture

Although there were no significant effects on plant yield in the pot trials, the longer term field trial would have be expected to show effects due to the increased time for rock weathering. However, in the field trial there were no significant yield effects due to rockdust addition. The field trial investigated the addition of rockdust alone or in combination with NPK fertilizer, manure and compost. As there were no significant interactions with rockdust and organic/inorganic amendment in the field trial, rockdust did not improve plant yields in any treatments. The lack of significant effects in the field trial show that even in the longer term, insufficient amounts of plant nutrients were released by weathering of the rockdust. These findings are in agreement with the rockdust extraction experiments that showed that even 'stronger' strength extractants only extracted low levels of micronutrients. The addition of micro-nutrients by rockdust addition to agricultural soil was therefore unproven. However, by using the XRF analysis of minor constituents of rockdust, a maximum dosage can be calculated (Chapter 4).

Other authors mainly focused on the addition of K by rockdust samples but showed similar results to those reported here. Bakken *et al.* (2000) showed that rock weathering rates were too low for plant-K demands in the short term. Weathering of rockdust and hence rate of nutrient release depends on the stability of minerals present in the rockdust sample. As was shown by CIPW rockdust mineralogical analysis (Chapter 4), basaltic rock is high in plagioclase and orthoclase feldspars. Calcium, sodium and potassium are likely to be supplied by weathering of SEER rockdust. In agreement with this, O'Brien *et al.* (1999) showed that basaltic rockdust or glacial moraine fines could increase extractable Ca levels. As plagioclase feldspars are amongst the most easily weathered minerals, more calcium and sodium would be provided by rockdust weathering than potassium from orthoclase. Results published by Sanz Scovino and Rowell (1988) were in agreement with this. They showed no significant plant growth or uptake of K after feldspar application.

9.1.3 Value of rockdust as fertilizer

The calculations shown in Table 9-3 show the possible maximum value of rockdust as a fertilizer assuming total elemental release. The mineralogical analysis shows that iron, calcium and sodium are added in the highest quantities by rockdust. The calculations show plant yields that could theoretically be supported by complete release of the nutrient from rockdust when all other nutrients are available in unlimited quantities. While sodium is provided in large quantities by the rockdust, it is only needed in small quantities by grasses (Table 9-1). Therefore possible plant growth supported by sodium from rockdust is high. However, this plant growth would require all other macronutrients in high quantities to provide this growth. In terms of P and K supply, there is a large plant demand for these elements; however, they are available in lesser quantities than sodium from rockdust. The possible plant growth supported by P and K addition from rockdust are therefore much lower. These calculations again demonstrate the ineffectiveness of rockdust as macro-element fertilizers as total dissolution of the rock is required to release the nutrients described in Table 9-3.

As plants have low requirements for micronutrients (Table 9-1 and Table 9-2), rockdust may be more useful as a trace-element fertilizer. Table 9-3 and Table 9-4 show that iron and cobalt provided by weathering of rockdust would be the most likely elements provided to sustain plant growth. There is a vast difference between the potential growth upon total dissolution compared with partial dissolution (as indicated by dilute nitric extractable concentrations). Using the figures in Table 9-3 and Table 9-4, rockdust could provide significant quantities of trace metals. However, the important factor in these calculations is the length of time required for elements to be released by weathering of the rockdust. Since the potential increase in plant yield was not realized in the field experiment or pot experiments, two possible conclusions can be made. Either:

1. The rate of weathering is too slow to provide micro-nutrients to the plants in the short term trials; or

2. The parent soil is not deficient in the trace elements released by rockdust weathering into the soil

It is not clear from the experiments which of these two conclusions is most likely. However, the extraction experiments carried out in Chapter 4 highlighted the slow nutrient release from rockdust.

Using the data from Table 9-3 and Table 9-4, it would be expected that rockdust could be applied to remedy some specific trace element deficiencies in soil. However, as the weathering rate is so slow, even large doses may not increase micro-nutrient levels – especially in the short-term.

	Weight in plant material (% in dry matter)					ppm in dry matter	
	Calcium	Phosphorus	Potassium	Magnesium	Sodium	Iron	Manganese
Content in grasses	0.4 – 1.0	0.2 – 0.5	1.5 – 3.5	0.08 – 0.25	0.02 – 0.05	50 - 200	20 - 200

Table 9-1 Content of some elements in grasses (MAFF/ADAS, 1975)

	ppm in dry matter				
	Copper	Molybdenum	Zinc	Nickel	Cobalt
Sufficient range in plants	5 - 20	0.1 – 0.5	20 – 100	0.1 – 5.0	0.2 – 0.5

Table 9-2 Normal concentration range of micronutrients in plants (as described in Fageria *et al*. (2002)

	Weight in rockdust (g kg^{-1})	Rockdust application rate (t ha^{-1})	Element supply by rockdust application (kg ha^{-1})	Possible plant growth supported at maximum nutrient content (t ha^{-1})	Possible plant growth supported at minimum nutrient content (t ha^{-1})
Calcium	38.6	40	1546	154.6	386.4
Phosphorus	1.2	40	49	9.8	24.5
Potassium	14.7	40	587	16.8	39.2
Magnesium	24.8	40	991	396.5	1239.1
Sodium	30.3	40	1211	2421.7	6054.2
Iron	55.3	40	233	1162.9	4651.6
Manganese	0.9	40	34	170.4	1703.5
Copper	0.0185	40	0.74	37.0	148.0
Molybdenum	0.0006	40	0.02	44.4	222.0
Zinc	0.086	40	3.44	34.4	172.0
Nickel	0.0125	40	0.50	100.0	5000.0
Cobalt	0.023	40	0.92	1840.0	4600.0

Table 9-3 Possible grass growth that could be supported by total dissolution of nutrients from Collace quarry rockdust (2006 sample analysis) using typical nutrient content of grass from Table 9-1 and Table 9-2

	Extractable concentration in rockdust (g kg^{-1})	Rockdust application rate (t ha^{-1})	Element supply by rockdust application (kg ha^{-1})	Possible plant growth supported at maximum nutrient content (t ha^{-1})	Possible plant growth supported at minimum nutrient content (t ha^{-1})
Calcium	4.20	40	168	16.8	42.0
Phosphorus	0.50	40	20	4.0	10.1
Potassium	0.04	40	2	0.1	0.1
Magnesium	0.76	40	30	12.1	37.8
Sodium	2.01	40	80	160.7	401.8
Iron	1.25	40	50	249.4	997.6
Manganese	0.09	40	40	18.6	186.2
Copper	0.0009	40	0.04	1.8	7.2
Molybdenum	bdl	40	bdl	bdl	bdl
Zinc	0.0028	40	0.11	1.1	5.6
Nickel	0.0004	40	0.02	3.2	160.0
Cobalt	0.0007	40	0.03	56.0	140.0

Table 9-4 Possible grass growth that could be supported by partial dissolution of nutrients from Collace quarry rockdust (nitric acid extract of SEER field trial rockdust sample) using typical nutrient content of grass from Table 9-1 and Table 9-2

To further demonstrate the effectiveness of rockdust as a trace element fertilizer, the XRF analysis from Chapter 4 was recalculated into an application dose of trace elements (in kg ha^{-1}) per 40 t ha^{-1} application of rockdust (Table 9-5). The concentrations of trace elements supplied by rockdust are shown to be variable but low across all rock types. Although it has been shown, for example in Table 9-1 and Table 9-2, that plants have low requirements for trace elements it is unlikely that rockdust would supply these trace elements in sufficient quantities to impact on plant growth rates. Indeed, this was shown in the field trial using Collace rockdust. Only barium, calcium, copper, iron, lithium, manganese, lead and zinc could be detected in plant material harvested during the field trial and the contents of these metals were not influenced by rockdust application. In addition extractable aluminium, barium, copper, iron, manganese, nickel, lead and zinc contents of soil were not positively affected by rockdust application.

	Trace elements supplied by rockdust samples (kg ha^{-1})																
	Ba	Co	Cr	Cu	Li	Ni	Sc	Sr	V	Zn	Zr	Pb	U	Th	Rb	Nb	Cs
Collace 2006	14.68	0.92	0.74	0.74	0.28	0.5	0.6	18.56	4.1	3.44	8.64	0.45	0.07	0.20	1.54	0.48	0.03
Duntilland	-	-	2.08	2.53	-	2.02	1.12	16.91	15.48	5.05	7.26	0.28	-	0.14	1.34	0.65	-
Furnace	-	-	0.48	0.14	-	0.30	0.17	50.11	1.46	1.53	3.02	0.48	-	0.03	1.36	0.12	-
Clatchard	-	-	0.16	0.32	-	0.22	0.53	19.15	4.43	4.34	10.45	0.51	-	0.25	1.79	0.52	-
Orrock	-	-	14.18	2.12	-	9.13	0.92	34.84	9.03	3.27	10.06	0.14	-	0.20	0.92	2.30	-
Duntilland Fines	-	-	2.4	2.74	-	2.51	1.07	14.94	13.98	5.83	7.61	0.32	-	0.18	1.12	0.7	-

	Hf	Ta	Tl	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu	Mo	Sn
Collace 2006	0.19	0.03	0.01	1.15	0.89	1.90	0.24	1.12	0.24	0.07	0.18	0.19	0.03	0.10	0.11	0.02	0.02	0.04
Duntilland	-	-	-	1.25	-	2.08	-	1.19	-	-	-	-	-	-	-	-	-	-
Furnace	-	-	-	0.26	-	0.88	-	0.48	-	-	-	-	-	-	-	-	-	-
Clatchard	-	-	-	1.15	-	2.56	-	1.29	-	-	-	-	-	-	-	-	-	-
Orrock	-	-	-	1.10	-	3.29	-	1.49	-	-	-	-	-	-	-	-	-	-
Duntilland Fines	-	-	-	1.32	-	2.34	-	1.25	-	-	-	-	-	-	-	-	-	-

Table 9-5 Maximum trace element addition to soil based on a 40 t ha^{-1} application

9.2 Use of compost

A second aim of this work was to assess the viability of greenwaste compost for use in both agriculture and horticulture. In horticulture, this material would be used either partly or wholly to replace peat in the manufacture of plant growth media. Agricultural applications were tested as annual amendments of the material to grassland.

9.2.1 Compost in horticulture

The use of greenwaste compost in the manufacture of plant growth media was tested in Chapter 8. Plant growth in greenwaste compost with and without rockdust was compared to that obtained from a peat based medium. Growth of 3 different plant types was tested over a period of 8 weeks. The results from these experiments showed that greenwaste compost as a growth medium performed as well as a peat based product for each of the plant types tested. These results suggest that the available nutrients from greenwaste compost were sufficient for plant demands. Even the treatment that had 1/5 (vol) acid washed sand produced statistically the same growth as the peat based control and the greenwaste compost alone. This showed that there was an excess of plant available nutrients in the greenwaste compost that could sustain plant growth for even longer periods of time. This was confirmed in a 21 week growth trial using ryegrass and cropping every 7 weeks. This trial showed that the medium could be used for longer periods of time than the 8 weeks used in the main trials.

Disadvantages to the use of greenwaste compost in horticulture are mainly based around the bulk density differences between this and peat based products. In the 'fresh' state, Dundee City Council compost had a bulk density of 0.68 g cm^{-3} while B&Q peat based compost was 0.31 g cm^{-3}. The bulk density increased further when sand or rockdust was added at a rate of 20 % (by volume). This shows that greenwaste compost alone is the most attractive alternative to peat based growing media.

It has been suggested that composted materials will only be a viable alternative to peat based media when the issue of variability has been addressed (Ozores-

Hampton *et al.*, 1999). Compost available nutrient extractions (Chapter 8) have shown that an average figure can be used to calculate 'typical' nutrient content, although some variation will be expected in this natural product. Also, PAS 100 certification proves that the compost is a stable, sanitized product and must be renewed annually. This will go some way towards improving the market acceptability of composted products. In addition to this, any extra information that composters supply in addition to obligatory PAS 100 parameters (for example total nutrients and trace nutrients, 'available' nutrients, water soluble nutrients) will also help to promote the use of these materials.

9.2.2 Compost in agriculture

As discussed earlier, a potential major outlet for composted greenwaste has been identified as agriculture. This material is certainly likely to prove more attractive to farmers than sewage sludge (biosolids) due to lower metal contents and lower risk to human and animal health. As long as the compost achieves PAS 100 certification, the potentially toxic elements applied to land will be maintained at low levels although regular soil testing is also recommended (Environment Agency and WRAP, 2007).

Nutrient analysis of greenwaste compost showed that it was much lower in available-N than the recommended inorganic N application for the field trial. However, compost is also high in organic-N and could prove to be a long-term source of nitrogen for plant growth with repeated applications. This was shown in the field trial where increased plant yields compared to the control were only shown after 2 applications of compost.

The rate of compost application in this trial was at the low end of applications used by other researchers (Table 9-6).

Author	Composted material application rate (t ha^{-1})
Agassi *et al.* (2004)	40 and 120
Bernal *et al.* (1998b)	48
Cabrera *et al.* (1989)	14
Cambardella *et al.* (2003)	80
Cogger *et al.* (2001)	6.7, 13.4 and 20.2
Erhart *et al.* (2005)	9, 16 and 23
Garcia *et al.* (1991)	30, 60, 120 and 180
Guidi *et al.* (1983)	30 (dry matter basis)
Soumaré *et al.* (2003)	25, 50 and 100
Sullivan *et al.* (2003)	155

Table 9-6 Compost application rates used in studies by other authors

It would be possible to apply compost at higher rates than those used in the field trial, but care should be taken to ensure that the guideline value of 250 kg ha^{-1} total nitrogen in organic waste addition per year is not exceeded (MAFF, 1998a; MAFF 1998b). Guidelines for farmers in nitrate vulnerable zones states that organic manure loadings should not exceed 250 kg ha^{-1} of total nitrogen each year averaged over the area of grass on the farm, and 170 kg ha^{-1} of total nitrogen each year averaged over the area of the farm not in grass (DEFRA, 2002). However, the Soil Code also states that wastes such as sewage sludge cake or composted organic wastes which contain very little plant available nitrogen may be applied up to 500 kg ha^{-1} total nitrogen in one application every two years in catchment areas less sensitive to nitrate leaching (MAFF, 1998a). Care should also be taken to avoid large applications of potentially toxic elements. As the content of PTEs in applied compost is detailed as part of PAS 100 certification, a record of the dose of these elements applied can be kept. Analysis when the PTE content of soil is expected to be high after repeated applications of compost would be advised to avoid this risk. During the three year field trial, only small changes in extactable levels of some PTEs were noted in the compost treated soil compared to the control, manure and NPK treatments.

Another excellent reason for the use of greenwaste compost in agriculture is the increase in plant quality compared to plants grown with NPK fertilizer. Although there was less of a yield effect in compost treated plots compared to NPK treated plots, the quality (in terms of nutrient content) of the plant matter grown on compost plots was better than that of those grown on NPK plots. Greenwaste compost would be a valuable addition in organic agriculture systems due to the long-term supply of N, P and K but it could also be used in addition to chemical fertilizers with the potential for reduced rates of fertilizer addition with repeated compost applications. Compost was shown by the field trial to compete favourably with farmyard manure applications. Although compost took longer than manure to produce plant growth effects significantly above that of the control, by the second year of application the two treatments performed similarly. Nutrient content of the harvested material was also similar between the two treatments. It was noted that the application of composted greenwaste were more easily managed compared to manure application due to the friable texture of the compost that also made it is easier to obtain an even coverage.

One of the most important steps in realizing the potential for the use of composted materials is the change in status from a waste material to a valuable product. Increasing standards in the composting industry by introduction of PAS 100 and the Quality Protocol for compost have helped to promote composted material. However, one of the main problems of the use of compost in agriculture is the high cost of transport of the material. In this area, it is likely that composted materials would be seen as competing with sewage sludge. However, as previously discussed, compost that has achieved PAS 100 certification would have far fewer disadvantages than sewage sludge (specifically in the areas of PTEs and micro-organisms). Rather than free disposal of a waste material (as is the case with sewage sludge) compost use in agriculture should be seen as a valuable addition of organic matter, plant available nutrients and micronutrients and a long-term, low level addition of N, P and K. Due to the high cost of transport, the economic value of compost would be at its highest near to the areas of production. Hence other uses of compost would include professional and amateur horticulture and landscaping. This is already the case for many compost suppliers.

Figures from the 2004/05 State of Composting in the UK (The Composting Association, 2006) show that compost producers were able to sell almost half of the material produced (49 %) while 31 % was used on-site and 20 % was given away free of charge. There are a diverse range of uses of composted material, the data from the State of Composting report shows that agriculture represents the single largest outlet for composted materials (30 % of material); other uses such as professional and amateur horticulture, landscaping and land restoration are growing outlets; while landfill engineering and sports turf are diminishing uses of this material. The growing use in high value markets shows the change in opinions on composted material from being considered as a waste material to a valuable product.

The implementation of targets for the reduction in waste sent to landfill mean that there will be increasing levels of material composted in the future. Landfill targets emanating from the Landfill Directive (EC/31/99) are as follows:

- A reduction to 75 % of the amount of biodegradable municipal waste landfilled in 1995 by 2010

- A reduction to 50 % of the amount of biodegradable municipal waste landfilled in 1995 by 2013

- A reduction to 35 % of the amount of biodegradable municipal waste landfilled in 1995 by 2020

Therefore, over the next 10 years, an increase in output from composting facilities is expected. By producing compost to a high standard, outlets in horticulture and agriculture are viable uses for this material and will ensure that it is viewed as a product rather than a waste material.

9.3 Conclusions

The work presented in this thesis tested several hypotheses. The first hypothesis was that application of rockdust, either alone or together with organic materials or inorganic fertilizers to agricultural soil would lead to:

- increased harvested plant yields
- increased plant quality indicated by increased plant nutrient content
- increased levels of soil nutrients (including trace elements)
- changes to the soil microbial community

However, no increase in plant yield was measured in an agricultural scale field trial of rockdust alone or in combination with various fertilizers. There were also no effects on nutrient content of the harvested material due to rockdust addition. Soil from the field trial was analysed during the project but no positive effect of rockdust (alone or in combination with fertilizers) could be seen on soil nutrient levels. The long-term effect of rockdust on the microbial community in the soil as a result of application of the above materials was assessed using a physiological profiling technique. However, rockdust was not shown to give rise to long-term changes in the soil microbial community.

The second hypothesis was that the use of composted greenwaste material, either alone or in combination with various types of rockdust, as plant growth media for several types of crops would lead to:

- increased plant yields
- improved plant quality indicated by increased plant nutrient content

Plant growth media manufactured using one greenwaste compost source and various rockdust types were used in a greenhouse pot trial. Plant dry matter yield was not increased in these mixtures compared to growth in a peat based media. The plant quality data (as measured by the nutrient content of harvested material) showed that greenwaste compost supplied nitrogen as effectively as peat based growth medium. The growth experiments also showed that greenwaste compost provided sufficient plant available-P while the peat based medium was over fertilized with respect to phosphorus.

The field trial also investigated the effects of organic and inorganic amendments on plant growth. Annual applications of composted greenwaste, farmyard manure and NPK fertilizer were applied during the trial. Differences between the treatments were apparent from the first year when the NPK treatment gave significantly higher plant yield than the two organic treatments. This effect continued throughout the trial. Differences between the organic treatments were less well defined with compost taking slightly more time than manure to produce a significant yield effect compared to the control.

A final hypothesis was that the possible beneficial effects gained from rockdust use are a result of:

- the macronutrient content of rockdust
- the micronutrient content of rockdust
- the high pH of rockdust materials

To assess these possible benefits, a suitable procedure for the analysis of extractable plant nutrients from rockdust was developed for use with a range of extractants. Various rockdust samples were analysed using the nutrient extraction technique. The results showed that basic rocks or fine material showed the highest potential for nutrient release. Micronutrients concentrations in the extract solutions were very low showing that rockdust would be unlikely to add significant amounts of trace elements especially in the short-term. As trace elements could not be detected until the dilute nitric acid extraction, this is recommended as an appropriate test for extractable nutrients from rockdust. However, it is not clear what degree of weathering of rockdust this extraction represents.

Overall, although in this thesis rockdust was not shown to increase plant yields, soil or plant nutrient contents or lead to changes in the soil microbial community in the field trial; the research showed that PAS 100 standard composted greenwaste materials could be used in both agriculture and horticulture to sustain plant growth either alone or in combination with conventional fertilizer or peat based growth medium. The quality of plant material grown in soil treated with these materials or in greenhouse growing media composed of these materials was shown to have be as good as, or in some cases better than, the alternative treatments of NPK fertilizer or peat based growing media.

9.4 Future research into rockdust and composted materials

While the research detailed in this thesis assessed the potential for these materials in both agriculture and horticulture, the long-term plant growth effects were not assessed using a deep-bed system similar to that of the SEER Centre terraces. As rockdust materials did not enhance plant growth in the pot trial experiments or in the field trial, a longer term trial using the compost/rockdust mixtures from the pot trial would be an appropriate future step for research into these materials. A trial on this scale would require substantial extra funding to set-up a replicated system.

As the data from the field trial gave mostly positive results with respect to compost use in agriculture, it is recommended that further work be carried out to investigate the long-term effects on soil chemistry, microbial communities and plant growth. More work could be carried out to assess nitrogen turnover in compost treated plots to show the build-up and release of nitrogen reserves. Alongside this, the build-up of PTEs should be assessed to determine how long compost could be applied to agricultural soil before guideline limits are reached. The microbial community physiological profiling technique used in this thesis could be further developed to assess short term effects of compost addition to agricultural soil and to determine the longevity of any changes to the soil microbial community gained by compost applications. Long-term plant growth and nutrient content data using the same organic and inorganic fertilizer treatments in this project could provide even more useful information on the possible benefits of an organic system compared to the conventional inorganically fertilized system. For example, this work could show if compost treated plant growth ever ‘catches up’ with the growth shown in NPK treated soil; it could also show the long-term effects on plant quality as annual applications of the fertilizing materials are made.

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