# Evaluation Of Near-Infrared Spectroscopy For Analysis Of Soil And Plant In Agriculture

by

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# Abstract

In this research, a critical scientific appraisal of Near Infrared (NIR) spectroscopy for the analysis of soil and plant is presented. Near Infrared measurements in the study were collected using a KESNIR spectrometer with a scanning range of 400–1700 nm and a large scanning area. NIR was shown as the instrument of choice because of its versatility, non-destruction of sample on analysis and rapid measurement times.

The focus of this study was to derive and test correlations between NIR spectra of soil and plant samples and concentrations of nutrient-related variables in these samples (as measured using conventional techniques). These NIR correlations effectively constitute a series of calibrations. The concentrations of a number of elements (or other soil or plant physicochemical properties) will then be able to be reliably estimated on the basis of a sample's NIR spectrum alone. Part of this project is devoted to deriving calibrations, and the rest will focus on assessing how well these NIR calibrations perform, by comparison of NIR-predicted values to those obtained using conventional chemical extraction followed by analyte-specific instrumental analysis.

In order to achieve the above for soil testing, calibrations included samples from all 15 New Zealand soil orders and subsoil types, geographical regions, and land use. Most of the soil and plant samples analysed have been taken from the pool of such samples routinely submitted to *AgResearch* for analysis. In addition, to date, no studies have been reported in which NIR spectra have been recorded for a full range of soil orders in a country.

In the case of the NIR measurements, field-moist soil and plant samples could be used, rather than dried and ground samples. This represents a considerable saving of time and effort. One aim of this project was to investigate and validate measurements for soil and plant samples by NIR using field-moist samples. This would then enable the measurement of nutrient status in the field.

Soil nutients and parameters looked at in this study were pH, Olsen P, sulphate-S, available K, Mg, Ca and Na, soil type, P retention, reserve K, soil total N (TN), soil total S (TS), soil total C (TC), available N and nitrate-N.

The study also aimed to determine that if key nutrients could not be ultimately measured accurately and rapidly in the field using NIR, a rapid alternative method was to be investigated. It was found that NIR could not accurately predict pH, Olsen P, sulphate-S, available K, Mg, Ca and Na and nitrate-N from a direct soil scan for New Zealand soils. However, a rapid sample preparation method/complexing ('signal enhancement') of field-moist or dried soils for the measurement of Olsen P and available K prior to presenting to the NIR could enable accurate measurements. NIR via the 'signal enhancement' method could measure Olsen P with results obtained for New Zealand soils with accuracy comparable to Olsen P determined by the traditionalby method. Therefore Chapter 8 in this thesis is dedicated towards determining exactly how the 'base reference method' (Olsen P) behaved for New Zealand soils.

Furthermore, pH could be rapidly and accurately measured after a 10-minute extraction on field-moist or dried soils using a pH meter. The accuracy of pH mesurements using NIR was improved when compared to direct soil scans when the soil solution was complexed by an indicator and presented to the NIR. Soil nitrate-N can be measured by complexing prior to presentation to NIR using the same pH water extract.

Soil type, P retention, reserve K, soil total N (TN), soil total S (TS), soil total C (TC), and available N could be measured via a direct soil scan.

A patented procedure using $CO_2$ to determine parameters in wet plant was developed. Key plant nutrients looked at in this study was nitrate-N, N, P, S, Mg, Ca, K and plant moisture. Plant moisture could be accurately determined by NIR. Nitrogen, nitrate-N and Ca in dry and wet plant material could be measured with a high degree of accuracy while NIR did not have the desired accuracy for the other major elements. This study also showed that transfereable calibrations was possible with the KESNIR instruments for the measurement of plant N.

Two major topics within the overall aim were also identified. These were the N status test and a soil Sulphur test which both have a large agronomic advice and significant NIR component to them.

A pot trial study using soils from throughout New Zealand was used to develop a soil nitrogen test for New Zealand pastoral soils. Currently, soil tests for N availability have proven difficult to develop, and no single test has been universally adopted. A total of 52 soils comprising the major soil groups in New Zealand were collected for the pot trial. Soils collected were from Northland, Waikato, Bay of Plenty, Central Plateau, King Country, Taranaki and all major districts of the South Island.

The study found that inorganic-N in the soil drives pasture production. The N content in grass can be used to accurately predict N responses to fertiliser application. There is always a response to N application. N status varies greatly across New Zealand, and therefore varies due to soil type and land use. Using multivariate analysis, 81% of the variation was accounted for when dry matter yield was correlated against inorganic-N soil TN, and Anion Storage Capacity (ASC). Soil TN, ASC and soil type can be accurately and rapidly measured using NIR. Soil and grass N can be categorised into Low, Medium or High N status. Soil nitrate-N can be measured by complexing prior to presentation to NIR.

The aim of the work on a new Sulphur test was to determine if the Total S pool in soil is a better measure of the sulphur status than sulphate-S or easily mineralisable organic-S. Total S accounted for 71% of the variation when compared with relative yield for 43 field trials, whereas mineralisable-S accounted for 58% and sulphate-S accounted for 59%. Sulphate-S is easily influenced by external sources – such as urine and dung from grazing animals, leaching, fertiliser and atmospheric inputs. Organic-S accounted on average for 97% of the TS, of which EOS consisted of on average 3%. The sulphate-S component consists on average 3% of the TS. The Total Sulphur pool, because of its magnitude, is not influenced to the extent that EOS and particularly sulphate-S are by external sources. It is therefore proposed that Total S is a better and more robust measure of the Sulphur status for New Zealand pastoral soils.

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# Chapter 1. Introduction

***Contents:***

## 1.1 General Overview of Soil and Plant Testing in NZ

Each year in New Zealand (NZ), approximately 115 000 soil samples (*Pers. comm.* major NZ, Hills Laboratories, Gribbles E-Lab and ARL, 2004) and 50 000 plant samples, are chemically analysed for their fertility status. NZ has a total land area of 268 021 km$^2$, of which 58% is in grazing, horticulture, planted production forests or other land use and provides 67% of NZ GDP (Statistics NZ). This equates to 0.43 soil samples analyzed per km$^2$ for NZ's total land area, and 0.74 if only area covered by farming, forestry and other land use is taken into account. Comparatively, in the United States, 3 million soil samples (10 samples per km$^2$) and in Australia, 135 000 (0.34 samples per km$^2$) are analysed each year for agricultural land. The cost of soil testing in New Zealand is about NZ $45, for the United States NZ $39, Australia NZ $100 and South Africa NZ $14–27 (Bramley and Cook, 2000). This suggests the larger the number of agricultural soil samples analyzed per km$^2$ per annum in a country the lower the cost per soil sample analysis, or, more likely, the lower the cost, the more samples measured.

Currently, almost all of the agricultural soil and plant analyses in NZ are carried out using chemical extraction techniques, followed by analysis of each specific target element or compound in the extract solution using one or more instrumental methods of analysis. All such testing is invariably done on dried and ground plant and soil samples.

Soil and plant testing in agriculture is used as a means of monitoring nutrient deficiencies and imbalances, measuring toxicities, and for maintaining soil fertility for maximum or sustainable crop or pasture production. The results from plant and soil testing are, therefore, integral for formulating lime and fertiliser recommendations. It is estimated that over two million tonnes of fertilizer are applied to New Zealand pastures and crops annually (Horrell *et. al*, 1999). Soil and plant testing will be used as a tool to monitor environmental impact of farming practises. Nutrients could be classed into low, medium or high levels. Any nutrient in a system which is deemed to be high and poses an environmental risk can be identified and appropriate action taken by utilising the information gathered from testing.

Local Government in New Zealand is divided into Regional Councils, and Territorial Authorities (City and District Councils). Regional Councils are primarily responsible for resource consenting issues associated with discharges of contaminants into the environment.

In order to streamline their regulatory functions, Regional Councils develop legally binding Regional Plans. In the future, many of these Regional Plans are likely to require nutrient budgeting. For example, the proposed Waikato Regional Plan will require nutrient budget models to be supplied before fertiliser can be applied. These rules are under appeal and therefore not operative at present (Environment Waikato Regional Council, 2004). However, the general trend is toward more nutrient budgeting. Environment Waikato is looking at taking a more focused approach to target high-risk areas, such as the Taupo catchments and surface waterways. Recent work has shown that surface water quality in the Waikato Region, which reflects changes in land practices, has been generally declining due to diffuse-source nutrient contamination from agricultural sources (Vant, 2004).

Agreements between local government and the agricultural industry are also being developed: arguably the most significant of these to date is known as '*The Fonterra Accord*' (Fonterra Accord, 2003), and this also encourages farmers to use a nutrient budget. A driver toward better nutrient budgeting is the farm-management expectations of international trading partners: there is a progressive shift toward environmental quality assurance as a prerequisite for various favourable trading opportunities.

For these reasons, the need for routine nutrient analysis is progressively increasing. It is probable that in the future, nutrient levels, particularly nutrients such as nitrate-N that poses risks environmentally (see Chapter 7) and phosphate, will need to be monitored prior to applying fertiliser.

For plant analysis the total nutrient or elemental content is determined, whereas with soil testing, the labile or an extracted fraction of that particular nutrient is determined.

## 1.2 Soil Analysis

Before analysis, soil samples are prepared by drying between 30–35 °C, and grinding to allow passage through a 2 mm sieve. The nutrient status of soils is determined by the amounts of elements extracted from soils using chemical extracting solutions, which usually contain weak acids, neutral salts, or a mixture of the two. The best correlation between soil nutrient status and plant nutrient status/crop yield (or crop response) for the constituents studied is the determining factor for the chosen soil extractant.

In a routine soil fertility test, the aim is to provide an indication of the fertility of a soil and this is done by measuring the level of major available nutrients and soil acidity. In NZ, a basic soil test includes extractable P, extractable Mg, Na, Ca and K, extractable sulphate-S and a measure of soil acidity, pH. Other commonly-used soil tests include extractable organic-S, organic carbon (OC) or total carbon (TC), organic matter, total nitrogen, cation exchange capacity (CEC), anion storage capacity (ASC), extractable B, Reserve K, nitrate-N and ammonium-N.

## 1.3 Plant Analysis

Generally, plant nutrient status is determined as the total amount of each element present in the plant material. Plant tissue samples are first prepared by drying at 60–70 °C, followed by grinding. Samples are then acid digested, which involves use of either a single concentrated acid or a mixture of concentrated acids to quantitatively extract the elements from the plant material. Once the elements are extracted into the liquid phase, a variety of analytical methods are available to measure element concentrations. The analysis of major and trace elements in plants is also carried out to determine animal and pasture nutritional requirements. The constituents analysed for are N, P, S, Mg, Ca, Na, K, Mn, Zn, Cu, Fe, Mo, Co, Se, B, nitrate-N and Cl.

## 1.4 NIR

### 1.4.1 Brief Overview

Near Infrared (NIR) Spectroscopy is a fairly recent instrumental technique in which an indirect measurement is made of the species under investigation. NIR spectroscopy is also generally considered a *non-destructive* technique – the sample is not destroyed or altered significantly during analysis. The NIR region of the electromagnetic spectrum covers from the end of the visible out to about 2500 nm. Spectral interaction in this region are complex overtones of major effects, allowing probing of quite subtle interactions between species and physical parameters. The absorptions in the NIR region are caused by vibration modes of particularly the O-H, C-H and N-H groups within molecules. These are the more reactive molecule ends in most organic materials, and subtle covalent bonding effects manifest as subtle alterations in relative absorbances throughout the NIR region.

In recent years it has been shown that the NIR spectrum is rich in information, and can be used to estimate a number of the more significant characteristics of samples, including the concentrations of (at least some) elements (see Chapter 2: Literature Review). In order to do this, the approach used has been to ascertain which parts of the NIR spectrum correlate with the results of conventional tests, and then use these spectral features as proxies for the variable. Spectral features in the NIR spectrum can therefore be calibrated to sample properties and parameters by quantitatively relating these to results obtained by conventional instrumental, chemical and physical techniques. In doing this, use is made of statistical approaches such as partial least-squares regression (PLS) that are only made possible through the great recent advances in computer technology. The availability of sufficient computer power has meant that most of the developmental work carried out on NIR to date has been performed since 1980s. This is evident with the large rise in number of publications in the 1980s and 1990s.

In other wavelength regions, spectroscopic methods are usually based on sharp spectral signatures, with relatively simple deconvolution of the spectra into constituent component signatures, allowing a tight link to be derived between wavelength intensity and unknown sample. An NIR spectrum of a sample contains many broad and overlapping spectral features. These often cannot be deconvolved due to the fundamental interaction of the absorbances. If the instrumentation has sufficient specificity and signal to noise capability, while the spectral components cannot be separated on a fundamental level, the spectra for identical samples remain identical. Therefore statistical techniques can be used to probe the critical interactances and derive spectral relationships without ever needing to define the underlying fundamental causes.

Consequently the way a sample is presented to the spectrometer is important in getting accurate and reproducible results. Furthermore, in a single scan, NIR spectroscopy is able to measure a wide range of chemical analytes and physical characteristics of material in a matter of seconds. An operator does not need specialist knowledge about NIR as long as samples are presented in a consistent manner.

A range of chemical and physical determinations can be obtained from one scan. Cost per analysis by the NIR should make testing cheaper than traditional wet chemistry methods.

Almost all organic compounds have absorbance effects in the NIR region. Some inorganic species (with covalent bonds) also absorb in this region. Those species which do not absorb in the NIR region may nevertheless be detected indirectly because of their influence on the other constituents present.

NIR spectroscopy technique is unusually fast compared to other analytical techniques (a few seconds). It is non-destructive, and often no or minimal sample preparation is required. It is also remarkably versatile. If samples contain covalent bonds such as C–H, N–H, S–H or O–H, and if the concentration of the analyte exceeds 0.1% of the total composition, then it is also very likely to yield accurate results.

### 1.4.2 Transferable Calibration

One of the largest challenges facing NIR has been the inability to transfer calibrations between instruments. This has posed problems if a component such as a bulb was changed in a single instrument. If NIR is to gain wide acceptance and gain further momentum, calibrations will need to be transferable. This is only possible if different instruments output very similar data on the same samples. For this to happen the wavelength axis, optical resolution and photometric axes must be identical among instruments (Anderson *et al.,* 2002) or at least accurately modelled between the instruments.

### 1.4.3 Data Analysis and Chemometrics

In this context chemometrics is the science of linking physical or chemical methods with indirect methods such as NIR. Chemometrics has revolutionised NIR: Near infrared spectroscopy would be difficult to use without chemometrics because of the overlapping bands.

Typical of any chemometric method, the price to be paid is in the preliminary work. The computer system must be 'taught' what is important in the sample. This is not difficult, especially with current software, which offers the spectroscopist such choices of regression as multiple linear regression (MLR), partial least squares (PLS), principal components regression (PCR) and neural networks (NN) among others. If a parameter needs to be continuously measured, is difficult or expensive to measure, NIR spectroscopy may be a good solution. The trade-off can be good even after several hours of calibration development.

Calibrations need to be maintained over time and frequently updated to ensure they are robust. They need to be continuously monitored because factors which will affect calibrations include seasonal variations, temperature, subtle changes in methodology (sample presentation) and instrument changes.

### 1.4.5 NIR-Soil and Plant Analysis

NIRS is currently being used to assess grain, feed quality and food quality, but its uses in plant and soil testing are relatively new. A review of the literature shows that to date, studies have published calibrations in general for total concentrations (Malley *et al.*, 1999; Udelhoven *et. al.*, 2002) of some elements in soil with little on the plant available form of the constituent studied. These studies dealt with one soil group and a small number of samples. Many of the studies have also been limited to studying elemental composition in a single sample type. An example of this is the work done by the South African sugar cane industry (Meyer, 1998). The reason for this is that it is very difficult to have a range of sample types and ensure that calibrations are robust. All variations need to be covered in order for calibrations to be robust.

NIR technology has the potential to make routine plant and soil testing substantially faster, cheaper, and simpler than it is at the moment. Sample preparation can also be minimal. In addition to simplifying current testing programmes, availability of a reliable NIR method would be likely to increase the total number of samples which can be analysed. This may enable growers to fine-tune their application of soil treatments and possibly reduce their costs.

### 1.4.6 Conclusion

Currently, apart from measuring feed quality, the use of NIR for soil and plant testing is very limited (or nil) in NZ. The greatest variability in soil and plant testing is contributed by spatial and temporal rather than the laboratory. This variability can be considerably reduced with NIR use (larger number tested at site due to reduced costs) and the benefits to New Zealand agriculture from appropriate application of NIR technology could be immense.

From the perspective of routine soil and plant testing, NIR has some real advantages over the traditional wet chemistry techniques. These are:

- The technique is rapid. Spectra can be obtained in a matter of seconds or minutes.
- Minimal sample preparation is required and field moist samples can be used.
- Environmental risks are low because chemicals are not generally used.
- The development of calibrations is time consuming but this is offset by rapid generation of results once this is in place.
- An operator does not need specialist knowledge about the technique as long as samples are presented in a consistent manner.
- A range of chemical and physical determinations can be obtained from one scan.
- Cost per analysis by the NIR should be cheaper than traditional soil or plant testing methods.

## 1.5 Study Scope-Aim

The emphasis of this thesis is on application of NIR technology, other technology, analytical techniques and field/glasshouse calibrated soil tests to further improve soil and plant testing and agronomic advice for NZ.

The aim of the thesis is to contribute to expanding the technical capability in New Zealand for effective plant and soil testing by:

- Reviewing published literature on plant and soil analysis by NIR (Chapter 2).
- Improving methods of soil and plant preparation and presentation to a diode-array NIR instrument. Outline NIR calibration development, chemometrics and other methods for study (Chapter 3).
- Evaluating the performance of rapid NIR for plant sample analysis (Chapter 4). Calibration developed on wet & dry plant.
- Evaluating the performance of rapid NIR for NZ soils (Chapter 5).
    - Key nutrients: Can they be analysed accurately and rapidly?
    - Direct soil scan & sample 'enhancement' procedure.
    - Effect of soil drying: Important for calibration development on field moist soils if calibrations built from 'reference dried soil tests'.
    - method of rapidly drying soil.

- Exploring the relative advantage of the soil test for total soil S over those for sulphate-S and easily mineralisable organic-S (Chapter 6).
- Development of a new N test for pastoral farming (Chapter 7).
- Standardizing the Olsen P soil test (Chapter 8).
  'Accurate reference NIR method is required' in order to get an accurate NIR calibration.
- Evaluate 'Transportable' calibrations: Are they possible using a diode array NIR (Chapter 9).
- Outputs from thesis-Patents and papers (Chapter 10).

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# Chapter 2: Literature review of soil and plant testing using NIR

## 2.1 Introduction

NIR Spectroscopy is more versatile and user friendly than any other analytical technique currently available in the market. This is reflected in the number of NIR related publications. There are at least 23,000 published papers and patents on NIR spectroscopy (CNIRS Bibliography, 2002) and a high proportion of these are directly associated with agriculture.

The Council for Near Infrared Spectroscopy (CNIRS) maintains a bibliography of near infrared literature (including patents) that covers all forms of NIR technology from 1800 to the present. This bibliography, called the *CNIRS Bibliography (CNIRS-B)*, is in three chronologically ordered libraries (1800-1995, 1996-Present and Patents,1971-2002). The CNIRS-B contains more than 23,000 citations. It is the single most complete bibliography of NIR technology currently in existence.

William Herschel is thought of as the discoverer of the NIR region. He discovered the NIR region on 17 March 1800 when he conducted an experiment to measure the relative heating effect of differently refracted rays of sunlight. He did this by measuring the temperature changes of the different colours in the visible spectrum when he dispersed light by a prism on to a table. Using mercury glass thermometers to measure the temperature changes, he noticed the maximum heating effect was half an inch beyond the red end of the visible spectrum with a temperature rise of 9 degrees (Herschel, 1800). Figure 2.1 shows the NIR region 770-2500 nm, with respect to the rest of the electromagnetic region.

The near infrared (NIR) region of the spectra is taken as that adjacent to the visible region, (Figure 2.1), usually wavelengths of 750-2500 nm. However, commercial instruments available for NIR spectroscopy may cover slightly wider areas of the spectrum. Instruments may also cover narrower ranges such as diode array that go to 1700 nm.

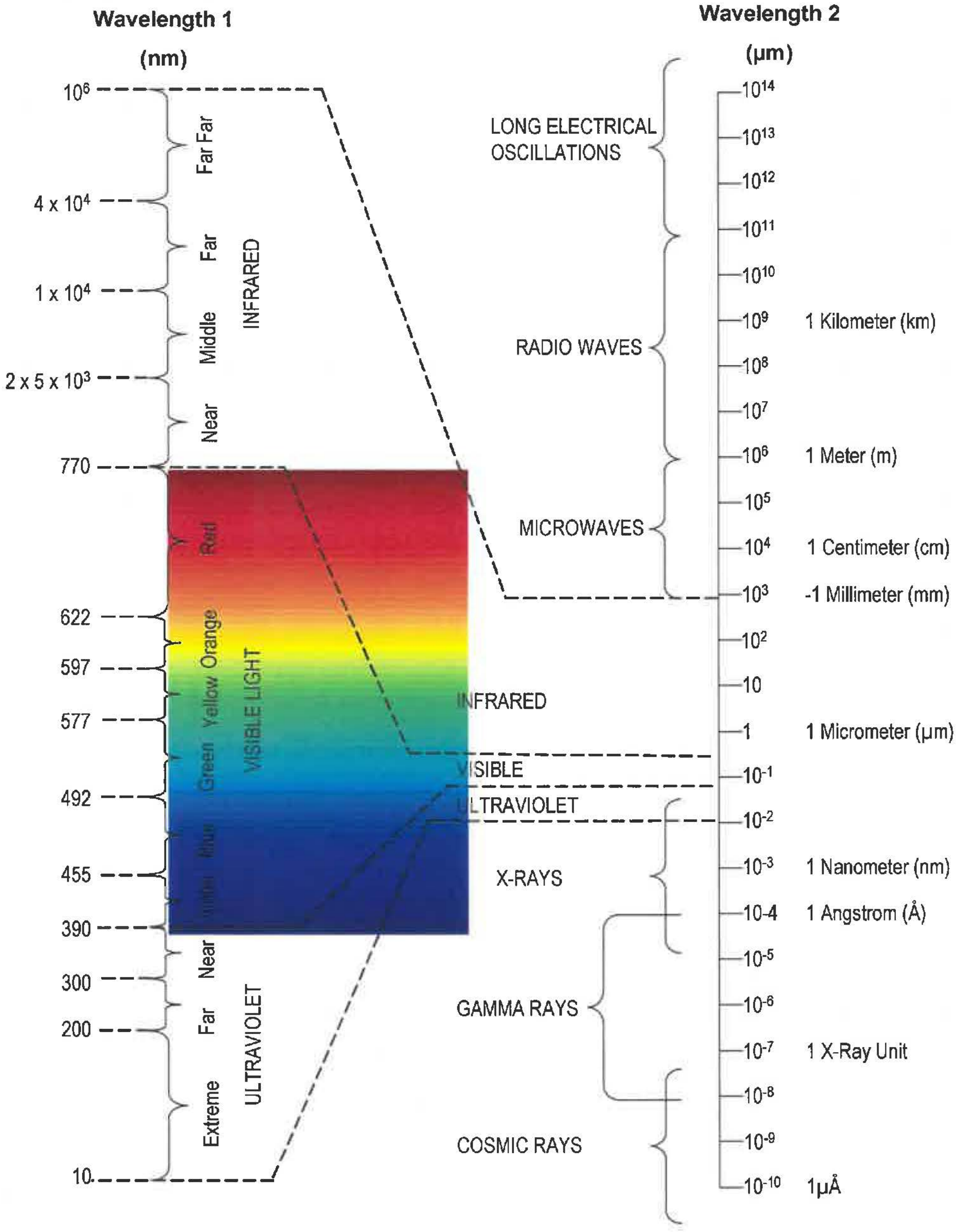

**Figure 2.1:**
NIR region and its place within the electro-magnetic spectrum.

There are 4 types of NIRS instruments available in the market at present. These are Filter, Dispersive, Diode array and Fourier Transform. NIR instruments can either measure from a sample the reflectance or transmittance or both simultaneously. The NIR region has the advantage in that the sample preparation is less critical than for the mid and far-infrared regions. Virtually all organic compounds absorb in NIR region, as do many inorganic minerals. Even inorganic species which do not absorb in this region may be detected because of their influence on the organic constituents present (Ciavarelli *et al.*, 1998). This makes the potential of NIRS applications in analysis very wide.

NIR measures overtones and combinations of the molecules vibrational modes, principally those involving hydrogen. Therefore, NIR is particularly useful for the study of hydrogen bonding. A disadvantage is that most of the useful features in NIR spectra are 'overtones' or combinations of overtones, and therefore less easy to assign than the distinct fundamentals in the mid-IR and far-IR spectra. The information found in the mid-IR and far-IR is repeated in the NIR region but is convoluted. However, today's chemometrics software and computer technology overcome this problem. Therefore, NIR analysis has become a practical choice for many applications.

Although it is not generally easy to identify the wavelengths at which specific absorbers absorb, a main advantage of the NIR region is that absorbances are lower than in the IR region, and are proportional to concentration. Therefore, NIR absorbance can be used to quantify concentrations of the absorbers.

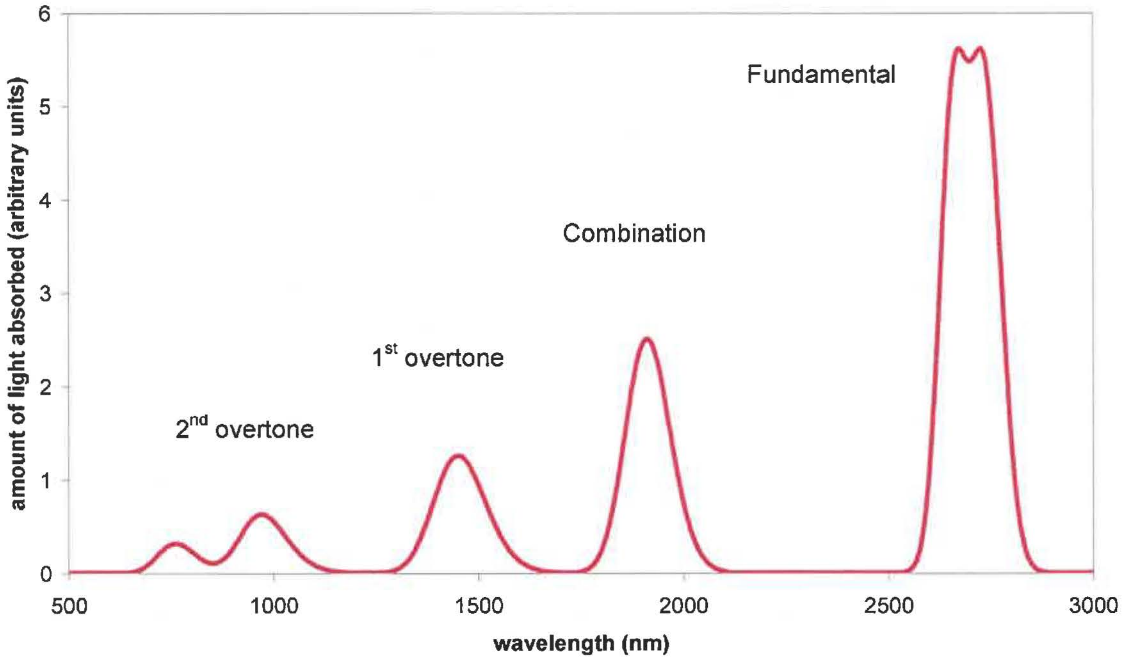

**Figure 2.2:**
An idealised drawing of the fundamental bands for water and its respective overtones and combinations bands found in the NIR region.

NIR has a wide range of agricultural applications; food and feed quality, pharmaceutical, polymer, cosmetics, environmental, oil, textile and medical fields. It is being used for process monitoring on-line, near line or in-line in the above industries.

## 2.2 NIR in Agriculture

The contribution by NIR to agriculture began as far back as the 1960's (Batten, 1998). It offered to agriculture the possibilities of non-destructive routine analysis in very short times. NIR proved to be more rapid, less expensive and more environmentally friendly than traditional laboratory and wet chemical techniques. Much of the development of early applications using NIR has been attributed to agricultural scientists. These initial researchers faced problems of data analysis, reliability of instrumentation and availability of reliable traditional analytical methodology for calibrations. Instrumentation has now become more powerful, compact and robust in terms of even portable instruments on the market to enable analyses to be performed in the field. The rapid advance in the power of computer technology and software has enabled NIR to obtain improved, robust and accurate calibrations which were not possible in the past. The use of analytical instruments such as ICP, ICP-MS and HPLC and the improved detection limits and accuracies that the above methods possess has increased the use of NIR.

The growth of the modern NIR technology particularly in the agricultural sector can be attributed to Carl Norris. The father of NIR is considered to be Carl Norris. In 1965, initial work by Norris detected differences in the moisture content in grain when working for the US agriculture dept, (Massie and Norris, 1965). Norris's subsequent work showed that diffuse reflectance and transmittance spectra of agricultural products contained information about the chemical compounds or structures and each structure had specific absorption properties.

Early applications using NIR were for the determination of feed quality of forages and grains (Williams, 2002). Tests included protein content, ADF, ash and moisture. There have been numerous studies on these applications. Now the feed quality of forages and grains is routinely analysed by commercial labs. AgResearch's feedTECH laboratory in Palmerston North, NZ, routinely offers at least 15 NIR feed quality tests to the agricultural sector. The tests are available on feeds such as grass, baleage, hayleage, hay, grass silage, and maize silage.

## 2.3 Soil Analysis

### 2.3.1 Soil literature review: Summary

A major cause of inaccurate NIR predictions is when models developed are applied to samples which are not adequately represented in the group of samples used for the calibration model. Aplications of NIR soil analysis has been less successful than feed analysis because the calibrations have been less accurate, because the species tested for is not optically sensitive in the NIR region and samples not adequately represented in the calibration. A large number of soil samples will be needed to cover all variations for calibrations and the samples must cover the entire range for it to be successful.

The soil matrix is a complex medium for the NIR to deal with when comparing to a matrix such as plant material or milk powder which is more uniform in nature. NIR absorption by soil is not linearly related to individual components of the soil matrix (Couillard *et. al.*, 2003). The reason for this is attributed to differences in particle size, absorption intensities of soil minerals, and surface coating effects of clays and fine organic matter on larger soil particle (Russell, 2003). The best calibrations are deemed to be the ones with the lowest SEP for NIR work.

In recent years there have been reports of the use of NIRS to measure a range of soil characteristics. Many of these papers have been restricted to showing good calibrations for a range of soil analyses or properties and raising the possibility of the use of NIRS for routine soil analysis. However, Meyer's groups at the South African Sugar Research Institute routinely apply NIRS in the analysis of soils, as well as sugar cane. In 1996 they reported that they had applied this technique to more than 140,000 soil samples (Meyer, 1996) and described the field use of a portable NIRS instrument for soil analysis (Schumann, 1999).

Most publications of NIR measurements on soils have investigated a relatively small number of samples, often from a small group of soils. An exception to this are the studies by Chang *et al.*, 2001. This may mean that better correlations have been reported than would be achieved in practice for routine soil testing. On the other hand, if calibrations are made with large numbers of soils from diverse soil groupings, better correlations may be possible. Effectively, separate calibrations appropriate to specific soil groups could be used. Because NIRS measurements provide good estimates of organic matter, CEC, soil water and soil texture, it is possible that soil type determination could be part of the NIRS measurement. Malley *et al.*, 2004 reviewed NIR studies where soil physical, biological, nutrient and mineral measurements have been conduted.

The majority of soil testing applications using NIR have been investigated only in the last decade. The total number of publications dedicated to soil testing with emphasis on soil fertility are less than 100. Literature review indicates that less than 20 studies have been devoted to soil applications up to 1994. A large proportion of publications have been published since 1994 with about 60% published on the topic since 2000. Most of these studies have been conducted in and on soils from USA. Canada, Australia and South Africa have also made significant contributions. Yet other studies have also been conducted in Japan, Israel, Korea, Hungary, Spain, Sweden, Italy, Brazil, Taiwan, Korea, Norway, Germany, Eastern and Southern parts of Africa, Netherlands, France and Uruguay. To date there has not been any studies published on New Zealand soils using NIR.

Tables 2.1-2.19 show results obtained for NIR soil studies discussed in the following sections. The tables list a range of soil analytical applications where NIRS has shown promise. Most of these papers provide data showing the possibilities for using this technique in soil analyses. However, only a few groups are using NIRS as a routine soil analytical procedure. The tables give information on the soil test, study reference, year of study, location, instrumentation, wavelength range(λ), whether sample was scanned dry or field moist, soil particle fraction scanned, soil depth (mm) sampled, number of samples in study, the range of the test parameter studied, the repeatability of the wet chemisty test $S_r$ (wetchemistry), $R^2$, RMSECV and RMSEP.

Researchers using NIR for soil testing have reported different degrees of accuracies for their calibrations. There are many reasons for this and some of these are outlined below:

- Sets of soils used only one soil series, soil type or from one location and obtained good correlations whereas those which had a variety were not as successful.
- Small number of samples in studies. This leads to better accuracies obtained than if larger more varied sample set is used.

- The use of different soil fractions (finely ground, < 1mm, < 2 mm etc.). Majority of studies used the <2 mm fraction which is the standard soil testing practice.
- Steadily increasing power of the NIRS instruments, the software and PCs used in recent years.

A review of the NIR literature on soil studies suggests that:

- Most researchers have only demonstrated the possibilities with a relatively small number of samples with some exceptions (Chang, 2001; Shepard and Walsh, 2002).
- Better calibration statistics was obtained when determining total elemental composition compared to the available form. This is possibly due to the lower concentration encountered for available nutrients. These available nutrients possibly have minimal or no optical activity directly in the NIR region.
- Indirect measurement of an analyte or parameter due to co-correlation. An example being CEC.
- The majority of NIR measurements were performed on dried material than field moist soil. The exceptions being studies conducted by (Schumann, 1999; Chang, 1999; Malley *et al.,* 1999c). These studies demonstrated the feasibility of using field-moist soils instead of air-dried soils.
- The possibility of using a portable NIRS instrument in the field. This would have real advantages for precision agriculture, especially for cropping situations.
- Majority of studies have been performed using NIRSystems 6500 Instrument. This review estimates that 80% of studies have been conducted using this instrument.
- Most studies used PLS for calibration development. For future work neural network software (NT) will need to be used if testing is to be routine since thousands of samples will need to be in a calibration.
- Earlier studies used certain wavelengths to build calibrations.
- Calibrations are non-linear for measurements such as C and N where a variety of soil types or groups are used. Use of individual soil type calibrations to overcome this improves calibration statistics.
- The literature suggests that routine determination of soil moisture, C, N mineralizable N, CEC, soil texture (sand silt and clay fraction) and some of the total elemental composition of some elements such as Ca, Mg and Fe may be routinely possible.

- Most of the soil studies reviewed have shown the possibilities of using NIR, rather than its routine use. One of the exception being (Meyer, 1989 & 1998 and Schumann 1999) of South African Sugar Experimental Station. They have integrated routine NIRS measurements for soil, cane leaves, and shredded cane into their procedures to improve agricultural efficiency. Their NIR measurements include tests such as mineralisable N for soil, N in cane leaves and Brix, fructose and moisture in shredded cane.
- Calibration results are superior where NIR is measuring analytes (i.e. moisture, C or N) that are spectrally active in the NIR region , rather than those that are predicted by virtue of their correlation with spectrally active analytes or because they shift the absorption band of water (i.e. pH, Cd or Mg).
- In order for routine soil testing to be a possibility robust calibrations will need to be developed for a wide range of soils which encompasses the concentration range for the test.

The literature review covers studies on soil and plant testing and is given in chronological order. Studies conducted on soil are separated into 1800-1994 and 1995- present.

### 2.3.2 Studies from 1800-1994

One of the earliest studies to be carried out on the reflection of soil was that by Bowers and Hanks (1965). They looked at the influence of moisture content, organic matter and particle size. Their study indicated that moisture content, particle size and organic matter influenced reflection from soils. Bowers measured reflectance of soil using a wavelength range of 185-3500m$\mu$. They used a Beckman DK-2A & DU spectrometer.

It was found that wet soil samples have lower reflectance curves than dry soils. They found that the reflectance decreased as the surface moisture content increased, increasing the surface moisture content increases the absorbance. Their work found the absorbance band of water at approximately 1440, 1900 and 2200. They found that moisture content could be accurately and reproducibly determined by reflectance measurements. Elevated daytime temperature of dark coloured soils is attributed to their greater absorbance of solar energy. This would mean that reflectance is lower from darker soils. Organic matter influences soil colour therefore differing organic matter content in soil will influence reflectance. They found that wavelengths of a sample with less organic matter had a greater reflectance. Increases in reflectance with fine milling was attributed to increased interface between opacifier and frit. They found lower reflectance for clay minerals. Also different reflectance properties between clay minerals bentonite and kaolinite were found and attributed to kaolinite structural characteristics and lower mass density relative to bentonite. An exponential increase in reflectance is seen with decreasing particle size with the most noticeable increases occurring at sizes less than 400 microns. Changes in reflectance could also be attributed to surface roughness. As particle size decreased the surface become smoother. Thus the roughness of the surface is in turn a function of the particle size. Moisture content, organic matter and particle size strongly influence the reflectance and therefore absorbance of radiant energy. At all wavelengths, on all samples, reflectance decreased and absorption increased as moisture content increased.

Baumgardner *et al., 1970* found that organic matter plays a principal role in reflection of soils with organic matter content >2.0%. As OM drops to < 2.0% it becomes less effective in clouding the effects of other soil constituents on spectral responses of soils.

Spectral reflectance of soils and the content of organic matter were investigated by Al-Abbas *et al.*, 1972. Organic matter and clay were found to be significantly correlated. The relationship between clay content and relative reflectance could be secondary because of the high correlation between organic matter and clay content. Therefore, it is unclear whether the relationship is real. When soil organic matter decreases, the spectral response increases. A similar relationship held between clay content and spectral data. This suggests a good correlation exists between organic matter and clay content. They found that there were wavelength bands which contributed significantly to the prediction of organic matter in the soils with 720 – 800 nm having greatest influence.

Krishnan *et al., 1980* collected soils from Illinois, USA for their study. Samples high in organic matter content showed a marked response near the 800nm. The study found that 92% of the variation in soil organic matter content of 10 Illinois soils could be explained by a regression equation using transformed soil reflectance i.e. absorbance data.

Dalal and Henry, 1986 simultaneously determined moisture, organic C and total N by NIR using a Infra Alyzer 500C instrument on 72 Queensland soils. Calibrations were based upon selection of the best three wavelengths in a multiple regression analysis. Their study found that the SEP to be greater for coarsely ground soils (> 2mm) than finely ground soil (<0.25mm). Their study found that NIR spectrum of soils has a wide range in absorbance. The visual differences in the absorbance in NIR spectrum were mainly due to moisture in the soils. The spectra of soil containing different C and N concentrations showed only small differences in absorbance but C and N concentrations could be reliably predicted in soils. It is imperative for NIR determinations that particle sizes are similar. The technique would be less reliable if soils with a wide range of particle sizes are used in a calibration.

Meyer, 1989 of Natal, South Africa, was able to simultaneously determine soil organic matter, total soil N, N mineralization rating (4 point scale) and Texture for South African soils using Technicon 300, 400 and 450 series instruments.

Ben-Dor and Banin, 1990 used FTNIR to measure carbonate in soils with a range of 10% - 75%. A group of 91 soils from arid-zone regions were used. Forty-three soils were used for calibration and 48 soils were used to test the prediction. Standard error of prediction (SEP) were similar to standard error of cross validation (SECV) with values of 7.9% and 5.9%, respectively.

Morra *et al.,* 1991 obtained $r^2$ (SEP) values of 0.93 (0.6%) and 0.89 (0.06%) for total C and N respectively in coarse clay and silt fractions of soil.

Krischenko *et al*., 1992 found that soil spectra are dependent on the mineral composition. Their paper stated that in order to ensure accurate predictions are obtained, the NIR instrument should only be calibrated on soils of the same type. Soils were obtained from Moscow and Stavropol regions of USSR and from middle Asia. The soil spectra from these different regions were very similar even though they were formed under different climatic and geological conditions. They found that the absorption spectra of soils decreased from 1100-1800 nm and then increased sharply from 2000-2500 nm, with the main difference between the spectra of soils studied was the level of background absorption. An NIRSystems models 6500 and 4500 were used for their study. They found that NIR gave the same results as the chemical methods for many of the tests in the study. They obtained calibrations of $r^2$ (SEP) for OM, 0.95 (0.26 %); TC 0.94 (0.08 %); Humic acid, 0.95 (0.03 %) and Fulvic acid, 0.63 (0.06 %). Determination of some soil fertility parameters yielded results for pH, 0.65 (0.34); exchangeable Ca, 0.89 (1.05); exchangeable Mg, 0.81 (0.35); sum of absorbed bases 0.91,(1.33); TN, 0.93 (0.03 %); mineral nitrogen ($NO_3$ and $NH_4$), 0.48 (12.8 ppm); available phosphorus, 0.42 (145 ppm) and available potassium, 0.83 (38.6 ppm).

Matsunanga and Uwasawa, 1992 obtained correlation coefficients > 0.9 for moisture content, bulk density, TC, TN, CEC and phosphate sorption coefficient. They obtained correlation coefficients <0.7 for pH, available P, and exchangeable Ca, Mg, and K.

Henderson *et al.,* 1992 found that although bands in the visible region gave a better correlation with soil organic C there was significant interference from Fe and Mn oxides. They concluded that the best correlation for soils derived from different parent materials was found with middle IR bands and obtained a correlation coefficient (r) of 0.964.

Suddith and Hummel, 1993 used a portable NIR instrument with a wavelength range of 1670-2630 to measure OC, CEC and moisture content for 30 Illinois soils. Calibrations yielded $r^2$ (SEP) of 0.89(0.23%), 0.86(3.59 mEq/100g) and 0.97 (1.59%) for the above tests respectively.

Fox *et al.*, 1993 compared NIR and other soil N availability quick tests for corn. The work indicated that NIR was able to predict corn response to N fertiliser in Pennsylvania. The prediction was as good as or even better than the then current method and was an attractive alternative because NIR was rapid and cheap. Measurements were made on a 6500 NIRSystems spectrometer with reflectance measurements obtained between 400-2500 nm.

### 2.3.3 1994-current

Ben-Dor and Banin (1995) studied NIR using 91 soil samples from Israel. These 91 soil samples represented 12 groups of Israel soils which covered the Arid and semi arid climate zones of Israel. The samples were measured on a FTIR spectrometer (alpha centarui madson). They looked at ten soil constituents total iron ($Fe_2\ O_2$ ), aluminium ($A1_2O_2$) silica ($SIO_2$) , potassium ($K_2O$) and phosphorous ($P_2O_5$) loss on ignition residual (LOI), free iron oxides (Fed), aggregate size (1.5-2mm) fraction (F1), average aggregate size (mm; AVGR) and sodium adsorption percentages (CNaP) which were measured by routine methods employed in soil laboratories. They concluded that NIR was very promising for rapid and non-destructive analysis of soil. The calibration performance of $r^2$ (SEP) for measured tests for their study is $SiO_2$, $r^2 = 0.82$ ( 11.19%); LOI, $r^2 = 0.85$ (4.03 %); FI, $r^2 = 0.65$ (3.77 %); Fed, $r^2 = 0.62$ (2789 ppm); $Al_2O_3$, $r^2 = 0.66$ (1.77 %); $Fe_2O_3$, $r^2 = 0.55$ (1.18 %) and AVGR, $r^2 = 0.60$ (0.11 mm). In the same year they obtained calibration performances of $r^2$ (SEP) for clay content $r^2 = 0.76$ (8.6%) CEC $r^2 = 0.82$ (6.72 $cmol_c\ kg^{-1}$) OM $r^2 = 0.69$ (1.63%) and $CaCO_3$ $r^2 = 0.70$ (12.9%) for 91 soil samples that represented 12 soil groups of Israel. These soils were air dried and passed through a 2 mm sieve (Ben-Dor and Banin, 1995 b). They had a calibration set of 35 samples and a validation set of 56 samples. The $r^2$ and SEC and SEP were very similar for calibration and validation sets.

Stenberg *et al.*, 1995 evaluated NIR for the determination of clay content, soil organic matter, cation exchange capacity and base saturation. They used 146 air dried samples from cultivated areas of Sweden. They estimated that NIR analysis could reduce costs by up to 70% compared to wet chemistry.

Malley *et al.*, 1996 used NIR to predict OC, N and P in fresh water sediments in Canada. The samples were dried at 104 $^0$C and passed through 150 micron mesh. The 90 samples in the study were scanned over wavelength 1100-2498 nm using NIRSystems 6500 spectrometer. They found that high $r^2$(SEP) values could be obtained for organic C $r^2 = 0.99$ (3.95 mg $g^{-1}$), N $r^2 = 0.99$ (0.508 mg $g^{-1}$) and for P $r^2 = 0.97$ (0.069 mg $g^{-1}$). They concluded that NIR has the capacity to predict the above parameters in the range encountered in fresh water sediments.

Couillard *et al.,* 1997 scanned 96 undisturbed, dried and ground (62mm) turf soil profiles with a NIRSystem 6500 from 400-2500nm. Tests looked at included moisture content, OM, bulk density, sand, silt, clay, available P, exchangeable Mg, Ca and K, TN pH, CEC and TC. The predictions of the above tests performed better on the undisturbed samples than the dried and ground. Calibration performance of $r^2$ (SEC) for the undisturbed turf samples for tests were moisture $r^2 = 0.92$ (2.43 mg $g^{-1}$), OM $r^2 = 0.90$ (0.57 mg $g^{-1}$), bulk density $r^2 = 0.80$ (0.11 g $cm^{-3}$ ), sand $r^2 = 0.93$ (1.26 mg $g^{-1}$), silt $r^2 = 0.92$ (1.16 mg $g^{-1}$), clay $r^2 = 0.77$ (0.42 mg $g^{-1}$), pH $r^2 = 0.82$ (0.12), P $r^2 = 0.82$ (18.94 kg $ha^{-1}$), K $r^2 = 0.86$ (0.15 cmol $kg^{-1}$), Mg $r^2 = 0.50$

(0.34 cmol kg$^{-1}$), Ca $r^2$= 0.42 (3.44 cmol kg$^{-1}$), CEC $r^2$ = 0.28 (3.07 cmol kg$^{-1}$), TN $r^2$ = 0.37 (0.04 %) and TC $r^2$ = 0.28 (1.06 %).

Biological decomposition process was monitored by Ben-Dor *et al* (1997) using NIR (400-2500nm). They noted that the NIR region was very sensitive to slight changes and were able to pick up subtle changes to OM during the composting cycle.

A study of NIR on soil contaminated by oil and fuel was carried out by Zwanziger and Forster (1998). They used a Bruins Omega 20 spectrometer with a wavelength range of 800-2700 nm. The study indicated that soils spiked with the above contaminants could be predicted well using NIR. Particle size fractions influence predictions with coarse fractions (> 800$\mu$m) had SEC three times higher than medium (500-800 $\mu$m) or fine (< 500 $\mu$m) fractions.

Cho *et al.*, 1998 used eighty five soil samples of mainly paddy and upland areas of Korea to determine TN, inorganic nitrogen and available N. The samples were scanned over a wavelength range of 1100-2500 nm using Technicon InfraAylser 500. Correlation coefficients of R and (SEP) for TN R = 0.93 (0.03%), inorganic-N R = 0.87 (1.16 mg/100g) and available-N of R = 0.77 (1.1 mg/100g) were obtained. They concluded that NIR could be used to predict the above tests.

NIR was used by Peng *et al.,*1998 to determine soil moisture, OM and TN in 126 Chinese soils. The calibration and validation sets had very similar correlation coefficients (R), SECV and SEPs. For soil moisture, OM and TN they obtained the following calibration performances where R (SEC) = 0.97(1.08 %), 0.94(0.23 %) and 0.94(0.04 %) respectively. The study found that the NIR predicted results were very similar to the results obtained by wet chemistry. Calibration performance was slightly better for the <0.25 mm fraction soil than for the < 1mm soil fraction.

Seven different soil characteristics using NIR were studied by Salgo *et al.*, 1998 on 108 Hungarian soils. The tests studied were humus, calcium carbonate, TN, dead water content, yarn test by Arany, mechanical composition and hygroscopic water content. The humus content was accurately predicted by NIR (SEP = 0.3 %). Mechanical compostion and hygroscopicity showed significant correlation with the water content in soils with acceptable

NIR accuracies obtained for the two tests. The other four tests were not predicted well and were attributed to lack of spectroscopic information or to the poor quality of reference methods.

Meyer, 1998 of South Africa used an NIRSystems 6500 instrument to measure air dried topsoil samples (<0.25mm fraction), representing 20 forms of varying organic matter, TN, clay, silt, sand and fertility status. Measurements of OM content, total N, clay, silt and sand fractions were determined. He stated in this work that preliminary results suggested that NIR could provide acceptable calibrations for determining soil pH, N status, CEC and P fixation. This paper was presented in 1998 and gave an overview of the NIR work done in South African sugar industry. In their work they obtained N mineralisation potential where a score of 1-4 was given and obtained accalibration where $r = 0.86$ and a $SEC = 0.3$. For TN, OC and sand fraction calibration performance of r (SEC) of 0.9(0.01%), 0.92(0.46 %) and 0.94(3.8%) were achieved respectively.

A feasibility study by Malley and Currie, 1999 on the rapid analysis of available N and P in hog manure using NIR showed that calibrations for soil N achieved $r^2 = 0.9$ for both field moist and air dried soil. Tests such as nitrate N, ammonium M, available P, sulphate S, K, Na and Ca and Mg were also determined on both soil and hog manure. Calibrations were superior for hog manure tests with respect to the tests measured on soil.

The feasibility of using NIR analysis for the determination of C, N, P and calcium carbonate was determined by Malley *et al.*, 1999. Sediment cores were obtained from a German Lake in 1993. The cores, sliced into 1 or 2 cm thick slices, were freeze dried and scanned without sample grinding over wavelength range of 1100-2500 nm using a NIRSystems 6500 spectrometer. Correlation coefficients $r^2$ and (SEP) of 0.93 (7.0 mg $g^{-1}$ ) for C, 0.81 (3.8 mg $g^{-1}$) for carbonate, 0.94 (0.7 mg $g^{-1}$) for N, 0.99 (0.16 mg $g^{-1}$) for P were achieved. The study indicated that the prediction of TC, Ca carbonate, N and P by NIR was feasible in soil cores that reflected varied water quality history. The authors concluded that the study samples came from one lake. For practical analytical purposes, samples from many lakes would need to be collected and calibrations developed for NIR to be useful.

Ehsani *et al.,* 1999 study looked at soil mineral content from two types of soils a Yolo loam and Capay clay from California, USA. They looked at the nitrate-N content in soils spiked with nitrate N. The concentration range of nitrate in the soil was between 0 and approximately 110 ppm. They obtained calibrations equations with correlation coefficients greater than 0.9 with SEP of between 2-5 ppm. They used the wavelength range of 1800-2300 nm to determine the nitrate content in soil. They concluded that calibrations will work as long as soil samples used for prediction purposes came from the same location as calibrations samples. They also stated the calibration would fail if the prediction set includes interfering chemical(s) which were not part of the original calibration set.

The amount of N taken up in plant parts during the growing season using initial soil N, a soil incubation method, soil OM via NIR predictions were studied by Borjesson *et al.*, 1999. Soil samples were from 15 plots cropped with winter wheat on a farm in south-western Sweden. All methods predicted crop uptake of N well. The results from NIR predictions were as good as the results obtained from the best traditional method used for predicting crop N which is initial soil nitrate-N. They found that wavelenghts around 1400 and 1700 nm and above 2000 nm coincided with the wavelengths to be important for the prediction of soil OM and other soil components influencing mineralization.

The feasibility of using NIR to determine N and C mineralization rates in dairy manures was studied by Reeves *et al.*, 1999. Manure was incubated with soil for various time periods and scanned using NIR between wavelengths 1100-2500 nm. Calibrations for ammonia-N, nitrate-N and ammonia + nitrate (total inorganic N) were developed. They used 593 samples from several mineralization experiments for this study. They concluded that NIR had the potential for analyzing manure-amended and non-amended soils from mineralization experiments.

The feasibility of using NIR was investigated for the analysis of pH, electrical conductivity (EC), P, S, Ca, Mg, Na, K, Fe and Mn in 28 Canadian soil samples by Malley *et al.*, 1999. Field moist soil samples were scanned for pH and EC, and air dried samples were scanned for the rest of the tests. The NIR-predictions were highly correlated with traditional wet chemistry (r2>0.9) for P, Ca, Mg, K, Fe, and Mn, and almost as highly correlated ($r^2$>0.8) for

S and Na and pH. The study concluded that elemental concentrations in dry soils may be analysed routinely using NIR.

Reeves *et al.,* 1999 obtained 179 soil samples from Maryland, USA for their NIR study. The samples were passed through a 4 mm sieve. Total C and N were determined on samples dried at 105 $^0$C. Mineralisable N as soil N mineralised during a 21 day aerobic incubation at 25 $^0$C was determined. The soil pH with a water to soil ratio of 2:1 was also determined. Samples were scanned using NIRSystems 6250 (1100-2500 nm) on finely ground soil. Correlation coefficients ($R^2$) for C, N, mineralisable N and pH were 0.95, 0.95, 0.08 and 0.80 respectively. Their work showed that NIR could measure total C and N successfully but had variable success with pH and could not measure mineralisible N based on a 21 day incubation period under aerobic conditions. Their work showed that differences in soil were not a problem in developing accurate calibrations but this did not mean that location is irrelevant. They showed that calibrations obtained from one location can be used to determine samples from another location with outlier predictions attributed to soil location differences. In addition, a likely source of prediction errors could have been slight differences in composition of organic matter contributed by different crops grown and due to the soil temperature and rainfall differences.

Biolgical activity in agricultural soils using NIR was investigated by Reeves *et al.*, 2000 for the above 179 soil samples obtained from two locations from experimental plots. Biological activity as measured by four enzymes (dehydrogenase, phosphatase, arylsulfatase and urease) and nitrification potential was determined. Their work showed that NIR is capable of determining biological activity as reflected by the four enzymes. Correlation coefficients as high as $R^2 = 0.8$ were obtained. On the same sample set TC and TN using NIR were found to give superior correlation coefficients and lower prediction errors. Discrimination into high, medium and low activity values were not successful. Correlation analysis indicated that measures of biologically-active nitrogen might be the basis for these determinations. They concluded that NIR might be of use where rapid determination and in cases where extreme accuracy are not required.

Swelling clays such as smectites can cause structural damage to buildings unlike clay minerals such as Illites and Kaolinite that do not swell significantly. Clay minerals are often found in differing mixes in the soil and therefore have varying soil swelling capability. NIR was used by Goetz *et al.,* 2001 to look at the application of determining these clay minerals in soils using a portable field spectrometer. The study showed that smectite content with a SECV error of 10% was possible. They found that loadings showed that 1800-2000 and 2150-2250 nm regions contained the most relevant information for the detection and quantification of smectites content. These above two regions corresponded to the bound water in the clay lattice interlayer and Al-OH combination bands respectively.

Confalonieri *et al.*, 2001 looked at the potential of NIR in determining TC, TN, exchangeable K and available P for 142 soil samples obtained from Northern Italy. Samples were taken to a depth of 300 mm, dried, sieved and passed through a 2 mm sieve. These were scanned via NIRSystems 5000 spectrophotometer between wavelengths of 1100 and 2500 nm. They found that TC and TN could be determined with good accuracy. Calibration performances of $r^2$ (SECV) for TN and TC were 0.85 (0.01%) and 0.87 (0.06%) respectively. Results with exchangeable K were less successful and mainly used for providing good separation of samples into groups. The study indicated that for available P the NIR technique seemed useful for only giving a rough estimate of the available P value. Calibration performances of $r^2$ (SECV) for exchangeable K and available P were 0.57 (6.8 ppm) and 0.72 (6.7 ppm) respectively. Wet chemistry base tests for available P and exchangeable K were separately determined by the Olsen P and 1.0 M ammonium acetate methods.

Thirty three chemical, physical and biochemical properties were studied for 802 soil samples collected from 4 major land resource areas in the US by Chang *et.al.*, 2001. Spectral reflectance of soil samples were measured on an NIRSystems 6500 instrument where air dried soil was packed into quartz cells. Spectra were recorded between 400-2500 nm. To evaluate the application of NIR for soil testing under more realistic and practical applications the <8mm sieved soil fraction samples were analysed. The 2mm sieved soil fraction was also analysed. Total C, TN, moisture, CEC, water content, basal respiration, sand, silt, Mehlich III extractable Ca were successfully predicted by NIR ($r^2 > 0.80$). The Study also found some Mehlich III extractable metals (Fe, K, Mg and Mn) and exchangeable cations (Ca, Mg and K), sum of exchangeable bases, acidity, clay, potentially mineralisable N, total respiration rate, biomass C and pH were also estimated but with less accuracy ($r^2 = 0.8\text{-}0.50$). The study also found that Mehlich III extractable Cu, P, Zn and exchangeable Na could not be predicted ($r^2$ <0.50).

Combination of organic matter and soil using NIR was studied by Fidencio *et al.*, 2002. For their study they collected two different types of soils (oxisol and ultisol). Soil samples were collected from different depths with the end result being 100 soil samples with different organic matter content. Soil samples were dried at 40 $^0$C and passed through a <2mm sieve. Spectral measurements made from 1000-2500 nm were recorded on a Cary 5G spectrometer. These samples were from Brazil, with a OM concentration range of 0.4-4.8%. They accomplished correlation coefficients R=0.95 with a SEP of 0.2%.

Reeves *et al.*, 2002 investigated the use of NIR and Mid-IR for the determination of carbon in soils. The study focussed on four sets of samples collected in the USA. Samples were analysed on a NIRSystems model 6500. Scans were taken between 400-2500 nm. Results indicated that OC and possibly inorganic C can be measured by NIR fairly rapidly and accurately. They concluded that NIR is more advanced in terms of sampling options and understanding the effects of particle size and moisture on calibrations. They found out, though, that Mid-IR appears to offer greater accuracy for the determination of C in soils particularly as the soil sample diversity increased.

The nutrient content in hog manure amended soils and hog manure by use of NIR was studied by Malley *et al.*, 2002. Both field moist and air dried soil samples were measured using NIR. The samples were collected from Winnipeg, Canada. The study found for field moist soil correlation coefficients ($r^2$) for N, OM, Mg and moisture content was >0.84 and for sulphate-S was 0.7. For dry soils the results were similar for N but better for Mg, sulphate-S, Ca and K. Samples were analysed on a Foss NIRSystems 6500 spectrometer with spectra recorded between 400-2500nm.

Martin *et al.*, 2002 used NIR for the analyis of OC and organic N in the A horizon of soils within a single field in Manitoba, Canada. Useful calibrations for C were developed where 75-80% of the variations were accounted for when the range of C was between 0-4.0 %. These were improved to 80% when calibrations were developed for OC in the range of 0-2.0

%. A calibration for organic N proved unsuccessful with only 30% of the variation accounted for by the model.

Chang and Laird (2002) evaluated the ability of NIR to measure OC, inorganic C and TN content of 108 soil samples. The samples were collected from Iowa and Minnesota, USA. The samples were prepared by mixing soil with calcium carbonate, humic acid and composite materials. Tests measured were OC, inorganic C, TC, TN, C:N ratio and organic C:N ratio. Soil samples were crushed in a motar and dried in an oven at $105^0$C. A total of 108 samples were used for this work and spectra were obtained between 400-2500 nm using the NIRSystems 6500 spectrometer. All tests had $r^2 > 0.86$ for calibration sets. Similar results were obtained for the analysis of the validation set where $r^2 > 0.85$ was achieved.

Organic carbon, TN and pH were measured on 332 soil samples obtained from different regions of Uruguay, South America by Moron and Cozzolinio *et al.,* 2002. Two hundred of the samples were randomly selected to develop the calibrations while the remaining 132 were used to validate it. Samples were scanned on a Foss NIRSystems 6500 spectrometer. Samples were scanned between 400-2500 nm. Samples were obtained down to a depth of 150 mm. Soil samples were dried at 40 $^0$C overnight and crushed and passed through a 2mm sieve. Correlation coefficient $r^2$ and (SECV) of 0.94 (0.19%) for OC, 0.91 (0.02%) for TN and 0.93 (0.18) for pH were achieved by the study. The correlation coefficient for the validation set was lower than for the calibration set with SEPs twice that of SECVs for all three tests.

Eighty top and sub soil samples were collected from 40 grassland field trials distributed within three agricultural regions in Norway by Fystro (2002). NIR calibrations were obtained for OC, TN and potential mineralisation using the 80 grassland soil samples. Calibrations with $r^2 > 0.8$ were achieved for both OC and TN, with SEP of 5.7 g C $kg^{-1}$ and 0.497 g N $kg^{-1}$ achieved for each. The study found that moist samples were predicted more accurately than dried samples with no benefit gained from grinding dry samples.

Dunn *et al.*, 2002 looked at the potential of NIR for soil analysis from soils obtained from the Riverine Plain of South Australia. Over 550 top soils to a depth of 100 mm and 300 sub soils to a depth of between 400 and 500mm were air dried and ground before scanning using a NIRSystems 6500 spectrometer. They found that NIR was able to successfully determine other soil properties in both top and sub soils. In the top soil CEC, exchangeable Ca and Mg, and pH were able to be measured with a high level of accuracy. It was found that OC and exchangeable Na were predicted with an acceptable level of accuracy. In the sub-soil, CEC, exchangeable Na, Ca, Mg and pH were all predicted with a high level of accuracy.

Chodak *et al.,* 2002 measured the organic levels of forest soils using NIR. They measured several chemical biological properties of the organic layers in spruce, beech and mixed spruce and beech stands. Four hundred and six samples were collected from forest soils from Solling, Germany. The humus samples were analysed for C, N, P, S, Na, K, Ca, Mg, Mn, Fe and Al. NIR predicted the contents of C, N, P, S, Na, Ca, K, Fe and Al well with regression coefficients of $r > 0.9$. Measurements were made on dried material using Foss NIRSystems spectrometer with a wavelength range of 400-2500 nm.

Clay and soil OM content of a sample set consisting of 2750 top-soils which represented all Swedish agricultural area was studied by Stenberg *et al.,* 2002 using NIR. All soils were air dried, crushed and passed through a 2mm sieve. Measurements were made between 1100-2500 nm using a Bran and Lubbe InfraAnalyser 500 spectrometer. A global clay calibration had a $r^2 = 0.85$ with an RMSEP = 5.6%. The range of clay content in the soils was 0 to approximately 70%. The performance of the models were improved when six regional models consisting of adjacent districts were calibrated $r^2=0.9$ for wet and an RMSEP = 3.9% was achieved. A global model for soil organic matter did not perform satisfactorily and therefore division of Swedish farm sites into regional classes (as done for clay content) did not improve the results. They found that if smaller data sets for single fields or field experiments were used that soil OM could be better predicted if the models were restricted to soils with a fairly high clay content. It was found that the performance of the calibration increased with increasing clay content.

Evaluation of total P, Bray P, Olsen P and Truog P using NIR reflectance was made by Ryu *et al.*, 2002. One hundred and forty eight soils with a wide range of soil characteristics were collected from paddy, upland and orchard areas of Kyong book province in Korea. The soil samples were air dried and passed through a 2 mm sieve. NIR measurements were made on a Foss 5000 with a wavelength range of 1100-2500 nm. Separate correlation coefficient of $R = 0.91$, 0.82, 0.80 and 0.72 were obtained for the above tests. Standard error of prediction (SEP) were very high for all four tests. Therefore they will not be of any use for analytical purposes particularly in New Zealand.

Mid-infrared (MIR) and NIR for soil C measurement was looked at by McCarty *et.al.*, 2002. Two hundred and seventy three samples were collected from 14 geographically diverse locations from the central United States. Mid-infrared analysis was measured using a FT spectrometer with wavelength range of 2500-25000 nm. NIR spectra were obtained using a NIRSystems 6500 instrument with wavelength range 1100-2500 nm. Samples were air dried and ground to pass through a 180 micron mesh. Comparison between MIR and NIR in measuring TC and inorganic C showed that MIR calibrations performed significantly better than those of NIR. The SEPs for MIR were found to be approximately half that of NIR. They concluded that there was strong evidence that MIR spectra contained better information related to soil C than for NIR.

Ludwig *et al.*, 2002 looked at 120 soil samples which were collected from two mountain ash sites in Victoria, Australia, after 10 years of forest harvesting. The soil samples were collected to a depth of 300 mm and were air dried and ground prior to analysis. Samples were analysed for TC, TN, microbial C and N, available P and N content in salt solutions. The 120 samples were scanned using a Foss NIRSystems 6500 spectrometer with wavelength range 400-2500 nm. Calibrations yielded correlation coefficients (r) = 0.97 for TC, 0.94 for TN, 0.69 for Bray P and 0.73 for Olsen P. Bray P and Olsen P had SEPs of 1.6 mg kg$^{-1}$ and 1.0 mg kg$^{-1}$ each. These are fairly low SEPs but the P range for the sample set was between 0.1-9.0 mg kg$^{-1}$. This range is very narrow and extremely low when compared to normal levels encountered in agriculture.

Reflectant measurements were made on 1000 top soils from central Africa by Shepherd and Walsh (2002). The samples included soils from Malawi, Kenya, Rwanda, Tanzania, Uganda, Zambia and Zimbabwe. These samples were taken from a variety of landscape positions, parent materials and land use. The soils were air-dried and passed through a 2 mm sieve. Reflectant measurements were made using a FieldSpec spectrometer with a wavelength range of 350-2500 nm. Validation $r^2$ for exchangeable Ca, CEC, exchangeable Mg, organic C and clay content was >0.8. Sand content and soil pH had $r^2$ between 0.7 and 0.8.

Russell *et al.*, 2002 looked at the potential of NIR to predict nitrogen mineralisation in rice soils in the Southern region of Australia. Soils to a depth of 100 mm were sampled from 25 farms throughout the rice growing region of South Australia. Then the soil was air dried and crushed and passed through a 2 mm sieve. The soil samples were scanned using a 6500 NIRSystems instrument with a wavelength range of 400-2500 nm. They obtained a calibration with r = 0.89 for mineralisable-N and SECV = 16 mg N kg$^{-1}$. The data had a range of between 50-175 mg N kg$^{-1}$.

Use of 228 Japanese soil samples which represented 7 soil groups were used by Ootake *et al.*, 2000 to study the non-linearity of soil calibrations. The soils were air dried and the 2 mm fraction used. A Bran-Luebbe InfraAlyzer 500 with a wavelength range 1100-2500 nm was used to collect spectra. The constituents measured were TN, TC, CEC and phosphate sorption coefficient (PSC). They postulated that the difficulty in developing calibrations which could be used for any sample/site prediction is due to the non-linearity of soil calibrations. The non-linearity was attributed to soils from different groups having varied characteristics. They developed calibration equations separately for each soil group. This improved calibration performance for some soil groups. It was also found where non-lineraity was not a problem for some soil groups; the groups could be bulked together and robust calibration obtained with better performance than if the groups were treated separately.

Soil chemical properties from different location of SW Germany were evaluated by Udelhoven *et al.*, 2003. One hundred and sixty five soils samples were collected between 150-300 mm depth. These samples were air dried and sifted through 2mm sieve before being scanned by a ASD FieldSpec II spectrometer. Spectral readings were made between 400-2500 nm. Reliable estimations were obtained for total amounts of Ca, Mg, Fe, Mn and K. Estimations of organic C and TN were less successful. Extracable K, Mg and P were not satisfactorily estimated.

NIR assessment of soil Cd and Zn contamination in river flood plains in the Netherlands was investigated by Kooistra *et al.*, 2003. Soil samples were dried at 40°C and sifted through a 2 mm sieve. The samples were scanned via NIRSystems 6500 instrument with wavelength range of 400-2500 nm. Calibration statistics for Cd were r=0.94 and RMSECV=0.68 mg kg$^{-1}$. Likewise for Zn they were r=0.95 and RMSECV=81 mg kg$^{-1}$.

The feasibility of measuring NIR measurements in a field was assessed by Christy *et al.*, 2003 in Iowa, USA. One hundred and forty soil samples were used for the study. Calibrations were developed for TC, TN, moisture and pH. For the calibrations they obtained $r^2$ and (RMSEP) each of 0.87 (0.45%), 0.86 (0.03%), 0.82 (3.0%) and 0.72 (0.46) for the above tests.

Determination of OM fractions in coniferous forest soils were studied using NIR by Couteaux *et al*, 2003. The objective of their work was to assess the usefulness of NIR in determining biological fractions of C and N in soils. The 200 soil samples were from forests in Sweden and south France. The samples were air dried and passed through a 1 mm sieve before being analysed on NIRsystems 6500 spectrometer with wavelength range 400-2500 nm. Tests evaluated were TC, TN, ammonium-N, mineral-N, Biomass-C and BiomassN. Correlation coefficients and (SEP) of 0.99(1.6%), 0.99(0.08%), 0.84(31 mg $kg^{-1}$), 0.80(38 mg $kg^{-1}$), 0.96(0.55 g $kg^{-1}$) and 0.97(25 mg $kg^{-1}$) were achieved respectively. They concluded that NIR is useful in determining TC, TN, labile N and C, biomass C and N. They also noted that NIR is able to pick up analytical errors and predictive performances can be due to laboratory error rather than a genuine lack of prediction by NIR.

Dematte *et al.*, 2003 studied the change in reflectance from addition of fertilisers to Brazilian soils. The soils were dried at 45 °C and passed through a 2 mm sieve. The samples were placed in Petri dishes and scanned using an Iris spectrometer with a wavelength range 400-2500 nm. The study indicated addition of fertiliser to soils resulted in changes in reflectance intensity but did not change the original absorption features of the soils. Liming of soil increased the spectral reflectance between 700-2500 nm and application of OM resulted in a decrease in reflectance intensity between 600-2500 nm. Their study indicated that it was possible to measure Ca and Mg contents in soil using NIR.

Russell, 2003 studied the effects of different sample preparation techniques for TC, TN and mineraliseable-N for soils from the Riverine plain of south-eastern Australia. There were seven soil preparations which included treatments of 2 mm fraction, fine grinding using puck and ring grinder, pure mineral samples (elimination of OM) and scanning samples through plastic bags. The finely ground soils gave an absorption spectrum noticeably lower and of slightly different pattern than the 2 mm fraction. Fine grinding of soil had little effect on SEP for TC, TN and mineraliseable-N when compared to the 2 mm fraction. Soils scanned through plastic bags gave slightly better prediction for mineraliseable-N but more error for TC and TN (>35%). The study found that different soil preparations influenced soil spectra and calibration success. High correlation between TC and TN suggested that NIR calibrations for the two parameters utilised absorptions at common wavelengths. The study also noted that TC and TN correlated well with mineraliseable-N. This is an indication that mineraliseable-N predictions are strongly influenced by specific information of the above two properties.

Three hundred and thirty three agricultural soils from Uruguay were used by Moron and Cozzolino (2003) to study the content of silt, clay, sand, Fe, Cu, Mn and Zn using NIR. The samples were collected to a depth of 150 mm and dried and ground to <2 mm before analysed on a NIRSystems spectrometer with a wavelength range of 400-2500 nm. They obtained coefficient of determinations and (SEC) for sand, silt, clay, Cu, Fe, Mn and Zn of 0.81(5.1%), 0.83(5.3%), 0.92(2.6%), 0.87(0.7 mg kg$^{-1}$), 0.92(21.7 mg kg$^{-1}$), 0.72 (83.0 mg kg$^{-1}$) and 0.72 (1.2 mg kg$^{-1}$) for respective samples. Their study indicated that NIR had the potential to determine soil texture , Fe, Cu and Zn on a routine basis.

Islam *et al.*, 2003 collected 161 soils representing 11 of the 14 soil orders of the Australian classification system to study several soil properties using NIR. One hundred and forty tree samples were from NSW and the other 18 sample were from Queensland district. Samples were dried at 40 $^{0}$C and passed through 2mm sieve before being scanned using a Cary 500 spectrometer with a wavelength range of 250-2500 nm. Their results showed that pH, air dried water content, OC, clay, CEC, exchangeable Ca and Mg could be reasonably ($r^2$ >0.7) predicted by NIR.

A study by Confalonieri and Odoardi, 2003 on Italian cropping soils indicated that NIR could, with good accuracy, determine TC and TN but exchangeable K and available P were not as successful via NIR. One hundred and forty two air dried soils were scanned using a Foss NIRSystems 5000 instrument. They obtained $r^2$ and (SECV) using stepwise regression of 0.87(0.06%), 0.85(0.01%), 0.57(6.8 mg kg$^{-1}$) and 0.72(6.7 mg kg$^{-1}$) for the above tests respectively.

van Groenigen *et al.*, 2003 assessed the potential of NIR and diffuse reflectance Fourier transformed mid-infrared spectrometry for predicting crop and soil parameters in a California rice field. Soil samples taken from the upper 100 mm in spring were dried at 65 °C and milled in a Wiley mill. Tests studied were TC, TN, mineralizable N, Olsen P, CEC and exchangeable cations (Ca, Mg, Na and K), as well as yield and N uptake. PLS was used for calibration development. For soil, predictions for CEC, Ca and Mg were the most accurate with $r^2$ (RMSEP) = of 0.83(1.4 cmol $kg^{-1}$), 0.80(0.66 cmol $kg^{-1}$) and 0.90(0.69 cmol $kg^{-1}$) for NIR and $r^2$= 0.56 (2.1 cmol $kg^{-1}$) , 0.60 (0.93 cmol $kg^{-1}$) and 0.61(1.0 cmol $kg^{-1}$) for FT-MIR. Correlation coefficient and (RMSEP) for NIR and FT-MIR for Olsen P were 0.71(1.6 mg $kg^{1}$) and 0.55 (1.9 mg $kg^{-1}$) and for mineralizable N 0.46 (0.03 mg $kg^{-1}$) and 0.21(0.04 mg $kg^{-1}$)in each case. They found no significant correlations for total soil C or N. For their study they stated that standard errors of prediction were lower than reported in the literature. The reason for this could be the small range of variability found within a single field.

## 2.4 Plant Analysis

### 2.4.1 Summary

Some of the early NIR work were applications related to feed quality of forages and grains with numerous studies carried out on these applications. Tests included protein content, ADF, ash and moisture. Currently feed quality of forages and grains are routinely analysed by commercial labs for the above tests. This study will not cover feed quality of forages and grains.

The focus is on evaluating NIR capability in determining elemental composition of plant materials. Also, the study focuses on the toxic parameter nitrate-N which is harmful to animals. A review of the NIR literature on plant analysis studies suggests that:

- the measurement of N with a high degree of accuracy comparable to wet chemistry is possible.
- the measurement of P, K, Mg, Ca and S (the major elements) is possible.
- the measurement of minor elements Mn, Fe, Cu, B, Mo, Se, Zn and Co will not be possible where these elements exist at normal plant concentrations.
- there are no absorption bands for minerals, ionic forms and salts in the NIR region, but detection of organic complexes and chelates is possible.

### 2.4.2 Major and minor elements

Shenk *et al.*, 1981 analysed forages of diverse species and growth stage obtained from many locations. The study used a scanning monochromatic NIR instrument. They reported standard errors for Ca, P and K of 0.16%, 0.04% and 0.37% respectively. The precision of the NIR determined samples was better than the laboratory results for most of the tests. Shenk *et al* 1981 on NIR study on forage and grain stated that an unknown sample can only be predicted with certainty when:

- its NIR spectrum is similar to that of the calibration set.
- the quality of the laboratory measurements should be excellent.
- precise NIR measurements must be made.
- appropriate transformations are applied to NIR data.
- wavelengths chosen are useful for the entire populations studied.

In choosing wavelengths which fitted the calibrating sample well there is always the danger of not accurately predicting unknown samples. They found this to be the case for 45 wheat samples they studied.

The measurement of nitrogen content in cured tobacco lamina samples was carried out by Rosa and Pandeya, 1981. The samples were obtained from manufacturing companies, farms, markets and genetic experiments. Therefore, they had a wide range in constituent variability. Yet they obtained $r^2 = 0.76$ for nitrogen. Near infrared spectroscopy was able to detect many inaccuracies in laboratory wet chemistry values.

Nitrogen, P and S content in samples of Trifolium in natural grassland using NIR was measured by Ciudad *et al.*, 1983. They obtained correlation coefficient and (SEP) 0.87 (0.16), 0.69 (0.02) and 0.67 (0.02) each for the three elements.

McClure, 1984 measured B, Ca, Cl, Cu, Fe, Mg, Mn, N-$N0_3$ N, P, K, Na, S and Zn in freeze dried tobacco leaves. He obtained $R^2 > 0.89$ for all that's measured. The calibrations were not validated. He did comment that in their North Caroline State University Lab, if the coefficient of variation is less than 10%, the calibration has some validity.

The measurement of Ca and P using NIR on 82 samples consisting legumes, grasses and legume/grass mixtures were studied by Redshaw *et al.*, 1986. They selected certain wavelengths to predict chemical parameters. For Ca the wavelength in order of importance were found to be 1958, 2018, 1258, 2458, 1438, 1378 and 2138mm respectively. For P, the wavelengths in order of importance were 2098, 1338, 1538, 2258 and 1258 mm respectively. For moisture they were 1948, 2228, 1928 and 1888 respectively. They obtained calibration statistics of $R^2$(SEP), for moisture 0.90 (0.2), Ca 0.87 (0.15) and P 0.71 (0.02).

Clark *et al.*, 1987 studied NIR ability to determine concentrations of Na, K, Ca, P, Mg, Fe, Mn, Cu and Zn in three forages (alfalfa, wheat grass and tall fescue). They found that the major elements Ca, P, K and Mg could be accurately measured by NIR. The minor elements and Na were not accurately predicted. The study showed that NIR was indirectly measuring Ca, Mg and K by their association with organic molecules such as chlorophyll.

The measurement of elements N, P, K, Nn and Mg using NIR was studied by Ferri *et al.*, 1991 using forages, sunflower, heat, sugar-beet and soyabean. Individual calibrations for each species was developed. It was found that calibrations could accurately predict the major elements N, P, K, Ca and Mg but not Na.

Two hundred and fifty senescent and fresh foliage of woody plants were analysed for their nitrogen content using NIR by McLellan *et al.*, 1991. An $r^2$=0.96 with and SECV of 0.12 was obtained. Their study showed that repeated NIR measurements of the same sample set at yearly intervals over a 2-year period showed no significant drift with time (long-term storage) for N content.

Yoshikawa *et al.*, 1991 measured the concentrations of N, Mg and K in rice leaves using NIR. They obtained $r^2$ and (SEP) of 0.73 (0.38%), 0.78 (0.02%) and 0.58 (0.16%) respectively for the above elements.

A calibration model was developed by Batten *et al.*, 1991 which accounted for 96% of the N content of rice leaves. The model was validated and a SEP of 0.15% was obtained. As a result of this work a N tissue testing NIR service was established. Farmers in NSW, Australia, can now determine their N content within 1-2 days of sampling using the service. The measurement of N status in farmer's cane leaves is also routinely measured in Natal at the South African sugar experimental station where >10,000 samples are analysed annually.

The study by Smith *et al.*, 1991 showed that NIR could be used to determine Mg concentration in perennial rye grass. They obtained correlation coefficient of $r^2 = 0.68$ and an SEP of 0.02%.

The measurement of TP in 19 vegetable feedstuffs using NIR was evaluated by De Boever *et al.*, 1994. Using 238 samples with a P range of 0.22 – 1.37 % they obtained $r^2 = 0.90$ and SEP = 0.08%. The reproducibility of the wet chemistry test was found to be 0.009%.

The content of major and minor elements was evaluated by deAldana *et al.*, 1995. Their study concluded that NIR could accurately measure N in grasslands with calibration having a performance of $r^2 = 0.98$ and SEP 0.908%. Acceptable performances were obtained for Ca and Mg with $r^2$ (SEP) obtained of 0.84 (0.02) and 0.88 (0.10%). For Cu, Mn and K the models had limited success, and for P, Na, Fe and Zn the models developed were not successful in predicting the elements in grasslands. However accuracies were obtained for the minor elements and not for the major elements N, P, K, Mg and Ca. Calcium and Mg were associated with compounds in the cell wall such Ca pictate and Mg in chlorophyll. Organic acids were found to be important plant metabolics and accumulate in grass from 2-8%. For instance K malate in grass samples had been identified.

The study by Masoni *et al.,* 1996 showed that deficiency of elements Fe, S, Mg and Mn of barley, wheat, corn and sunflower leaves could be observed using NIR. It was found that for all species studied a mineral deficiency caused an increase in reflectants which was well correlated with a decrease in chlorophyll levels.

Hallet and Hornbeck, 1997 evaluated the ability of NIR to predict the elements Al, Ca, Fe, K, Mg and Mn in white pine and red oak leaves. The study found that 79-88% of the variation of folia Al, Ca, K, Mn and Mg could be explained by NIR model. NIR was not successful in predicting Fe in red oak and white pine, possibly due to the low Fe concentration encountered.

The measurement of K in grape petiodes, grape leaves, rice shoots and orange leaves by NIR was evaluated by Ciavarella and Batten (1998). Correlation coefficient of $r^2 = 0.94 – 0.99$ and SEP = 0.12-0.18% were achieved on individual calibrations for the four species studied. They found the regions of the spectrum with the strongest correlations between wave length and K levels were due to absorption by carbohydrates such as sucrose, starch and cellulose. Potassium in plant tissue existed mainly in its ionic form and therefore did not have a NIR signature. The ability, therefore, to develop an accurate K calibration must be due to the influence of K on organic constituents in the plant. Potassium, also being a major element, is found in high concentrations in the plant (0.5-6.0%).

Gillon *et al.*, 1999 measured the N and P content at different stages from living to litter of pine needles. Both individual and a global calibration (lumping several growth stages) were produced. It was found that N and P could be accurately predicted and the global calibration was just as accurate as the local calibration.

NIR was used by Ramos *et al.,* 1999 to estimate P, K, Ca and Mg in semi arid grasslands. NIR was able to predict the concentrations of the above elements with $r^2$ and (SEP) of 0.88 (0.02), 0.87 (0.17), 0.91 (0.09) and 0.08 (0.02) for the individual cases. They concluded that NIR was well suited as a quick method to determine the above elements.

The N in a diverse group of cereal products was accurately predicted using NIR by Kays *et al.*, 2000. A total of 222 samples were used in the study which had a range of 0.41-3.31% N. The standard of the laboratory determination was calculated as 0.034% N. The $r^2$ for calibration and (SEP) was 0.97 (0.09%).

Rodriquez and Miller, 2000 obtained $r^2 = 0.92$ for N content in two dwarf type Bermuda grasses using NIR. The measurement of K, Ca, Mg, Fe, Zn, Mn and Cu were not successful with $r^2 < 0.50$ obtained for calibrations.

A study of the mineral content in mushroom compost showed that the standard error in the lab wet chemistry was about half that of the SECV (Sharma *et al.*, 2000).

The ability of NIR to measure P content in potato starch was shown by Thygesen *et al.*, 2001. The range of P content of the 97 samples studied were 0.029% - 0.11%. The study obtained a RMSECV of 0.006%. This error was smaller than prediction error obtained by a current chemistry wet method used for measuring P in potato starch. It was found, however, that the NIR model relied on weak spectral effects and was very sensitive to sample preparations.

NIR was used by Suehara *et al.*, 2001 to determine the N content of compost during the compost fermentation of toufu. An $r^2 = 0.97$ and SEP = 0.08% were obtained. The author stated that the prediction of N was as good as the predictions from their reference methods (dumas).

One hundred samples which included six grass species (Italian Rye grass, Perennial rye grass, Timothy, Orchid grass, Red Fescue, Meadow Fescue) and Red clover were used to access NIR's ability to predict the elements Ca, P, Mg, K, Na, Zn, Mn and Se by Lavrencic *et al.*, 2002. The work showed that the minor elements Zn, Mn, Se and the major element Na was unlikely to be predicted by NIR. The calibrations developed for the major elements Ca, P, Mg and K had $r^2 > 0.88$ and had low SECV's. This indicated that those elements could be predicted with some degree of accuracy for grass species.

The determination of N in dry and wet (field moist) grass (Fescue Kentucky 31) using NIR was studied by McClure *et al.*, 2002. The $r^2$ and SEP for dry and wet grass tissue calibrations was of 0.97 (0.29%) and 0.88 (0.97%) respectively. The range of N content for the study was 0.9 – 6.6%. Other studies have shown that $r^2$ and SEP for dry and wet samples could be measured with $r^2$ and (SEP) 0.99 (0.17%) and 0.93 (0.42%) for the different states (Norris, 1998). Water in the wet plant samples masked the spectral information that was imparted if the samples were dry. This lead to lower accuracies being obtained when measuring wet plant material (McClure *et al.*, 2002).

Chen *et al.*, 2002, showed that P in sugar cane leaves by NIR could be determined to the same level of accuracy as the reference chemistry. They obtained calibration equation when $r^2$ and SEP were 0.78 (0.02%) for a P range of 0.012-0.35%. Their calibrations were further improved when unneeded wavelength segments were eliminated using Martins uncertainty regression (Martins and Naes, 1989).

The measurement of DM and major elements (Ca, P, K and Mg) in corn silage using NIR was evaluated by Fontaneli *et al.*, 2002. Calibration statistics of $r^2$ and SEP for DM, Ca, P, K and

Mg were 0.99 (0.27%), 0.93 (0.03%), 0.92 (0.01%), 0.94 (0.06%) and 0.92 (0.01%) were achieved respectively.

Calibrations and SECV statistics obtained by Moron and Cozzolion, 2002 showed that N, P, Ca and K could be determined in alfalfa and white clover leaves using NIR. The calibrations for Mg and S were poor in comparison. When specific calibrations for alfalfa or white clover alone were developed the calibrations predicted S, Na and B well, but trace elements Fe, Zn, Cu and Mn were not. For B an $r^2 = 0.80$ and SEP = 4.2 mg $Kg^{-1}$ were achieved for the calibration developed. This work showed possibilities of NIR use as a screening tool for measurement of critical legume nutrients B and S.

Shepherd *et al.*, 2003, studied the measurement of N content in 319 samples which included 83 tropical crops and trees. The N content in the sample set ranged from approximately 0.6-5.0% N. The authors were able to achive calibration statistics of $r^2 = 0.85$ and SEP = 0.5%.

Study of NIR by Miller and Adams, 2003 to predict concentrations of P, K, Ca and Mg in Bermuda grass (turf-grass) was not successful. The determination of the above elements were via a Mehlich I extraction and then analysis via ICP. This is in contrast to other studies where total elemental composition via a digestion procedure was employed. This could account for the poor calibration statistics obtained by this study. Cozzolino and Morron 2004 evaluated the use of NIR to predict the trace elements Fe, Cu, Mn, Zn and B and major elements Na and S in legumes, and white clover. Three hundred and thirty dried samples with sample fraction <1mm were scanned over- nm using a NIRSystems spectrometer. Calibrations were developed using modified PLS. Studies by Halgerson *et al.*, 2004 showed that NIR could accurately predict Ca, K and P of leaves and stems of alfalfa. The predictions of Mg, S, A*l*, B and Si in leaves were not as good with failure to predict other elements.

## 2.5 Conclusion

The literature suggests that determination of moisture, mineralisable N, CEC, soil texture (sand silt and clay fraction) and some total elemental composition in soils is possible using NIR. The review of the NIR literature on plant analysis studies suggests that the measurement of moisture, N, P, K, Mg, Ca and S is possible while the measurement of minor elements is not possible.

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**Table 2.1:** Study references of soil moisture.

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range (%)** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Moisture (%) | Bowers and Hanks | 1965 | USA | Beckman DK-2A & DU | 185-3500 | Water added |  | <20 mesh sieve | 6 | 0.8-20.2 |  |  |  |  |
| Moisture (%) | Dalal and Henry | 1986 | Queensland Australia | InfraAlyser 500C | 1100-2500 | Dry (25$^{O}$C) | 0-600 | <2 | 72 | 3.5-13.0 |  | 0.85 |  | 0.58 |
| Moisture (%) | Dalal and Henry | 1986 | Queensland Australia | InfraAlyser 500C | 1100-2500 | Dry (25$^{O}$C) | 0-1200 | <2 | 72 | 3.5-13.0 |  | 0.93 |  | 0.60 |
| Moisture (%) | Sudduth and Hummel | 1993 | Illinois USA | Portable NIR | 1670-2630 | Field moist |  | <2 | 30 | 4.1-39.7 |  | 0.97 | 1.48 | 1.59 |
| Moisture (%) | Ping *et al.* | 1998 | China |  |  | Dry |  |  |  |  |  | 0.97 | 1.08 |  |
| Moisture(%) | Couillard *et.al* | 1997 | USA Michigan | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 93 | 3.1-54.9 |  | 0.92 | 0.24 |  |
| Moisture (%) | Couillard *et.al* | 1997 | USA Michigan | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 91 | 0.33-4.26 |  | 0.62 | 0.02 |  |
| Moisture (%) | Peng *et.al* | 1998 | China |  |  | Dry |  |  | 126 | 3.7-13.2 |  | 0.95 | 1.08 | 1.14 |
| Moisture (%) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine Ground | 147 |  |  | 0.75 |  | 4.9 |
| Moisture (%) | Malley and Currie | 1999 | Manitoba Canada | Foss NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 |  |  | 0.89 |  | 3.4 |
| Moisture (%) | Chang *et.al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 802 | 0.0-16% |  | 0.84 | 0.5 |  |
| Moisture (g Kg$^{-1}$) | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet |  | Field Moist 'as is state' | 46 predict | 78-705 |  | 0.89 | 34.1 |  |

**Table 2.1:** Study references of soil moisture.

| Test | Reference | Year | Location | Instrument | λ (nm | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | S$_r$ (chem) | r$^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Moisture (g Kg$^{-1}$) | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Drying and grinding | 46 | 78-705 | | 0.89 | 34.1 | |
| Moisture (%) | Christy *et.al* | 2003 | Iowa USA | Diode Array | 350-1700 | Wet | 0-100 (on the go) | As is in the field | 148 | | | 0.82 | 3.0 | |
| Water Content (gIg) | Islam *et.al* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface and sub-surface soils | <2 | 161 | <0.01-0.11 | | 0.82 | 0.01 | 0.01 |

**Table 2.2:** Study references of soil OM, OC and TC.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| O.M (%) | Al-Abbas *et.al.* | 1972 | Indiana USA | Airborne optical scanner | 400-2600 | Dry | | Soil surface | 197 | 0.75-6.2 | | 0.57 | | |
| O.M (%) | Krishan *et.al.* | 1980 | Illinois USA | Cary model 14 monochrmator | 400-2400 | Dry (105°C) | | <10 mesh sieve | 10 | 1.1-5.1 | | 0.87 | | |
| O.C (%) | Dalal and Henry | 1986 | Queensland Australia | Technicon InfraAlyser 500C | 1100-2500 | Dry (25°C) | 0-600 | <2 | 72 | 0.42-2.5 | | 0.86 | | 0.16 |
| O.C (%) | Dalal and Henry | 1986 | Queensland Australia | Technicon InfraAlyser 500C | 1100-2500 | Dry (25°C) | 0-1200 | <2 | 72 | 0.27-2.5 | | 0.86 | | 0.22 |
| O.M (%) | Meyer | 1989 | Natal South Africa | Technicon InfraAlyser 300,400 &450 | 1445-2348 (19 filter λ) | Dry | 0-250 | <2 | 96 | 0.3-7.1 | | 0.90 | | 0.5 |
| TC (%) | Morra *et al.* | 1991 | Idaho | Pacific Scientific Neotec 6250 | 1100-2500 | Dry silt/clay | 0-350 | <2 | 68 | 0.05-9.02 | | 0.93 | 0.62 | 0.59 |
| TC (%) | Morra *et al.* | 1991 | Idaho | Pacific Scientific Neotec 6250 | 1100-2500 | Dry silt | 0-350 | <2 | 68 | 0.06-7.80 | | 0.96 | 0.41 | 0.32 |
| TC (%) | Krischenko *et al.* | 1992 | USSR | NIRSystems 6500& 4500 | 1100-2500 | Dry | | | 21 | | | 0.94 | | 0.08 |
| O.M (%) | Krishchenko *et al.* | 199 | USSR | NIRSystems 6500 & 4500 | 1100-2500 | Dry | | | 131<br>74<br>57 | | | 0.95<br>0.95<br>0.62 | | 0.26<br>0.27<br>0.25 |
| O.C (%) | Sudduth and Hummel | 1993 | Illinois USA | Portable NIR | 1670-2630 | Dry | | <2 | 30 | 0.45-3.16 | | 0.89 | 0.22 | 0.23 |
| O.M. (%) | Ben-Dor And Banin | 1995 | Israeli (12 Soil groups) | FTIR Alpha Centauri | 800-2500 | Dry | 0-50 | <2 | 91 | 0.09-13.23 | | 0.69 | 1.63 | 1.34 |
| OC (%) | Malley *et al.* | 1996 | Canada (Lake sediments) | NIRSystems 6500 | 1100-2500 | Dry | 0-100 (sediment) | <150nm | 90 | 0.4-14.0 | | 0.99 | | 0.4 |
| TC (%) | Ootake *et.al* | 2000 | Japan (7 soil | Bran-Luebbe | 1100-2599 | Dry | | <2 | 228 | .27-9.19 | | 0.86 | 0.04 | |

**Table 2.2:** Study references of soil OM, OC and TC.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | sediments) | InfraAlyzer500 | | | | | | | | | | |
| OM (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 89 | 2.15-12.8 | | 0.90 | 0.06 | |
| OM (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 91 | 2.5-27.8 | | 0.74 | 0.09 | |
| T.C. (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 48 | 1.12-15.0 | 0.35 | 0.28 | 0.11 | |
| T.C. (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 48 | 1.12-15.0 | 0.35 | 0.29 | 0.11 | |
| OM (%) | Peng *et.al* | 1998 | China | | | Dry | | | 126 | 0.4-1.7 | | 0.88 | 0.23 | 0.28 |
| OM (%) | Salgo *et.al* | 1998 | Hungary | NIRSystems 6500 | 1100-2500 | Dry | | <2 | 108 | 0.2-5.3 | | 0.92 | 0.28 | 0.30 |
| OC (%) | Meyer | 1998 | Natal South Africa | | | Dry | | <2 | | | | 0.85 | 0.46 | |
| OM (%) | Malley and Currie | 1999 | Manitoba Canada | Foss NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 14.7 | | | 0.86 | | 3.6 |
| TC (%) | Malley *et.al* | 1999 | Germany (Lake sediments) | NIRSystems 6500 | 1100-2500 | Freeze Dried | 0-470 | No grinding | | 16.7-19.7 | 0.12 | 0.93 | | 0.7 |
| TC (%) | Reeves *et.al* | 1999 | Maryland USA | NIRSystems 6250 | 1100-2500 | Dry (105$^{0}$C) | 0-200 | Fine powder | 179 | 0.61-3.4 | | 0.95 | 0.09 | 0.09 |
| TC (%) | Confalonieri | 2001 | Northern Italy | NIRSystems 5000 | 1100-500 | Dry | 0-300 | <2 | 142 | 0.51-1.45 | | 0.87 | 0.06 | |
| TC (%) | Cheng *et.al* | 2001 | USA (4 major areas) | NIRSystem 6500 | 400-2500 | Dry | 0-300 | <8 | 743 | 0.13-28.6 | | 0.87 | 0.8 | |
| OM (%) | Fidencio *et.al* | 2002 | Brazil (Oxisol and Ultisol) | Cary 5G | 1000-2500 | Dry | 0-1000 (different depths) | <2 | 100 | 0.4-4.8% | | 0.90 | | 0.2 |

**Table 2.2:** Study references of soil OM, OC and TC.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TC (%) | Reeves *et.al* | 2002 | Maryland USA (4 locations) | NIRSystems 6500 | 400-2500 | Dry | 0-200 | | 179<br>64<br>136<br>136 | 0.53-3.4 | | 0.78-0.97 | 0.08-0.17 | |
| OM(g Kg) | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | | | 1-693 | | 0.84 | | 30.4 |
| OM (%) | Fidencio *et.al* | 2002 | Brazil (Oxisol and Ultisol) | Cary 5G | 1000-2500 | Dry | 0-1000 (different depths) | <2 | 100 | 0.4-4.8% | | 0.90 | | 0.2 |
| TC (%) | Reeves *et.al* | 2002 | Maryland USA (4 locations) | NIRSystems 6500 | 400-2500 | Dry | 0-200 | | 179<br>64<br>136<br>136 | 0.53-3.4 | | 0.78-0.97 | 0.08-0.17 | |
| OM (g Kg$^{-1}$) | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | | | 1-693 | | 0.84 | | 30.4 |
| OM (g Kg$^{-1}$) | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | | | 1-693 | | 0.97 | | 21.4 |
| | | | | | | | | | | | | | | |
| OC (g Kg$^{-1}$) | Martin *et.al* | 2002 | Manitoba Canada | NIRSystems 6500 | 1100-2500 | Dry | 0-1200 | Ground | 274 | 3.8-37.1 | | 0.75 | | 3.5 |
| OC (g Kg$^{-1}$) | Moron and Cozzalino | 2002 | Uruguay (different regions) | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 10.3-68.5 | | 0.94 | 1.9 | 5.0 |
| OC (g Kg$^{-1}$) | Fystro | 2002 | Norway (3 agriculture regions) | NIRSystems 6500 | 400-2500 | | 0-400 | 3 treatments | 80 | 6.0-79 | | 0.75-0.91 | 5.6-7.4 | 5.7-7.4 |
| OC (%) | Dunn *et.al* | 2002 | Riverine Plains South Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5) | 360 | 0.64-3.00 | | 0.62 | 0.26 | 0.25 |

**Table 2.2:** Study references of soil OM, OC and TC.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TC (g $Kg^{-1}$) | Chodak *et.al* | 2002 | Solling Germany | NIRSystems | 400-2500 | Dry | 0-200 (different depths) | Finely Ground | 406 | 181-499 | | 0.96 | 17 | 24 |
| TC (g $Kg^{-1}$) | M$^c$Carty *et.al* | 2002 | 14 locations Central USA | NIRSystems 6500 | 1100-2500 | Dry | 0-2000 | <180mm | 273 | 0.98-104 | | 0.86 | | 5.4 |
| TC (g $Kg^{-1}$) | Ludwig *et.al* | 2002 | Victoria USA | NIRSystems 6500 | 400-2500 | Dry | 0-300 | Finely ground | 120 | 15.1-213 | | 0.94 | 6.7 | 14.5 |
| TC (g $Kg^{1}$) | Groenigen *et al* | 2003 | Rice field CaliforniaUSA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 100 | 8.7-16.1 | | 0.01 | 1.6 | 1.6 |
| OC (g $Kg^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 674 | 2.3-36.8 | | 0.91 | | 2.2 |
| OC (g $Kg^{-1}$) | Udelhoven *et.al* | 2002 | SW Germany | Field Spec (II) | 400-2500 | Dry | 0-300 | <2 | 114 | 1.4-2.5 | | 0.60 | 1.4 | |
| TC (%) | Christy *et.al* | 2003 | Iowa USA | Diode array | 350-1700nm | Wet | 0-100 on the go | As is in the field | 148 | | | 0.87 | | 0.45 |
| TC (%) | Couteaux *et.al* | 2003 | Sweden & France/forests | NIRSystems 6500 | 400-2500 | Dry | | <1 | 150 | 2.1-45.9 | | 0.99 | 1.7 | 1.6 |
| TC (%) | Russell | 2003 | Riverine Plain SE Australia | NIRSystems 6500 | Dry | 0-100 | treatments (7 used) | | 25 | 1.15-2.43 | 0.81 | 0 | 0.15 | |
| OC (%) | Islam *et.al* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface & subsurface soils | <2 | 161 | 0.06-4.95 | | 0.61 | 0.42 | 0.44 |
| TC (%) | Confalonieri and Odoardi | 2003 | Cropping soils Italy | NIRSystems 5000 | 1100-2500 | Ry | 0-300 | Finely Ground | 142 | | | 0.87 | 0.06 | 0.08 |

**Table 2.3:** Study references of soil texture (clay/silt/sand fraction).

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Clay (%) | Al-Abbas *et.al.* | 1972 | Indiana USA | Airborne optical scanner | 400-2600 | Dry | | Soil surface | 134 | 8.4-31.3 | | 0.53 | | |
| Clay (%) | Meyer | 1989 | Natal South Africa | Technicon InfraAlyser 300,400 &450 | 1445-2348 (19 filter λ) | Dry | 0-250 | <2mm | 98 | 8-59 | | 0.94 | | 3.8 |
| Silt (%) | Meyer | 1989 | Natal South Africa | Technicon InfraAlyser 300,400 &450 | 1445-2348 (19 filter λ) | Dry | 0-250 | <2mm | 98 | 2-23 | | 0.81 | | 2.1 |
| Sand (%) | Meyer | 1989 | Natal South Africa | Technicon InfraAlyser 300,400 &450 | 1445-2348 (19 filter λ) | Dry | 0-250 | <2mm | 98 | 22-89 | | 0.83 | | 5.9 |
| Clay (%) | Ben-Dor and Banin | 1995 | Israeli (12 soil groups) | FTIR Alpha Centauri | 800-2500 | Dry | 800-2500 | <2 | 011 | 4:1-65.3 | | 0176 | 8.6 | 10.3 |
| Sand (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 46 | 82.6-99.5 | 0.28 | 0.93 | 0.13 | |
| Sand (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 46 | 82.6-99.5 | 0.28 | 0.92 | 0.14 | |
| Silt (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 46 | 0.52-14.7 | 0.37 | 0.92 | 0.12 | |
| Silt (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 48 | 0.52-14.7 | 0.37 | 0.87 | 0.16 | |
| Clay (%) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 49 | 0-2.9 | 0.26 | 0.77 | 0.04 | |
| Clay | Couillard *et.al* | 1997 | Michigan | NIRSystems | 400-2500 | Dry | 0-50 | <2 | 49 | 0-2.9 | 0.26 | 0.76 | 0.04 | |

**Table 2.3:** Study references of soil texture (clay/silt/sand fraction).

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (%) | | | USA | 6500 | | | | | | | | | | |
| Sand (%) | Meyer | 1998 | Natal South Africa | Technician Infra Analyser | 400-2500 | Dry | | <2 | | | | 0.88 | 3.8 | |
| Clay (%) | Chang *et.al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 743 | 0.7-35.2 | | 0.67 | 4.1 | |
| Silt (%) | Chang *et.al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 743 | 3.1-85.3 | | 0.84 | 9.5 | |
| Sand (%) | Chang *et.al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 743 | 1.2-95.2 | | 0.82 | 11.9 | |
| Clay (%) | Stenberg *et.al* | 2002 | Agriculture sites in Sweden | Bran and Lubbe Infra Analyser 500 | 1100-2500 | Dry | | <2 | 2750 | 0-70 | | 0.85 | 5.6 | |
| Sand (g Kg$^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 457 | 80-900 | | 0.91 | | 61 |
| Silt (g Kg$^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 457 | 0-420 | | 0.79 | | 30 |
| Clay (g Kg$^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 457 | 50-790 | | 0.88 | | 54 |
| Sand (%) | Moron and Cozzolino | 2003 | Agricultural soils Uruguay | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 2-71 | | 0.81 | 5.1 | |
| Silt (%) | Moron and Cozzolino | 2003 | Agricultural soils Uruguay | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 18-74 | | 0.83 | 5.3 | |
| Clay | Moron and | 2003 | Agricultural | NIRSystems | 400-2500 | Dry | 0-150 | <2 | 332 | 8053 | | 0.92 | 2.6 | |

**Table 2.3:** Study references of soil texture (clay/silt/sand fraction).

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range (%)** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (%) | Cozzolino | | soils Uruguay | 6500 | | | | | | | | | | |
| Clay (%) | Islam *et.al* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface and sub-surface soils | <2 | 161 | 1.7-71.7 | | 0.82 | 7.8 | 8.9 |
| Sand (%) | Islam *et.al* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface and sub-surface soils | <2 | 161 | <0.01-43.3 | | 0.34 | 7.1 | 9.8 |
| Silt (%) | Islam *et.al* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface and sub-surface soils | <2 | 161 | <0.01-43.3 | | 0.34 | 7.1 | 9.8 |

**Table 2.4:** Study references of soil Total N (TN) and Organic N (Org N)

| Test | Reference | Year | Location | Instrument | λ (nm | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TN (%) | Dalal and Henry | 1986 | Queensland Australia | InfraAlyser 500C | 1100-2500 | Dry | 0-600 | <2 | 72 | 0.04-0.23 | | 0.85 | | 0.01 |
| TN (%) | Dalal and Henry | 1986 | Queensland Australia | InfraAlyser 500C | 1100-2500 | Dry | 0-1200 | <2 | 72 | 0.02-0.23 | | 0.86 | | 0.02 |
| TN (%) | Meyer | 1989 | Natal South Africa | Technicon InfraAlyser 300,400 &450 | 1445-2348 (19 filterλ) | Dry | 0-250 | <2 | 98 | 0.03-0.60 | | | | 0.01 |
| TN (%) | Morra *et al.* | 1991 | Idaho | Pacific Scientific Neotec 6250 | 1100-2500 | Dry silt/clay | 0-350 | <2 | 68 | 0.02-0.75 | | 0.89 | 0.06 | 0.06 |
| TN (%) | Morra *et al.* | 1991 | Idaho | Pacific Scientific Neotec 6250 | 1100-2500 | Dry silt | 0-350 | <2 | 68 | 0.02-0.64 | | 0.94 | 0.04 | 0.04 |
| TN (%) | Krischenko *et al.* | 1992 | USSR | NIRSystems Model 6500 &4500 | 1100-2500 | Dry | | | 47 | | | 0.93 | | 0.03 |
| TN (%) | Ping *et al.* | 1998 | China | | | Dry | | | 126 | | | | 0.04 | 0.05 |
| TN (%) | Malley *et.al* | 1996 | Canada (Lake sediments) | NIRSystems 6500 | 1100-2500 | Dry | 0-100 | <150nm | 90 | 0.04-1.83 | | 0.99 | | 0.05 |
| T N (%) | Couillard *et al.* | 1997 | USA Michigan | NIRSystems 6500 | 1100-2500 | Wet | 0-100 | <150nm | 48 | | | | | |
| TN (%) | Couillard *et al.* | 1997 | USA Michigan | NIR Systems 6500 | 1100-2500 | Dry | 0-50 | <2 | 48 | | | | | |

**Table 2.4:** Study references of soil Total N (TN) and Organic N (Org N)

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range (%)** | **$S_r$ (chem.)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TN (%) | Ootake *et.al* | 2000 | Japan (7 soil groups) | Bran-Luebbe Infra Alyzer 500 | 1100-2500 | Dry | | <2 | 228 | 0.03-0.57 | | 0.83 | 0.04 | |
| TN (%) | Cho *et al* | 1998 | Korea (upland areas) | Technician Infra Alyser 500 | 1100-2500 | Dry | | Pulverized soil | 85 | 0.04-0.23 | | 0.86 | 0.025 | 0.028 |
| TN (%) | Peng *et.al* | 1998 | China | | | Dry | | | 126 | 0.04-0.14 | | 0.89 | 0.04 | 0.05 |
| TN (%) | Salgo *et.al* | 1998 | Hungry | NIRSystems 2500 | 1100-2500 | Dry | | <2 | 108 | | | 0.69 | 0.04 | 0.04 |
| TN (%) | Meyer | 1998 | Natal South Africa | | | Dry | | <2 | | | | 0.81 | 0.01 | |
| TN (%) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine Ground | 147 | | | 0.88 | | 0.15 |
| TN (%) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | 0.01 | 0.91 | | 0.05 |
| TN (%) | Malley *et.al* | 1999 | Germany (L. sedim.) | NIRSystems 6500 | 1100-2500 | Freeze Dried | 0-470 | No grinding | | 0.99-1.74 | 0.01 | 0.94 | | 0.07 |
| TN (%) | Reeves *et.al* | 1999 | Maryland USA | NIRSystems 6250 | 1100-2500 | Dry $105^0$c | 0-200 | Fine powder | 179 | 0.06-0.28 | | 0.95 | 0.007 | 0.009 |
| TN (%) | Confalonieri | 2001 | Northern Italy | NIRSystems 5000 | 1100-2500 | Dry | 0-300 | <2 | 142 | 0.06-0.14 | | 0.85 | 0.01 | |
| TN (%) | Chang *et.al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 744 | 0.02-1.65 | | 0.85 | 0.06 | |

**Table 2.4:** Study references of soil Total N (TN) and Organic N (Org N)

| Test | Reference | Year | Location | Instrument | λ (nm | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TN $(g\ Kg^{-1})$ | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Field moist | 46 | 1-6.93 | | 0.91 | 0.5 | |
| TN $(g\ Kg^{-1})$ | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Drying & Grinding | 46 | 1-6.93 | | 0.88 | 1.5 | |
| Org N $(g\ Kg^{-1})$ | Martin *et.al* | 2002 | Manitoba Canada | NIRSystems 6500 | 1100-2500 | Dry | 0-1200 | Ground | 285 | 0.1-3.9 | | 0.3 | 0.58 | |
| TN $(g\ Kg^{-1})$ | Chang and Laird | 2002 | Iowa & Minnesota. USA | NIRSystems 6500 | 400-2500 | Dry | | Ground | 108 | 1.5-5.5 | | 0.97 | 0.16 | 0.36 |
| TN $(g\ Kg^{-1)}$ | Moron and Cozzolino | 2002 | Uruguay diff. regions | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 0.9-6.2 | | 0.91 | 0.19 | 0.4 |
| TN $(g\ Kg^{-1})$ | Fystro | 2002 | Norway (3 agric. regions | NIRSystems 6500 | 400-2500 | Dry/moist | 0-400 | 3 treatments | 80 | 0.5-4.5 | 0.16 | 0.80-.098 | 0.53-0.57 | 0.49-0.63 |
| TN $(g\ Kg^{-1})$ | Chodak *et.al* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 | Finely ground | 406 | 9.7-24.4 | | 0.92 | 1.0 | 1.2 |
| TN $(g\ Kg^{-1)}$ | Ludwig *et.al* | 2002 | Victoria Australia | NIRSystems 6500 | 400-2500 | Dry | 0-300 | Finely ground | 120 | 0.6-10.9 | | 0.88 | 0.4 | 0.9 |
| TN $(g\ Kg^{-1})$ | Udelhoven *et.al* | 2002 | SW Germany | ASD FieldSpec (II) | 400-2500 | Dry | 0-300 | <2 | 114 | | | 0.62 | 0.1 | |
| TN (%) | Christy *et.al* | 2003 | Iowa USA | Diode Array | 350-1700 | Wet | 0-100 on the go | As is in the field | 148 | | | 0.86 | | 0.03 |
| TN (%) | Couteaux *et.al* | 2003 | Sweden and France/fores | NIRSystems 6500 | 400-2500 | Dry | | <1 | 150 | 0.05-1.81 | | 0.99 | 0.08 | 0.08 |

**Table 2.4:** Study references of soil Total N (TN) and Organic N (Org N)

| Test | Reference | Year | Location | Instrument | λ (nm | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TN (mg $Kg^{-}$) | Russell | 2003 | South E. Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | 7 treatment | 25 | 900-2030 | | 0.83 | | 138 |
| TN (%) | Confalonieri & Odoardi | 2003 | Cropping soils Italy | NIRSystems 5000 | 1100-2500 | Dry | 0-300 | Finely ground | 142 | | | 0.85 | 0.01 | 0.01 |
| TN (g $Kg^{-1}$) | Groenigen *et al* | 2003 | Rice field Calif., USA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 100 | 0.82-1.30 | | 0.20 | 0.1 | 0.01 |

**Table 2.5:** Study references of soil available N (Mineralizable N)

| | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range (%)** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Available Soil N (Kg $Nha^{-1}$) | Fox *et al.* | 1993 | Pennsylvania USA | NIR Systems 6500 | 400-2500 | Dry | 0-200 | <2 | 95 | 46-232 Kg N $ha^{-1}$ | | 0.49<br>0.52<br>0.61 | | |
| Available N (mg $Kg^{-1}$) | Cho *et al.* | 1998 | Korea (upland area) | Technicon Infra Alyser 500 | 1100-2500 | Dry | | Pulverised soil | 85 | 0-60 | | 0.62 | 9.0 | 11.0 |
| N mineralization potential score (1-4) | Meyer | 1998 | Natal South Africa | Technicon Infra Alyser | | Dry | | <2 | | | | 0.74 | 0.3 | |
| Mineralizable N 21d aerobic Incub. (mg $Kg^{-1}$) | Reeves *et al.* | 1999 | Maryland USA | NIRSystems 6250 | 1100-2500 | Wet | 0-200 | <4 | 179 | 0.2-33.5 | | 0.08 | 5.6 | |
| Mineralizable N (mg $Kg^{-1}$) | Chang *et al.* | 2001 | USA (4 major areas) | NIR Systems 6500 | 400-2500 | Dry | 0-300 | <8 | 764 | 0.4-555 | | 0.72 | 26.1 | |
| Mineralizable N (mg $Kg^{-1}$) 7d Anaerobic Incub. | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 604 | 0.1-30 | | 0.74 | 2.4 | |
| Mineralizable N (mg $Kg^{-1}$) | Russell *et al.* | 2002 | South Australia (25 farms) | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <2 | 22 | 50-175 | | 0.79 | 16 | |
| Mineralisable N 21D Anaerobic inc (mg $Kg^{-1}$) | Russell | 2003 | South Australia | NIR Systems 6500 | 400-2500 | Dry | 0-100 | <2 | 25 | 37-235 | | 0.79 | | 23 |
| Mineralizabl N ($mgKg^{-1}$) | Groenigen *et al* | 2003 | Rice field California USA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 99 | 2.7-11.2 | | 0.46 | 0.03 | 0.04 |

**Table 2.6:** Study references of soil mineral nitrogen ($NO_3$; $NH_4$).

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $NO_3 + NH_4$ (mg $Kg^{-1}$) | Krishchenko *et al.* | 1992 | USSR | NIRSystems 6500 &4500 | 1100-2500 | Dry | | | 47 | | | 0.48 | | 12.8 |
| In organic N (mg $Kg^{-1}$) | Cho *et al.* | 1998 | Korea (upland area) | Technicon Infra Alyser 500 | 1100-2500 | Dry | | Pulverised soil | 85 | 11-90 | | 0.76 | 15.8 | 16.3 |
| $NH_4$-N (mg $Kg^{-1}$) | Malley and Curric | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine ground | 147 | | | 0.66 | | 56.1 |
| $NH_4$-N (mg $Kg^{-1}$) | Malley and Curric | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | | 0.29 | | 4.7 |
| $NO_3$-N (mg $Kg^{-1}$) | Malley and Curric | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine ground | 147 | | | 0.45 | | 14.6 |
| $NO_3$-N (mg $Kg^{-1}$) | Malley and Curric | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | | 0.33 | | 7.5 |
| $NO_3$-N (ppm) | Ehsani *et al* | 1999 | California USA | NIRSystems 6500 | 1800-2300 | Dry | | | 660 | 0-110 | | 0.95 | | 2 |
| $NH_4$-N (mg $Kg^{-1}$) | Reeves *et al* | 1999 | Beltville USA | NIR System 6250 | 1100-2500 | Dry | | <2 | 593 | 0.0-272 | | 0.61 | 21.7 | 23.7 |
| $NO_3$-N (mg $Kg^{-1}$) | Reeves *et al* | 1999 | Beltville USA | NIR System 6250 | 1100-2500 | Dry | | <2 | 593 | 10.5-394 | | 0.76 | 31.2 | 37.8 |
| $NH_4$-N + $NO_3$-N (mg $Kg^{-1}$) | Reeves *et al* | 1999 | Beltville USA | NIR System 6250 | 1100-2500 | Dry | | <2 | 593 | 16.3-397 | | 0.63 | 36.9 | 44.2 |
| $NO_3$-N (mg $Kg^{-1}$) | Malley *et al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Field moist 'as | 46 (prediction) | 0.5-114 | | 0.34 | | 7.4 |

**Table 2.6:** Study references of soil mineral nitrogen ($NO_3$; $NH_4$).

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | is state' | | | | | | |
| $NO_3$-N (mg Kg$^{-1}$) | Malley *et al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Drying and grinding | 46 (prediction) | 0.5-114 | | 0.42 | | 15.7 |
| $NH_4$-N (mg Kg$^{-1}$) | Malley *et al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Field moist 'as is state' | 46 (prediction) | 0.9-494 | | 0.29 | | 4.9 |
| $NH_4$-N (mg Kg$^{-1}$) | Malley *et al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Drying and grinding | 46 (prediction) | 0.9-494 | | 0.66 | | 86.1 |
| $NH_4$-N (mg Kg$^{-1}$) | Coutenux *et.al.* | 2003 | Sweden & France/ Forests | NIRSystems 6500 | 400-2500 | Dry | | <1 | 120 | 1.1-280 | | 0.84 | 25 | 32 |
| Inorganic N (mg Kg$^{-1}$) | Coutenux *et al.* | 2003 | Sweden & France/ Forests | NIRSystems 6500 | 400-2500 | Dry | | <1 | 103 | 0.2-448 | | 0.81 | 27 | 38 |

**Table 2.7:** Study references of soil cation exchange capacity (CEC).

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CEC (mEq/100g) | Sudduth and Hummel | 1993 | Illinois USA | Portable NIR | 1670-2630 | Dry |  | <2 | 30 | 11.4-55.2 |  | 0.86 | 3.45 | 3.59 |
| CEC (mEq/100g) | Ben-Dor and Banin | 1995 | Isralei (12 soil groups) | FITR A Alpha Centauri | 800-2500 | Dry | 0-50 | <2 | 91 | 1.3-62.1 |  | 0.82 | 6.72 | 8.46 |
| CEC (mEq/100g) | Ootake *et.al* | 2000 | Japan (7 soil groups) | Bran-Luebbe Infra Analyzer 500 | 1100-2500 | Dry |  | <2 | 228 | 5/0-47.7 |  | 0.81 | 3.2 |  |
| CEC (c mol kg$^{-1}$) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 48 | 3.85-24.3 | 0.52 | 0.28 | 30.7 |  |
| CEC (c mol kg$^{-1}$) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 47 | 3.85-24.3 | 0.52 | 0.61 | 2.30 |  |
| CEC (c mol kg$^{-1}$) | Chang *et.al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 744 | 1.9-92.2 |  | 0.81 | 3.82 |  |
| CEC (Cmol kg-$^{1}$) | Dunn *et al* | 2002 | Riverine Plain South Australia | NIRSystem 6500 | 400-2500 | Dry | 0-100 | <0.5 | 562 | 2.7-33.6 |  | 0.88 | 2.2 | 1.9 |
| CEC (c mol Kg$^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 740 | 0.4-35 |  | 0.95 |  | 2 |
| CEC (c mol Kg$^{1}$) | Islam *et.al* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface and sub-surface soils | <2 | 161 | 15.6-311.5 |  | 0.75 | 38.0 | 43.3 |
| CEC (cmolKg$^{1}$) | Groenigen *et al* | 2003 | Rice field California USA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 100 | 21.6-38.0 |  | 0.83 | 1.4 | 2.1 |

**Table 2.8:** Study references of soil Potassium (K).

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Avail-able K (mg/kg) | Kischenko *et al.* | 1992 | USSR | NIRSystems | 1100-2500 | Dry | | | 83 | | | 0.83 | | 38.6 |
| $K_2O$ (%) | Ben-Dor and Banin | 1995 | Israeli (12 soil groups) | FTNIR | 800-2500 | Dry | 0-50 | <2mm | 91 | | | 0.55 | | |
| K MelichIII (cmol Kg$^{-1}$) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 46 | 0.06-2.96 | 0.1 | 0.86 | 0.15 | |
| K MelichIII (cmol Kg$^{-1}$) | Couillard *et.al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 46 | 0.06-2.96 | 0.1 | 0.87 | 0.14 | |
| K (mg Kg$^{-1}$ ) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-250 | Dry | 0-1200 | Fine ground | 147 | | 0.76 | | 121 | |
| K (mg Kg$^{-1}$ ) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-250 | Wet | 0-1200 | As is state | 147 | | | 0.59 | | 120 |
| Exch.K 1.0 $NH_4$ Acet. (mg Kg$^{-1}$) | Confalonieri | 2001 | Northern Italy | NIRSystems 5000 | 1100-2500 | Dry | 0-300 | <2 | 142 | 30-80 | | 0.57 | 6.8 | |
| K Melich 4 (mg Kg$^{-1}$) | Chang *et.al* | 2001 | USA<br>4 major areas | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 784 | 16-1757 | | 0.64 | 132 | |
| Exch.K (cmolKg$^{1}$) | Chang *et.al* | 2001 | USA<br>4 major areas | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 742 | 0.1-4.8 | | 0.55 | 0.42 | |
| Available K (mg Kg$^{-1}$) | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Field moist | 46 | 31-1300 | | 0.50 | | 155 |
| Available K (mg Kg$^{-1}$) | Malley *et.al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Drying & Grinding | 46 | 31-1300 | | 0.73 | | 121 |
| Exch.K (cmol Kg$^{-1)}$ | Dunn *et.al* | 2002 | Riverine P. SE, Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 559 | 0.20-2.10 | | 0.67 | 0.18 | 0.19 |
| Total K (mg g$^{-1}$) | Chodak *et.al* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 | Finely ground | 406 | 0.7-4.9 | | 0.92 | 0.3 | 0.3 |

**Table 2.8:** Study references of soil Potassium (K).

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exch.K (cmol $Kg^{-1}$ | Shepard and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 768 | | | 0.66 | | 0.3 |
| K (Ext.g $Kg^{-1}$) | Udelhouen *et.al* | 2002 | SW Germany | ASD Fieldspec II | 400-2500 | Dry | 0-300 | <2 | 114 | | | 0.15 | 0.05 | |
| Total K g $Kg^{-1}$) | Udelhouen *et.al* | 2002 | SW Germany | ASD Fieldspec II | 400-2500 | Dry | 0-300 | <2 | 52 | 8-16 | | 0.85 | 0.47 | |
| Exch.K (cmol $Kg^{-1}$) | Islam *et.al* | 2003 | NSW & QLD Australia | Cary 500 | 250-2500 | Dry | Surf. & subsurface | <2 | 161 | 1.3-36.9 | | 0.29 | 5.3 | 6.5 |
| Exch.K | Confalonieri & Odoardi | 2003 | Crop Soils Italy | NIRSystems 5000 | 1100-2500 | Dry | 0-300 | Finely Ground | 142 | | | 0.57 | 6.8 | 6.4 |
| Exch. K (cmol $Kg^{-1}$) | Groenigen *et al* | 2003 | Rice field Californ. USA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 100 | 0.36-0.82 | | 0.11 | 0.07 | 0.36 |

**Table 2.9:** Study references of soil pH.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | Krischenko *et al.* | 1992 | USSR | NIRSystems Model 6500 & 4500 | 1100-2500 | Dry | | | 78 | | | 0.65 | | 0.34 |
| pH | Couillard *et al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 48 | 6.8-7.95 | 0.02 | 0.82 | 0.12 | |
| pH | Couillard *et al.* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 49 | 6.8-7.95 | 0.02 | 0.87 | 0.10 | |
| pH | Malley *et al.* | 1999 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | 0-10 (metres) | <0.5 | 27 | 7.99-9.17 | | 0.66 | | 0.2 |
| pH | Reeves *et al.* | 1999 | Maryland USA | NIRSystems 6250 | 1100-2500 | Wet | 0-200 | <4 | 179 | 4.4-7.3 | | 0.80 | 0.2 | 0.3 |
| pH | Chang *et al.* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 743 | 3.9-8.5 | | 0.55 | 0.57 | |
| pH ($CaCl_2$) | Chang *et al.* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 743 | 3.5-8.0 | | 0.56 | 0.56 | |
| pH | Moron and Cozzolino | 2002 | Uruguay (different regions) | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 5.1-7.9 | | 0.93 | 0.18 | 0.28 |
| pH | Dunn *et al.* | 2002 | Riverine Plain South Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 555 | 3.8-7.3 | | 0.83 | 0.30 | 0.32 |
| pH | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 758 | 4.2-10.09 | | 0.83 | | 0.34 |
| pH | Christy *et al.* | 2003 | Iowa USA | Diode Array | 350-1700 | Wet | 0-100 | As is in the field | 148 | | | 0.72 | | 0.46 |
| pH[1] | Islam *et al.* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface and subsurface soil | <2 | 161 | 3.7-9.7 | | 0.73 | 0.62 | 0.61 |

**Table 2.10:** Study references of soil Ca.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exch. Ca | Kirshenko *et.al* | 1992 | USSR | NIRSystems Model 6500 & 4500 | 1100-2500 | Dry | | | 78 | | | 0.89 | | 1.05 |
| $CaCO_3$ (%) | Ben-Dor and Banin | 1995 | Israelei (12 soil groups) | FTIR Alpha Centauri | 800-2500 | Dry | 0-50 | <2 | 91 | 0-74.3 | | 0.70 | 12.9 | 11.6 |
| Ca Melich(II) (c mol $Kg^{-1}$) | Couillard *et al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Wet | 0-50 | Intact Cores | 49 | 2.8-22.6 | 0.5 | 0.42 | 3.4 | |
| Ca Melich(II) ($cmolKg^1$) | Couillard *et al* | 1997 | Michigan USA | NIRSystems 6500 | 400-2500 | Dry | 0-50 | <2 | 48 | 2.8-22.6 | 0.5 | 0.71 | 2.5 | |
| $CaC0_3$ (%) | Salgo *et al* | 1998 | Hungry | NIRSystems 6500 | 1100-2500 | Dry | | <2 | 108 | | | 0.83 | 2.1 | 2.4 |
| Ca (mg $Kg^{-1}$) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine ground | 147 | | | 0.86 | | 488 |
| Ca (mg $Kg^{-1}$) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | | 0.62 | | 596 |
| $C0_3^{2-}$ (mg $g^{-1}$) | Malley *et al.* | 1999 | Germany (Lake Sediments) | NIRSystems | 1100-2500 | Freeze dried | 0-470 | No grinding | | 31.1-66.4 | | 0.81 | | 3.8 |
| Total Ca (mg $g^{-1}$) | Malley *et al* | 1999 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | 0-10 (metres) | <0.5 | | 27.4-153.0 | | 0.98 | | 6.0 |
| Ca Melich III (mg $Kg^{-1}$) | Cheng *et al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 784 | 88-12,763 | | 0.80 | 564 | |
| Exch. Ca (cmol $Kg^{-1}$) | Cheng *et al* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 744 | 0.2-98.7 | | 0.75 | 4.0 | |
| Available Ca (mg $Kg^{-1}$) | Malley *et al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Field moist 'as is state' | 46 (prediction) | 2390-9400 | | 0.62 | 598 | |
| Available Ca | Malley *et al* | 2002 | Winnipeg | NIRSystems | 400- | Dry | | Drying and | 46 | 2390-9400 | | 0.85 | 488 | |

**Table 2.10:** Study references of soil Ca.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (mg Kg$^{-1}$) | | | Canada | 6500 | 2500 | | | Grinding | (prediction) | | | | | |
| Exch. Ca (c mol Kg$^{-1}$) | Dunn *et al.* | 2002 | Riverine Plain South Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 562 | 0.9-21.0 | | 0.87 | 1.23 | 1.26 |
| Total Ca (mg g$^{-1}$) | Chodak *et al.* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 (different depths) | Finely ground | 406 | 0.7-46.9 | | 0.88 | 2.8 | 3.1 |
| Exch. Ca (c mol Kg$^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field Spec | 350-2500 | Dry | 0-200 | <2 | 740 | 0.2-47 | | 0.94 | | 2.2 |
| Total Ca (g Kg$^{-1}$) | Udelhoven *et al.* | 2002 | SW Germany | ASD Field Spec II | 400-2500 | Dry | 0-300 | <2 | 52 | 0-100 | | 0.94 | | 52.9 |
| Exch Ca (m mol Kg-1) | Islam *et al* | 2003 | NSW&QLD Australia | Cary 500 | 250-2500 | Dry | Surface Sub-surface soils | <2 | 161 | <0.01-94.6 | | 0.70 | 13.4 | 13.4 |
| Exch. Ca (cmol Kg$^{-1}$) | Groenigen *et al* | 2003 | Rice field California USA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 100 | 11.7-19.4 | | 0.80 | 0.66 | 0.60 |
| OC (g Kg$^{-1}$) | Chang and Laird | 2002 | Iowa and Minnesota USA | NIRSystems 6500 | 400-2500 | Dry | | Ground | 108 | 15.4-145 | | 0.96 | 5.8 | 6.2 |
| Inorganic C (g Kg$^{-1}$) | Chang and Laird | 2002 | Iowa and Minn. USA | NIRSystems 6500 | 400-2500 | Dry | | Ground | 108 | 0.0-35.7 | | 0.97 | 1.6 | 1.5 |
| TC (g Kg$^{-1}$) | Chang and Laird | 2002 | Iowa and Minn. USA | NIRSystems 6500 | 400-2500 | Dry | | Ground | 108 | 15.4-145 | | 0.96 | 6.2 | 6.5 |

**Table 2.11:** Study references of soil S.

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S. $SO_4$ (mg $Kg^{-1}$) | Malley and Curric | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine ground | 147 | | | 0.85 | | 69.6 |
| S. $SO_4$ (mg $Kg^{-1}$) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | | 0.73 | | 73.6 |
| Total S (mg $g^{-1}$) | Malley *et al.* | 1999 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | 0-10 (metres) | <0.5 | 25 | 0.66-2.41 | | 0.97 | | 0.37 |
| S-$SO_4$ (mg $g^{-1}$) | Malley *et al.* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Field moist 'as is state' | 46 (pred. | 4-717 | | 0.73 | | 73.6 |
| S-$SO_4$ (mg $g^{-1}$) | Malley *et al.* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Drying and grinding | 46 (pred) | 4-717 | | 0.85 | | 69.8 |
| Total S (mg $g^{-1}$) | Chodak *et al.* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 (diff. depths) | Finely ground | 406 | 1.1-2.8 | | 0.92 | 0.1 | 0.2 |

**Table 2.12:** Study references of soil Phosphorous (P)

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Available P (mg/kg) | Krishenko *et al.* | 1992 | USSR | NIRSystems 6500 & 4500 | 1100-2500 | Dry | | | | | | 0.42 | | 145 |
| $P_2O_5$ (%) | Ben-Dor and Banin | 1995 | Isralei (12 soil groups) | FTIR | 800-2500 | Dry | 0-50 | <2 | 91 | 0.02-3.62 | | 0.23 | | |
| Total P (%) | Malley *et al.* | 1996 | Canada (Lake Sediments) | NIRSystems 6500 | 1100-2500 | Dry | <150mm | 90 | 0.004-0.183 | 5.0-322.7 | | 0.97 | 18.94 | 0.007 |
| Total P (%) | Couillard *et al.* | 1997 | USA Michigan | NIRSytems | 1100-2500 | Wet | 0-50 | Intact Cores | 47 | 5.0-322.7 | 9.8 | 0.81 | 18.94 | |
| Total P (%) | Couillard *et al.* | 1997 | USA Michigan | NIRSytems | 1100-2500 | Dry | 0-50 | <2 | 46 | 5.0-322.7 | 9.8 | 0.74 | 20.05 | |
| P Sorption Coefficient | Ootake *et al.* | 2000 | Japan (7 soil groups) | Bran-Leubbe 500 | 1100-2500 | Dry | | <2 | 228 | 110-2400 | | 0.71 | 222 | |
| PQ4$^{-P}$ mgKg$^{-1}$ | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine Ground | 147 | | | 0.49 | | 31.0 |
| PQ4$^{-P}$ mgKg$^{-1}$ | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | | 0.59 | | 29.3 |
| P Mgg$^{-1}$ | Malley *et al.* | 1999 | Germany (Lake Sediments) | NIRSystems | 1100-2500 | Freeze dried | 0-470 | No grinding | | 0.7-6.0 | | 0.99 | | 0.16 |
| Total P mg g$^{-1}$ | Malley *et al.* | 1999 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | 0-10 (metres) | <0.5 | 26 | 0.18-0.45 | | 0.92 | | 0.02 |
| Available P (Olsen P) (mg Kg$^{-1}$) | Confalonieri | 2001 | Northern Italy | NIRSystems 5000 | 1100-2500 | Dry | 0-300 | <2 | 142 | 28-92 | | 0.72 | 6.7 | |
| P Melich III (mg Kg-1) | Chang *et al.* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 779 | 0.7-508 | | 0.40 | 32.3 | |

**Table 2.12:** Study references of soil Phosphorous (P)

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PO4-p (mg Kg$^{-1}$) | Malley *et al.* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Field moist 'as is state' | 46 (prediction) | 3-301 | | 0.50 | | 29.3 |
| PO4-p (mg Kg$^{-1}$) | Malley *et al.* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Drying and grinding | 46 (prediction) | 3-301 | | 0.49 | | 31 |
| Colwell P (mg Kg$^{-1}$) | Dunn *et al.* | 2002 | Riverine Plain South Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 557 | 5-110 | | 0.27 | 16.1 | 18.0 |
| TP (mg g$^{-1}$ ) | Chodak *et al.* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 (different depths) | Finely Ground | 406 | 0.4-1.2 | | 0.86 | 0.1 | 0.1 |
| TP (mg Kg$^{-1}$) | Ryu *et al.* | 2002 | Kyong Province Korea | NIRSystems 5000 | 400-2500 | Dry | | <2 | 148 | 227-3676 | | 0.83 | 329 | 430 |
| Bray P$^{(I)}$ mg (Kg$^{-1}$) | Ryu *et al.* | 2002 | Kyong Province Korea | NIRSystems 5000 | 400-2500 | Dry | | <2 | 148 | 16.9-912 | | 0.67 | 146 | 162 |
| Olsen P (mg Kg$^{-1}$) | Ryu *et al.* | 2002 | Kyong Province Korea | NIRSystems 5000 | 400-2500 | Dry | | <2 | 148 | 4.2-317 | | 0.64 | 55 | 54 |
| Truag P (mg Kg$^{-1}$ | Ryu *et al.* | 2002 | Kyong Province Korea | NIRSystems 5000 | 400-2500 | Dry | | <2 | 148 | 0.0-718 | | 0.58 | 163 | 152 |
| Bray II P (mg Kg$^{-1}$) | Ludwig *et al.* | 2002 | Victoria Australia | NIRSystems 6500 | 400-2500 | Dry | 0-300 | Finely Ground | 120 | 0.5-8.7 | 0.48 | 048 | 0.5 | 1.6 |
| Olsen P (mg Kg$^{-1}$) | Ludwig *et al.* | 2002 | Victoria Australia | NIRSystems 6500 | 400-2500 | Dry | 0-300 | Finely Ground | 120 | 0.1-5.9 | | 0.53 | 1.2 | 1.0 |
| Olsen P (mg Kg$^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field spec | 350-2500 | Dry | 0-200 | <2 | 767 | 0.3-187 | | 0.32 | | 17 |
| P (ext) (g Kg$^{-1}$) | Udelhoven *et al* | 2002 | SW Germany | ASD Field spec (II) | 400-2500 | Dry | 0-300 | <2 | 114 | | | 0.54 | 0.05 | |
| Olsen P (mg Kg$^{-1)}$ | Confalonieri and Odoardi | 2003 | Cropping soils Italy | NIRSystems 5000 | 110-2500 | Dry | 0-300 | Finely Ground | 142 | | | 0.72 | 6.7 | 7.1 |

**Table 2.12:** Study references of soil Phosphorous (P)

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Olsen P (mg $Kg^{-1}$) | Groenigen *et al* | 2003 | Rice field California USA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 100 | 5.9-17.7 | | 0.71 | 1.6 | 1.9 |

**Table 2.13:** Study references of soil magnesium (Mg)

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable Mg | Krischenko *et al.* | 1992 | USSR | NIRSystems 6500 & 4500 | 1100-2500 | Dry | | | 88 | | | 0.81 | | 0.35 |
| Mg Melich III (c mol $Kg^{-1}$ ) | Couillard *et al* | 1997 | Michigan USA | NIRSystems 6500 & 4500 | 1100-2500 | Wet | 0-50 | Intact Cores | 48 | 0.7-6. 25 | 0.11 | 0.36 | 0.34 | |
| Mg Melich III (c mol $Kg^{-1}$ ) | Couillard *et al* | 1997 | Michigan USA | NIRSystems 6500 & 4500 | 1100-2500 | Dry | 0-50 | <2 | 48 | 0.7-6.25 | 0.11 | 0.50 | 0.38 | |
| Mg (mg $Kg^{-1}$) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Dry | 0-1200 | Fine Ground | 147 | | | 0.94 | | 194 |
| Mg (mg $Kg^{-1}$) | Malley and Currie | 1999 | Manitoba Canada | NIRSystems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | | 0.90 | | 194 |
| Total Mg (mg $Kg^{-1}$) | Malley *et al* | 1999 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | 0-10 (metres) | <0.5 | 25 | 14.5-61.2 | | 0.99 | | 2.1 |
| Mg Melich III (mg $Kg^{-1}$) | Chang *et al* | 2001 | USA, 4 major areas | NIRSystems 6500 | 200-2500 | Dry | 0-200 | <8 | 784 | 17-2886 | | 0.71 | 144 | |
| Exch.Mg (c mol $Kg^{-1}$) | Chang *et al* | 2001 | USA, 4 major areas | NIRSystems 6500 | 200-2500 | Dry | 0-200 | <8 | 742 | 0.1-17.6 | | 0.68 | 1.3 | |
| Available (mg $Kg^{-1}$) | Malley *et al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Dry | | Field moist | 46 | 142-2740 | | 0.85 | | 248 |
| Available (mg $Kg^{-1}$) | Malley *et al* | 2002 | Winnipeg Canada | NIRSystems 6500 | 400-2500 | Wet | | Drying & grinding | 46 | 142-2740 | | 0.92 | | 207 |
| Exch.Mg (cmol $kg^{-1}$) | Dunn *et al* | 2002 | Riverine P. SE Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 558 | 0.53-13.2 | | 0.91 | 0.88 | 1.05 |
| Total Mg (mg $g^{-1}$) | Chodal *et al* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 | Finely ground | 406 | 0.3-22.8 | | 0.44 | 1.6 | 2.3 |
| Exch.Mg (cmol $Kg^{-1}$) | Shepherd and Walsh | 2002 | Central Africa (7 countries) | Field spec | 350-2500 | Dry | 0-200 | <2 | 739 | 0.01-17.9 | | 0.91 | | 0.8 |

**Table 2.13:** Study references of soil magnesium (Mg)

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mg (Ext) (g $Kg^{-1}$) | Udelhoven *et al* | 2002 | SW Germany | ASD Field Spec (II) | 400-2500 | Dry | 0-300 | <2 | 114 | | | 0.71 | 0.03 | |
| Total Mg (g $Kg^{-1}$) | Udelhoven *et al* | 2002 | SW Germany | ASD Field Spec (II) | 400-2500 | Dry | 0-300 | <2 | 52 | 7.5-80 | | 0.91 | 38.4 | |
| Exch.Mg (mmolKg) | Islam *et al* | 2003 | NSW&QLD Australia | Cary 500 | 250-2500 | Dry | Surface and sub-surface | <2 | 161 | 0.4-94.8 | | 0.73 | 10.0 | 12.3 |
| Exch. Mg (cmol $Kg^{-1}$) | Groenigen *et al* | 2003 | Rice field Calif., USA | NIR System 6500 | 400-2500 | Dry | 0-100 | Finely ground | 100 | 8.3-16.1 | | 0.82 | 0.69 | 0.61 |

**Table 2.14:** Study references of soil sodium (Na)

| Test | Reference | Year | Location | Instrument | $\lambda$ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Na (mg Kg$^{-1}$) | Malley and Curric | 1999 | Manitoba Canada | NIR Systems 6500 | 400-2500 | Dry | 0-1200 | Fine ground | 147 | | | 0.54 | | 82.9 |
| Na (mg Kg$^{-1}$) | Malley and Curric | 1999 | Manitoba Canada | NIR Systems 6500 | 400-2500 | Wet | 0-1200 | As is state | 147 | | | 0.61 | | 110 |
| Total Na (mg g$^{-1}$) | Malley *et al.* | 1999 | Winnipeg Canada | NIR Systems 6500 | 400-2500 | Dry | 0-10 (metres) | <0.5 | 27 | 0.10-1.93 | | 0.90 | | 0.21 |
| Exch. Na (Cmol Kg$^{-1}$) | Chang *et al.* | 2001 | USA (4 major areas) | NIR Systems 6500 | 400-2500 | Dry | 0-300 | <8 | 439 | 0.1-1.8 | | 0.09 | | 0.13 |
| Available Na (mg Kg$^{-1}$) | Malley *et al.* | 2002 | Winnipeg Canada | NIR Systems 6500 | 400-2500 | Wet | | Field moist "as is state" | 46 (prediction) | 16-1330 | | 0.61 | | 110 |
| Available Na (mg Kg$^{-1}$) | Malley *et al.* | 2002 | Winnipeg Canada | NIR Systems 6500 | 400-2500 | Dry | | Drying and grinding | 46 (prediction) | 16-1330 | | 0.54 | | 82.9 |
| Exch Na (cmol Kg$^{-1}$) | Dunn *et al* | 2002 | Riverine Plain South Australia | NIR Systems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 550 | 0.04-3.91 | | 0.69 | 0.45 | 0.48 |
| Total Na (mg g$^{-1}$) | Chodak *et al* | 2002 | Solling Germany | NIR Systems 6500 | 400-2500 | Dry | 0-200 (different depths) | Finely ground | 406 | 0.07-0.31 | | 0.81 | 0.02 | 0.02 |
| Exch. Na (m mol Kg$^{-1}$) | Islam *et al.* | 2003 | NSW and QLD Australia | Cary 500 | 250-2500 | Dry | Surface and subsurface | <2 | 161 | 0.2-108.6 | | 0.46 | 19.4 | 14.6 |

**Table 2.15:** Study references of soil copper (Cu)

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range (%)** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu Melich III (mg $Kg^{-1}$) | Chang *et al.* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 762 | 0.1-373 | | 0.25 | 5.4 | |
| Cu (mg $Kg^{-1}$) | Moron and Cozzolino | 2003 | Agric Soils Uruguay | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 0.6-31.3 | | 0.87 | 0.7 | |

**Table 2.16:** Study references of soil Manganese (Mn)

| **Test** | **Reference** | **Year** | **Location** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Soil Depth (mm)** | **Soil Fraction (mm)** | **No.** | **Range (%)** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Total Mn (mg $g^{-1}$) | Chodak *et al.* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 (different depths) | Finely ground | 406 | 0.0-3.0 | | 0.85 | 0.3 | 0.4 |
| Total Mn (g $Kg^{-1}$) | Udelhoven *et al.* | 2002 | S W Germany | ASD Field Spec (II) | 400-2500 | Dry | 0-300 | <2 | 52 | 0.8-2.0 | | 0.81 | 0.19 | |
| Mn (mg $Kg^{-1}$) | Moron and Cozzolino | 2003 | Agric Soils Uruguay | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 94-878 | | 0.72 | 83 | |

**Table 2.17:** Study references of soil Zinc (Zn)

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zn Melich III (mg Kg$^{-1}$) | Chang *et al.* | 2001 | USA (4 major areas) | NIRSystems 6500 | 400-2500 | Dry | 0-300 | <8 | 761 | 0.3-130.6 | | 0.44 | 15.3 | |
| Total Zn (mg Kg$^{-1}$) | Kooistra *et al.* | 2001 | River Plains Netherlands | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <2 | 69 | 0-725 | | 0.90 | 81 | 65 |
| Zn (mg Kg$^{-1}$) | Moron and Cozzolino | 2003 | Agric Soils Uruguay | NIRSystems 6500 | 400-2500 | Dry | 0-150 | <2 | 332 | 2.3-55 | | 0.72 | 1.2 | |

**Table 2.18:** Study references of soil Aluminium (Al)

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exch. Al (cmol Kg $^{-1}$) | Dunn *et al.* | 2002 | Riverine Plain South Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 220 | 0.1-1.5 | | 0.60 | 0.22 | 0.23 |
| Total A*l* (%) | Dunn *et al.* | 2002 | Riverine Plain South Australia | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <0.5 | 220 | 0.4-22.8 | | 0.62 | 2.90 | 2.85 |
| Total A*l* (mg g$^{-1}$) | Chodak *et al.* | 2002 | Solling Germany | NIRSystems 6500 | 400-2500 | Dry | 0-200 (diff. depths) | Finely ground | 406 | 1.2-19.7 | | 0.96 | 1.0 | 1.1 |

**Table 2.19:** Study references of soil cadmium (Cd)

| Test | Reference | Year | Location | Instrument | λ (nm) | Dry or Wet | Soil Depth (mm) | Soil Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Total Cd (mg-Kg$^{-1)}$) | Kooistra *et al.* | 2001 | River Plains Netherlands | NIRSystems 6500 | 400-2500 | Dry | 0-100 | <2 | 69 | 0.0-5 | | 0.88 | 0.68 | 0.44 |

**Table 2.20:** Study references of plant moisture or dry matter (DM))

| **Test** | **Reference** | **Year** | **Instrument** | **λ (nm)** | **Dry or Wet** | **Plant Species** | **Plant Fraction (mm)** | **No.** | **Range (%)** | **$S_r$ (chem)** | **$r^2$** | **RMSECV** | **RMSEP** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Moisture (%) | Redshaw et al. | 1986 | Neotec 6100 | | | Legume, grass and legume-grass mixture | <1mm | 82 | 2.2-6.0 | | 0.90 | 0.3 | 0.2 |
| DM (%) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Wet | Mushroom compost | <0.5 | 190 | 26.3-36.2 | 1.0 | 0.92 | 0.9 | |
| DM (%) | Fontaneli *et al* | 2002 | NIR Systems 6500 | 1100-2500 | Dry | Corn silage | <1 | 246 | 8.61-99.2 | | 0.99 | 0.22 | 0.27 |

**Table 2.21:** Study references of plant nitrogen (N)

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N (%) | Rosa and Pandeya | 1981 | Infra Alyzer | | Dry | Cured tobacco lamina (29 lines) | <40 mesh screen | | 1.9-3.4 | | 0.76 | | |
| N (%) | Cuidad *et al.* | 1983 | Technician Infra alyzer 400R | | Dry | Natural grassland | <1 | 93 | 2.1-4.2 | | 0.87 | | 0.16 |
| N (%) | McClure | 1984 | Cary 17 | | Freeze dried | Tobacco (3 species) | | 152 | 1.59-5.20 | | 0.98 | 0.15 | |
| N (%) | Batten *et al* | 1991 | Infra Alyzer 500 | 1100-2500 | Dry | Leaves of rice plant | <0.5 | 146 | 0.8-3.50 | | 0.97 | 0.12 | 0.15 |
| N (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Wheat | | 93 | 0.2-1.85 | | 0.97 | 0.08 | 0.07 |
| N (%) | McLillan et al. | 1991 | | | | | | 255 | 0.45-2.78 | | 0.96 | 0.12 | |
| N (%) | Yoshikawa et al | 1991 | | 700-2500 | Dry | Leaves of rice plant | | | 0.53-3.55 | | 0.73 | 0.36 | 0.38 |
| N (%) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 0.68-2.90 | | 0.98 | 0.08 | 0.08 |
| N (%) | Norris | 1998 | | | Dry | | | | | | 0.99 | 0.17 | 0.17 |
| N (%) | Norris | 1998 | | | Wet | | | | | | 0.93 | 0.42 | 0.42 |
| N (%) | Meurens | 1998 | | | Dry | | | | | | 0.99 | 0.13 | 0.20 |
| | Meurens | 1998 | | | Wet | | | | | | 0.98 | 0.31 | 0.39 |
| N (%) | Gillion *et al* | 1999 | NIR Systems 6500 | 400-2500 | Dry | Growing, falling litter pine needles | <1 | 525 | 0.39-1.65 | | 0.94-0.99 | 0.25-0.38 | 0.42-0.71 |
| N(%) | Kays *et al* | 2000 | NIR Systems 6500 | 1100-2500 | Dry | Cereal Foods | <0.5 | 222 | 0.41-3.31 | 0.034 | 0.97 | 0.09 | 0.08 |
| N (%) | Rodriguez and Miller | 2000 | NIR Systems 6500 | 400-2500 | Dry | Bermuda Grasses | <1 | 200 | 2.0-4.0 | | 0.92 | | |

**Table 2.21:** Study references of plant nitrogen (N)

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N (%) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 189 | 1.98-3.01 | 0.03 | 0.95 | 0.08 | 0.17 |
| N (%) | Suehara | 2001 | NIRSystems 6500 | 400-2500 | Wet | Tofu compost |  | 108 | 0.7-2.6 |  | 0.94 | 0.07 | 0.08 |
| N (%) | Meurens | 1998 |  |  | Wet |  |  |  |  |  |  |  |  |
| N (%) | McClure *et al* | 2002 | NIR Systems 6500 | 400-2500 | Dry | Fescue (Kentucky 31) | <1 |  | 1.0-6.5 |  | 0.97 | 0.27 | 0.29 |
| N (%) | McClure *et al* | 2002 | NIRSystems 6500 | 400-2500 | Wet | Fescue (Kentucky 31) | <1 |  | 0.9-6.6 |  | 0.88 | 0.55 | 0.97 |
| N (%) | Moron and Cozzolino | 2002 | NIR Systems 6500 | 400-2500 | Dry | Alfalfa and white clover | <1 | 315 | 2.1-7.2 |  | 0.98 | 0.12 |  |
| N (%) | Shepherd *et al* | 2003 | Fieldspec | 350-2500 | Dry | 83 species | <1 | 319 | 0.6-5.0 |  | 0.85 |  | 0.50 |

**Table 2.22:** Study references of plant nitrate-N (N-$NO_3$).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N-$N0_3$ (%) | McClure | 1984 | Cary 17 |  | Freeze dried | Tobacco (3 species) |  | 152 | 0.03-0.33 |  | 0.91 | 0.03 |  |

**Table 2.23:** Study references of plant phosphate (P).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P (%) | Shenk *et al.* | 1981 | Neotec 6100 | 1200-2400 | Dry | Forage, grain, many species, maturity and location |  | 200 |  |  | 0.76 | 0.04 | 0.04 |
| P (%) | Cuidad *et al.* | 1983 | Technician Infra alyzer 400R |  | Dry | Natural grassland | <1 | <1 | 0.06-0.36 |  | 0.69 |  | 0.02 |
| P (%) | McClure | 1984 | Cary 17 |  | Freeze dried | Tobacco (3 species) |  | 152 | 0.23-0.44 |  | 0.95 | 0.02 |  |
| P (%) | Redshaw et al. | 1986 | Neotec 6100 | 1958 | Dry | Legume, grass and legume-grass mixture | <1mm | 82 | 0.11-0.30 |  | 0.71 | 0.02 | 0.02 |
| P (%) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 0.19-0.47 |  | 0.79 | 0.03 | 0.01 |
| P (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Forage | <1mm | 34 | 0.6-2.2 |  | 0.74 | 0.27 | 0.49 |
| P (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Sunflower | <1mm | 45 | 0.5-0.9 |  | 0.90 | 0.02 | 0.02 |
| P (%) | Ferri *et al.* | 1991 |  | 1100-2500 | Dry | Wheat |  | 76 | 0.05-0.30 |  | 0.94 | 0.01 | 0.01 |
| P (%) | DeBoevur *et al* | 1994 | Infra Alyzer 500 | 1100-2500 | Dry | 19 vegetable feeds tuffs | <0.75 | 238 | 0.22-1.37 | 0.009% | 0.90 |  | 0.08 |
| P (%) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 0.09-0.37 |  | 0.70 | 0.03 | 0.03 |
| P (%) | Gillion *et al* | 1999 | NIR Systems 6500 | 400-2500 | Dry | Growing, falling litter pine needles | <1 | 525 | 0.03-0.15 |  | 0.94-0.99 | 0.002-0.005 | 0.006-0.008 |
| P (%) | Ramos *et al* | 1999 | Technicon InfraAlyzer 500 | 1100-2500 | Dry | Semi-arid grasses & legumes | <1 | 92 | 0.10-0.36 |  | 0.88 | 0.02 | 0.02 |
| P (%) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 142 | 0.69-1.45 | 0.03 | 0.84 | 0.06 |  |

**Table 2.23:** Study references of plant phosphate (P).

| Test | Reference | Year | Instrument | $\lambda$ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P (%) | Thygisen *et al* | 2001 | NIR Systems 6500 | 700-2500 | Dry | Potato | | 97 | 0.029-0.11 | | | 0.006% | |
| P (%) | Lavrencic et al | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 0.16-0.55 | | 0.88 | 0.04 | |
| P (%) | Chen *et al* | 2002 | NIR Systems 6500 | 400-2500 | Dry | Sugar cane leaves | <1 | 302 | 0.012-0.35 | | 0.78 | 0.02 | 0.02 |
| P (%) | Fontaneli *et al* | 2002 | NIR Systems 6500 | 1100-2500 | Dry | Corn silage | <1 | 246 | 0.10-0.26 | | 0.92 | 0.01 | 0.01 |
| P (%) | Moron and Cozzolino | 2002 | NIR Systems 6500 | 400-2500 | Dry | Alfalfa and white clover | <1 | 316 | 1.9-5.7 | | 0.81 | 0.35 | |
| P (%) | Chen *et al* | 2003 | NIR Systems 6500 | 400-2500 | Dry | Sugar cane leaves | <1 | 307 | 0.08-0.35 | | 0.80 | 0.02 | 0.02 |
| P (%) | Miller and Thomas | 2003 | NIR Systems 5000 | 400-2500 | Dry | Bermuda grass | <1 | 388 | | | <0.71 | | |
| P (%) | Halgerson et al | 2004 | NIR Systems | 400-2500 | Dry | Alfaalfa | <1 | 388 | | 0.91 | | 0.03 | |

**Table 2.24:** Study references of plant potassium (K).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (□hem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K (%) | Shenk *et al.* | 1981 | Neotec 6100 | 1200-2400 | Dry | Forage, grain, many species, maturity and location | | 200 | | | 0.64 | 0.37 | 0.34 |
| K (%) | McClure | 1984 | Cary 17 | | Freeze dried | Tobacco (3 species) | | 152 | 1.81-4.20 | | 0.96 | 0.16 | |
| K (%) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 1.90-3.90 | | 0.88 | 0.26 | 0.31 |
| K (%) | Yoshikawa *et al* | 1991 | | 700-2500 | Dry | Leaves of rice plant | | | 1.44-3.75 | | 0.58 | 0.38 | 0.16 |
| K (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Sunflower | <1mm | 42 | 0.3-1.2 | | 0.85 | 0.05 | 0.04 |
| K (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Forage | <1mm | 35 | 1.0-1.7 | | 0.76 | 0.11 | 0.20 |
| K (%) | Ferri *et al.* | 1991 | | 1100-2500 | Dry | Wheat | | 70 | 0.4-3.60 | | 0.93 | 0.18 | 0.17 |
| K (%) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 0.48-2.42 | | 0.78 | 0.19 | 0.20 |
| K (%) | Hallett and Hornbeck | 1997 | NIR Systems 6500 | 400-2500 | Dry | White pine and red oak | <1 | 470 | 0.17-1.28 | | 0.88 | 0.08 | 0.10 |
| K (%) | Ciavarella and Batten | 1998 | NIR Systems 6500 | 1100-2500 | Dry | Orange Leaves | <0.5 | 89 | 0.44-2.07 | | 0.94 | 0.11 | 0.17 |
| K (%) | Ciavarella and Batten | 1998 | NIR Systems 6500 | 1100-2500 | Dry | Grape Petioles | <0.5 | 51 | 2.2-4.8 | | 0.99 | 0.08 | 0.18 |
| K (%) | Ciavarella and Batten | 1998 | NIR Systems 6500 | 1100-2500 | Dry | Grape Leaves | <0.5 | 91 | 0.59-1.9 | | 0.93 | 0.10 | 0.12 |
| K (%) | Ciavarella and Batten | 1998 | NIR Systems 6500 | 1100-2500 | Dry | Rice leaves | <0.5 | 94 | 2.3-4.5 | | 0.95 | 0.13 | 0.18 |
| K (%) | Ramos *et al* | 1999 | Technicon InfraAlyzer 500 | 1100-2500 | Dry | Semi-arid grasses & legumes | | 95 | 0.48-2.43 | | 0.87 | 0.17 | 0.17 |

**Table 2.24:** Study references of plant potassium (K).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (□hem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K (%) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 142 | 1.44-3.2 | 0.05 | 0.95 | 0.10 | 0.27 |
| K (%) | Lavrencic et al | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 1.31-4.38 |  | 0.94 | 0.21 |  |
| K (%) | Fontaneli *et al* | 2002 | NIRSystems 6500 | 1100-2500 | Dry | Corn silage | <1 | 246 | 0.61-2.14 |  | 0.94 | 0.08 | 0.06 |
| K (%) | Moron and Cozzolino | 2002 | NIR Systems 6500 | 400-2500 | Dry | Alfalfa and white clover | <1 | 302 | 0.89-3.9 |  | 0.90 | 0.23 |  |
| K (%) | Miller and Thomas | 2003 | NIR Systems 5000 | 400-2500 | Dry | Bermuda grass | <1 | 388 |  |  | <0.39 |  |  |
| K (%) | Halgerson *et al* | 2004 | NIR Systems 5000 | 400-2500 | Dry | Alfaalfa | <1 | 388 |  | 0.86 |  | 0.16 |  |

**Table 2.25:** Study references of plant sulphur (S).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (□hem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S (%) | Cuidad *et al.* | 1983 | | | | | | | 0.04-0.42 | | 0.67 | | 0.02 |
| S (%) | McClure | 1984 | Cary 17 | | Freeze dried | Tobacco (3 species) | | 152 | 0-0.21 | | 0.95 | 0.01 | |
| S (%) | Moron and Cozzolino | 2002 | NIR Systems 6500 | 400-2500 | Dry | Alfalfa and white clover | <1 | 296 | 2.1-7.2 | | 0.83 | 0.34 | |
| S (%) | Cozzolino and Moron | 2003 | NIR Systems 6500 | 400-2500 | Dry | White clover and cucerne | <1 | 332 | 0.02-0.72 | | 0.86 | 0.03 | 0.06 |
| S (%) | Halgerson *et al* | 2004 | NIR Systems | 400-2500 | Dry | Alfaalfa | <1 | 388 | | 0.60 | | 0.06 | |

**Table 2.26:** Study references of plant calcium (Ca).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (□hem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca (%) | Shenk *et al.* | 1981 | Neotec 6100 | 1200-2400 | Dry | Forage, grain, many species, maturity and location | | 200 | | | 0.91 | 0.13 | 0.16 |
| Ca (%) | McClure | 1984 | Cary 17 | | Freeze dried | Tobacco (3 species) | | 152 | 0.57-3.5 | | 0.99 | 0.12 | |
| Ca (%) | Redshaw *et al.* | 1986 | Neotec 6100 | 195 | | Legume, grass and legume-grass mixture | <1mm | 82 | 0.28-2.28 | | 0.87 | 0.18 | 0.15 |
| Ca (%) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 0.30-0.99 | | 0.82 | 0.10 | 0.04 |
| Ca (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Forage | <1mm | 34 | 0.12-0.80 | | 0.72 | 0.03 | 0.05 |
| Ca (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Sunflower | <1mm | 42 | 0.10-0.50 | | 0.82 | 0.05 | 0.05 |
| Ca (%) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 0.16-1.73 | | 0.88 | 0.09 | 0.10 |
| Ca (%) | Hallett and Hornbeck | 1997 | NIR Systems 6500 | 400-2500 | Dry | White pine and red oak | <1 | 468 | 0.07-0.95 | | 0.88 | 0.07 | 0.07 |
| Ca (%) | Ramos *et al* | 1999 | Technicon InfraAlyzer 500 | 1100-2500 | Dry | Semi-arid grasses & legumes | | 94 | 0.22-1.44 | | 0.91 | 0.08 | 0.09 |
| Ca (%) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 142 | 2.48-5.19 | 0.13 | 0.86 | 0.28 | |
| Ca (%) | Lavrencic et al | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 0.14-2.12 | | 0.96 | 0.10 | |
| Ca (%) | Fontaneli *et al* | 2002 | NIR Systems 6500 | 1100-2500 | Dry | Corn silage | <1 | 246 | 0.02-0.67 | | 0.93 | 0.03 | 0.03 |
| Ca (%) | Moron and Cozzolino | 2002 | NIR Systems 6500 | 400-2500 | Dry | Alfalfa and white clover | <1 | 322 | 0.98-4.0 | | 0.95 | 0.13 | |

**Table 2.26:** Study references of plant calcium (Ca).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (□hem.) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca (%) | Miller and Thomas | 2003 | NIR Systems 5000 | 400-2500 | Dry | Bermuda grass | <1 | 388 | | | <0.72 | | |
| Ca (%) | Halgerson *et al* | 2004 | NIR Systems 5000 | 400-2500 | Dry | Alfaalfa | <1 | 388 | | 0.88 | | 0.16 | |

**Table 2.27:** Study references of plant magnesium (Mg).

| Test | Reference | Year | Instrument | $\lambda$ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mg (%) | McClure | 1984 | Cary 17 | | Freeze dried | Tobacco (3 species) | | 152 | 0.31-0.83 | | 0.98 | 0.03 | |
| Mg (%) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 0.22-0.70 | | 0.73 | 0.06 | 0.02 |
| Mg (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Forage | <1mm | 36 | 0.03-0.30 | | 0.77 | 0.03 | 0.06 |
| | | | | | | | | | | | | | |
| Mg (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Sunflower | <1mm | 43 | 0.12-0.50 | | 0.82 | 0.04 | - |
| Mg (%) | Ramos *et al* | 1999 | Technicon InfraAlyzer 500 | 1100-2500 | Dry | Semi-arid grasses & legumes | | 91 | 0.05-0.20 | | 0.80 | 0.02 | 0.02 |
| Mg (%) | Yoshikawa et al | 1991 | | 700-2500 | Dry | Leaves of rice plant | | | 0.04-0.178 | | 0.78 | 0.01 | 0.02 |
| Mg (%) | Smith *et al* | 1991 | NIR Systems 6250 | 1100-2500 | Dry | Perennial ryegrass | <1 | 72 | 0.15-0.37 | | 0.68 | 0.04 | 0.02 |
| Mg (%) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 0.07-0.26 | | 0.84 | 0.02 | 0.02 |
| Mg (%) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 142 | 0.35-0.70 | 0.02 | 0.73 | 0.03 | |
| Mg (%) | Hallett and Hornbeck | 1997 | NIR Systems 6500 | 400-2500 | Dry | White pine and red oak | <1 | 470 | 0.04-0.24 | | 0.81 | 0.02 | 0.02 |
| Mg (%) | Lavrencic *et al* | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 0.07-0.48 | | 0.89 | 0.03 | |
| Mg (%) | Fontaneli *et al* | 2002 | NIR Systems 6500 | 1100-2500 | Dry | Corn silage | <1 | 246 | 0.12-0.32 | | 0.92 | 0.01 | 0.01 |
| Mg (%) | Moron and Cozzolino | 2002 | NIR Systems 6500 | 400-2500 | Dry | Alfalfa and white clover | <1 | 319 | 0.17-0.46 | | 0.75 | 0.03 | |
| Mg (%) | Miller and Thomas | 2003 | NIR Systems 5000 | 400-2500 | Dry | Bermuda grass | <1 | 388 | | | <0.37 | | |
| Mg (%) | Halgerson *et al* | 2004 | NIR Systems 5000 | 400-2500 | Dry | Alfaalfa | <1 | 388 | | 0.66 | | 0.25 | |

**Table 2.28:** Study references of plant sodium (Na).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Na (mg/kg) | McClure | 1984 | Cary 17 |  | Freeze dried | Tobacco (3 species) |  | 152 | 96-387 |  | 0.95 | 20 |  |
| Na (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Sunflower | <1mm | 37 | 0.01-0.10 |  | 0.67 | 0.02 | 0.02 |
| Na (%) | Ferri *et al.* | 1991 | InfrAlyzer 450 | 1100-2500 | Dry | Forage | <1mm | 30 | 0.07-0.30 |  | 0.26 | 0.03 | 0.03 |
| Na (%) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 0.005-0.73 |  | 0.79 | 0.06 | 0.07 |
| Na (%) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 190 | 0.02-0.04 | 0.01 | 0.83 | 0.003 |  |
| Na (%) | Lavrencic et al | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 0.005-0.045 |  | 0.52 | 0.006 |  |
| Na (%) | Cozzolino and Moron | 2003 | NIR Systems 6500 | 400-2500 | Dry | White clover and cucerne | <1 | 332 | 0.02-0.70 |  | 0.83 | 0.08 | 0.12 |
| Na (%) | Halgerson et al | 2004 | NIRSystems 5000 | 400-2500 | Dry | Alfaalfa | <1 | 388 |  | 0.16 |  | 0.05 |  |

**Table 2.29.:** Study references of plant boron (B).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B (mg/kg) | McClure | 1984? | Cary 17 | 900-2600 | Freeze dried | Tobacco (3 species) |  | 152 | 10-24 |  | 0.94 | 1.3 |  |
| B (mg $Kg^{-1}$) | Cozzolino and Moron | 2003 | NIR Systems 6500 | 400-2500 | Dry | White clover and cucerne | <1 | 332 | 21-66 |  | 0.80 | 4.4 | 4.2 |
| B (mg$Kg^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 73 |  |  | 0.86 | 13 |  |

**Table 2.30.:** Study references of plant chloride (Cl)

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cl (%) | McClure | 1984? | Cary 17 |  | Freeze dried | Tobacco (3 species) |  | 152 | 0.07-0.73 |  | 0.89 | 0.07 |  |

**Table 2.31.:** Study references of plant copper (Cu).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu (mg/kg) | McClure | 1984? | Cary 17 | | Freeze dried | Tobacco (3 species) | | 152 | 10-90 | | 0.92 | 1.4 | |
| Cu (mg $Kg^{-1}$) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 3.5-8.5 | | 0.46 | 0.8 | 0.6 |
| Cu (mg $Kg^{-1}$) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 1.3-10.0 | | 0.82 | 0.8 | 0.9 |
| Cu (mg $Kg^{-1}$) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 190 | 0.03-0.12 | 0.01 | 0.85 | 0.008 | |
| Cu (mg $Kg^{-1}$) | Cozzolino and Moron | 2003 | NIR Systems 6500 | 400-2500 | Dry | White clover and cucerne | <1 | 332 | 5-31 | | 0.76 | 0.83 | 2.3 |
| Cu ($mgKg^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 68 | | | 0.39 | 2.3 | |

**Table 2.32.:** Study references of plant Iron (Fe).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe (mg/kg) | McClure | 1984 | Cary 17 | | Freeze dried | Tobacco (3 species) | | 152 | 13-74 | | 0.91 | 9.0 | |
| Fe (mg $Kg^{-1}$) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 200-3900 | | 0.69 | 200 | 150 |
| Fe (mg $Kg^{-1}$) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 38-203 | | 0.74 | 15 | 16 |
| Fe (mg $Kg^{-1}$) | Hallett and Hornbeck | 1997 | NIR Systems 6500 | 400-2500 | Dry | White pine and red oak | <1 | 460 | 4-140 | | 0.15 | 22 | 23 |
| Fe (mg $Kg^{-1}$) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 190 | 0.86-2.79 | 0.08 | 0.89 | 0.18 | |
| Fe (mg $Kg^{-1}$) | Cozzolino and Moron | 2003 | NIR Systems 6500 | 400-2500 | Dry | White clover and cucerne | <1 | 332 | 66-861 | | 0.57 | 45.7 | 55.5 |
| Fe ($mgKg^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 62 | | | 0.52 | 11 | |

**Table 2.33.:** Study references of plant manganese (Mn).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mn (%) | McClure | 1984 | Cary 17 |  | Freeze dried | Tobacco (3 species) |  | 152 | 16-94 |  | 0.95 | 6.1 |  |
| Mn (mg $Kg^{-1}$) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 42-280 |  | 0.46 | 19 | 14 |
| Mn (mg $Kg^{-1}$) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 38-813 |  | 0.74 | 50 | 54 |
| Mn (mg $Kg^{-1}$) | Hallett and Hornbeck | 1997 | NIR Systems 6500 | 400-2500 | Dry | White pine and red oak | <1 | 468 | 76-4520 |  | 0.78 | 373 | 394 |
| Mn (mg $Kg^{-1}$) | Sharma *et al* | 2000 | NIR Systems 6500 | 400-2500 | Dry | Mushroom compost | <0.5 | 140 | 0.27-0.57 | 0.01 |  |  |  |
| Mn (mg $Kg^{-1}$) | Lavrencic et al | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 17-311 |  | 0.42 | 56 |  |
| Mn (mg $Kg^{-1}$) | Cozzolino and Moron | 2003 | NIR Systems 6500 | 400-2500 | Dry | White clover and cucerne | <1 | 332 | 32-282 |  | 0.78 | 20.9 | 33.7 |
| Mn ($mgKg^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 70 |  |  | 0.37 | 10 |  |

**Table 2.34.:** Study references of plant Zinc (Zn).

| Test | Reference | Year | Instrument | $\lambda$ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Zn (mg/kg) | McClure | 1984 | Cary 17 |  | Freeze dried | Tobacco (3 species) |  | 152 | 13-74 |  | 0.94 | 4.6 |  |
| Zn (mg $Kg^{-1}$) | Clark *et al.* | 1987 | Pacific Scientific 6350 | 1100-2500 | Dry | Wheat Grass | <1mm | 202 | 13-35 |  | 0.51 | 2.7 | 4.0 |
| Zn (mg $Kg^{-1}$) | de Aldana | 1995 | Infra Alyzer 500 | 1100-2500 | Dry | Semi natural grasslands | <0.5 | 170 | 10-50 |  | 0.72 | 3.8 | 3.4 |
| Zn (mg $Kg^{-1}$) | Lavrencic et al | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 4.4-38 |  | 0.64 | 4.4 |  |
| Zn (mg $Kg^{-1}$) | Cozzolino and Moron | 2003 | NIR Systems 6500 | 400-2500 | Dry | White clover and cucerne | <1 | 332 | 19-417 |  | 0.80 | 10.6 | 46.6 |
| Zn (mg$Kg^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 70 |  |  | 0.32 | 3 |  |

**Table 2.35.:** Study references of plant Aluminium (Al), cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), selenium (Se) and silicon (Si).

| Test | Reference | Year | Instrument | λ (nm) | Dry or Wet | Plant Species | Plant Fraction (mm) | No. | Range (%) | $S_r$ (chem) | $r^2$ | RMSECV | RMSEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al (mg Kg$^{-1}$) | Hallett and Hornbeck | 1997 | NIR Systems 6500 | 400-2500 | Dry | White pine and red oak | <1 | 465 | 11-458 |  | 0.82 | 42 | 44 |
| Al (mgKg$^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 60 |  |  | 0.76 | 11 |  |
| Cd (mgKg$^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 71 |  |  | 0.19 | 0.03 |  |
| Cr (mgKg$^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 70 |  |  | 0.56 | 0.06 |  |
| Ni (mgKg$^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 67 |  |  | 0.53 | 0.6 |  |
| Pb (mgKg$^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 66 |  |  | 0.54 | 0.04 |  |
| Se (mg Kg$^{-1}$) | Lavrencic et al | 2002 | Perkim Elmer FT NIR | 1000-2500 | Dry | Six grass species | <1 | 100 | 17-49 |  | 0.19 | 6.5 |  |
| Si (mgKg$^{-1}$) | Halgerson *et al* | 2004 | NIR Systems 6500 | 400-2500 | Dry | Alfaalfa | <1 | 41 |  |  | 0.87 | 53 |  |

# Chapter 3: Methods for Soil and Plant, NIR Instrumentation and Chemometrics.

- *3.1 Outline*
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- *3.3 Sample presentation*
- *3.4 NIR data preparation, data analysis, chemometrics and calibration development*
    - *3.4.1 Data preparation*
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## 3.1 Outline

This chapter outlines the methods, procedures and analytical instruments used for this study. It covers the NIR instrumentation used along with description of how soil and plant samples were prepared and presented to the NIR instrument. It covers how the wet chemistry base tests results were obtained and the analytical procedures and instrumentation used in obtaining them. A discussion on NIR data analysis, chemometrics and calibration development and validation is given. A brief method and procedure for the nitrate-N test, N test glasshouse experiment and sulphur test are also presented in this chapter (detailed descriptions are given in later, respective chapters). An outline of the sub-sections in this chapter is given below.

- The instrumentation section (3.2) gives the details of the KESNIR diode array instrument.
- The sample presentation section (3.3) covers how samples were presented to the NIR spectrometer.
- The NIR method and calibration development section (3.4) gives an account of procedures followed, in order to obtain robust calibrations for soil and plant tests. The section discusses chemometrics, data analysis, shows how data were handled, mathematical equations used and outlines calibration development.
- The section on plant method (3.5) covers plant preparation procedures for wet and dry plant material before presentation to NIR, the use of $CO_2$ for wet samples and also the wet chemistry base tests.
- The section on soil method (3.6) covers soil preparation procedures for field moist soil and dry soil. It also covers the wet chemistry analytical tests.
- The nitrate-N section (3.7) outlines the 70-day field trial that provided a range of nitrate-N levels encountered in pasture. A more detailed method is given section 4.4 of Chapter 4.
- The N test glasshouse experiment section (3.8) gives a brief description of the glasshouse study. The study, using soils from throughout New Zealand, is used to develop a soil nitrogen test for New Zealand pastoral soils. A more detailed method is presented in Chapter 7.
- The section on sulphur test (3.9) gives a brief description of the method carried out to develop the new proposed sulphur test for New Zealand. A more detailed method is presented in Chapter 6.

## 3.2 Instrumentation

All NIR measurements were performed on a KES Diode Array Spectrometer. The KES Spectrometer has short spectral measurement times (several hundred spectra per second). The spectral range is nominally 400-1700 nm. All wavelengths are measured simultaneously by a dual-array system, a silicon array covering 400-950 nm (nominal) and indium gallium arsenide (InGaAs) array covering 950-1700 nm (nominal). The spectrometer employs a dual-beam system, giving both an internal optical reference and a stray light spectrum for each measurement. There are no moving parts in the sensor module, which is an advantage over many other NIR instruments in the market. The sample area scanned by the spectrometer is approximately circular and about 33 $cm^2$ when the sample is placed 125 mm from the instrument. The instrument draws spectra at the rate of 500 per second (50Hz power supply), and corrects internally for stray light and ambient light variations. For the results discussed in this thesis, the spectra were internally averaged over some 30 corrected spectra within the KES, then further averaged within the PC, and 5 such "sub-spectra" produced for every spectral measurement. The total time to collect each "sub-spectra" was approximately 1.2 seconds., giving a total collection time of about 6 seconds.

There are 152 detectors in the two arrays. The first 76 are Si detectors (which measure in the visible/NIR (400–950 nm)) and the second 76 are InGaAs detectors (that measure in the NIR region (950–1700 nm)). The changeover between detector arrays can be clearly seen in Figures 3.1–3.4. The unit manufacturer provides an accurate wavelength centroid response for every diode and, critically, detector cross-response corrections. The final spectral wavelength scale is determined by cubic-spline interpolation at 5 nm steps from 400–1700 nm. Therefore, 261 raw energy values over this spectral range are obtained. Each spectrum produced contains a sample (1:152) and reference (153:304) energy readings. The spectra obtained were then averaged and a single spectrum used for data analysis.

## 3.3 Sample presentation

The KES has flexible sample presentation possibilities, and therefore a special mount was built by AgResearch. For this study, samples of plant, soil or liquid were placed in clear plastic Petri dishes (diameter 145 mm, depth 18 mm) and placed on the mount and scanned. The distance between the mount (where the sample was placed) and the KES instrument was

150 mm. The beam from the instrument penetrates the sample from the top by only 1–4 mm for solid samples, but penetrates deeper into liquids.

For NIR measurements to be accurate, the samples must be presented to the spectrometer in the most reproducible manner. NIR measurements are influenced by sample properties of particle size, moisture content and temperature, as well as unit specific issues, stray light changes, and even in extreme cases changes in ambient humidity. The KES design eliminates effects from ambient light variations. To ensure accurate NIR predictions, the sample presented needs to be homogeneous and representative of the parent sample.

BÜCHI Labortechnik AG (2001) examined precision of NIR measurements in relation to particle size distribution and homogeneity of the sample, for measurement of fat, water and protein content in meats. BÜCHI Labortechnik AG (2001) assessed four types of sample mixers. Reproducibility (precision of the results) was assessed by the Coefficient of Variation (CV) obtained from multiple measurements. Results confirmed that obtaining a small and consistent particle size, and homogeneity of the sample, are both important to reproducibility of the NIR measurement.

In order to ensure reproducible results in this work, the following procedures were followed:

- The KES instrument was allowed to warm up for at least 10 minutes before commencing measurements.
- Samples were scanned from the open top of Petri dishes.
- Solid samples (plant and soil) were scanned at least 3 times, producing at least 3 spectra for each sample. The samples were remixed before scan 2 and 3 were made. At the beginning of the study, the Petri dishes were rotated 8 times per remix for each sample. It was found that this was statistically not significant and therefore rotations were eliminated. The 3 remixes for each sample were found to be statistically different.
- Liquid samples were scanned only twice, because problems associated with homogeneity were not an issue.
- A physically robust calibration tile was scanned before and after every sample to correct for medium-time frame drift.
- A Spectralon tile (absolute reference tile) was usually scanned in the morning and at the end of the day.

## 3.4 NIR data preparation, chemometrics, data analysis and calibration development

### 3.4.1 Data preparation

Before and after each sample scan, a scan of the calibration tile was made. This was intended to allow a correction for any short to medium term drift, either from instrument or other sources. The Spectralon tile is a ceramic disk with nominally perfect reflectance. This is used as an 'absolute' reflectance standard and is generally used in the transfer or transport of calibrations between instruments (see Chapter 9).

Figure 3.1 illustrates raw energy spectra obtained from the KESNIR instrument for a Spectralon Tile, calibration Tile, Dry Plant, Wet Plant, Dry Soil and Field Moist Soil. The six sample spectra are on the left with the instrument reference spectra on the right. There are 304 data points in total.

Each sample spectrum had to be standardised before chemometric analysis could be applied. Spectrum Toolbox V7.04 developed by Dr Robert Burling-Claridge, AgReseach was used to standardise the KES spectra.

Spectrum Toolbox initially applies an instrument-specific diode cross-correlation correction matrix supplied by the manufacturer. The toolbox then incorporates the reference spectra, calibration tile and spectralon spectra to convert the raw energy to reflectance. Figure 3.2 is an illustration of reflectance spectra; once this is done there are 152 data points. The reflectance data are finally cubic-splined at 5 nm intervals (Figure 3.3), using the manufacturer supplied wavelength tables, and transformed to absorbance (Figure 3.4).. The following give mathematical expressions for reflectance and absorbance.

$$\text{Absorbance} = -\log\left(\frac{1}{R}\right)$$

$$R\ (\text{Reflectance}) = \frac{I}{I_0}$$

Where $I_o$ = incident light = instrument reference light, and $I$ = reflected light.

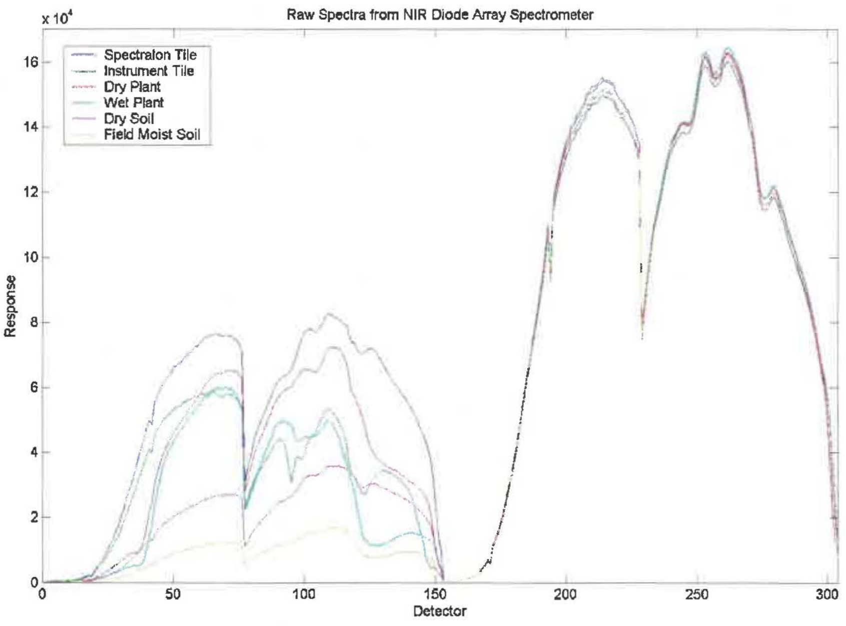

**Figure 3.1:**
Raw energy spectrum obtained from the KES instrument for the Spectralon Tile, Instrument Tile (calibration Tile), Dry Plant, Wet Plant, Dry Soil and Field Moist Soil. Detector refers to detector number in the diode array. Spectra to detector 152 (the left-hand side) represent samples and reference tiles; those on the right-hand side (spectra to detector 153–304) are from instrument.

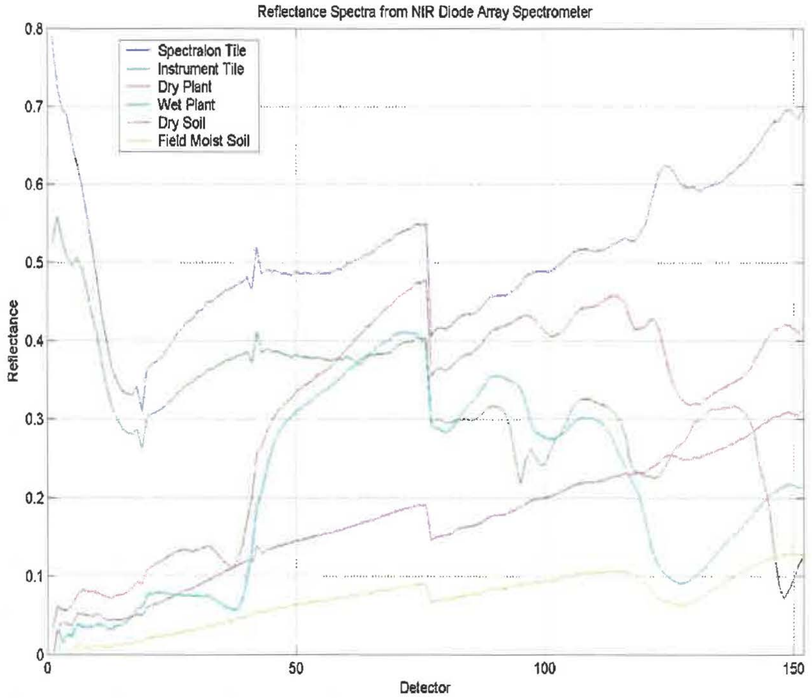

**Figure 3.2:**
Reflectance spectra corresponding to the raw spectra shown in Figure 3.1.

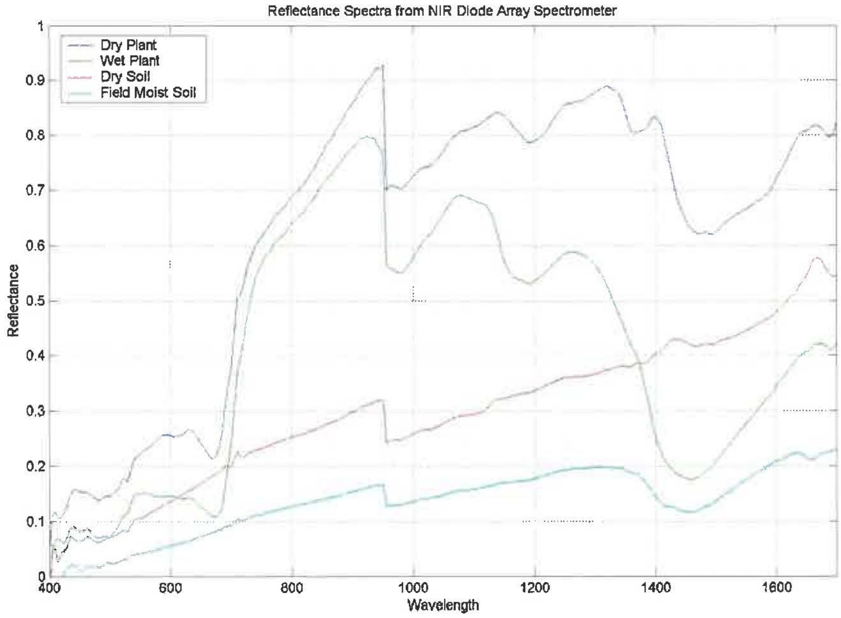

**Figure 3.3:**
Reflectance spectra for Dry Plant, Wet Plant equivalent, Dry Soil and Field Moist Soil equivalent.

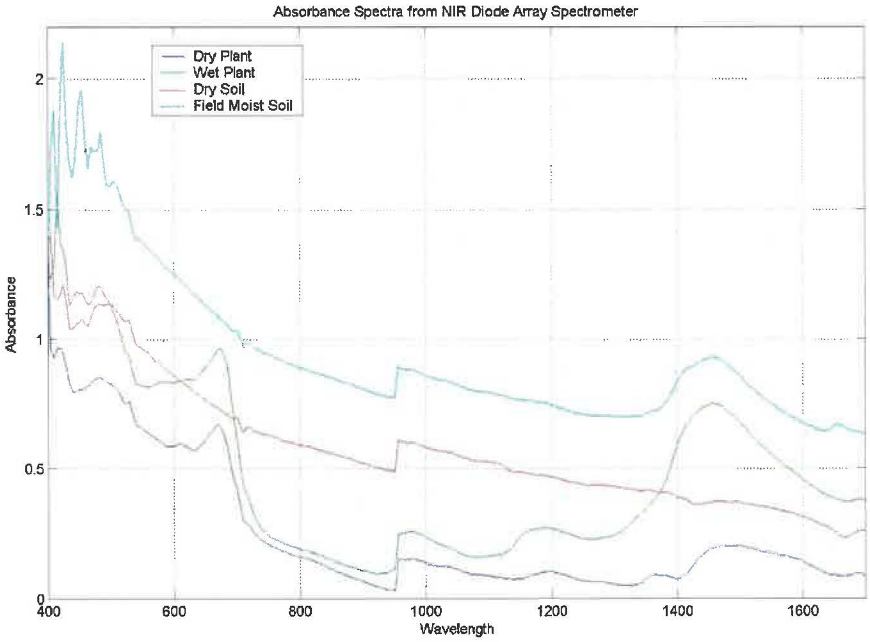

**Figure 3.4:**
Absorbance spectrum for Dry Plant, Wet Plant, Dry Soil and Field Moist Soil from wavelength to 400–1700 nm.

### 3.4.2 Data analysis and chemometrics

Chemometric analyses of the NIR spectra were performed using the software program Galactic Grams/32, Array Basic, a macro language allowing the user to program spectral processing, analysis and output.

The entered analytical wet chemistry sample values were paired with the appropriate NIR scan file names in a software file format that was directly imported into the calibration software package Grams/32 for partial least squares (PLS) and principal component analysis (PCA) chemometric analysis. Most of this NIR study was based on quantitative rather than qualitative measurement. A partial least squares regression approach (Martens and Naes, 1992) was used to ascertain which parts of the NIR spectra most closely correlated with the results of wet chemical and conventional tests.

The procedure for NIR data preparation analysis and calibration development was illustrated in Figure 3.5. In general, the following pre-treatments were used prior to calibration development unless specifically stated in preceding chapters of this study.

The first 30 wavelengths (400–550 nm) and the last 2 wavelengths were eliminated. It was found that the calibration performed better on elimination of these detectors. Responses from detectors at the ends are affected by the splining process. The outputs from the short visible region detectors were noisy, due to physical/engineering limitations.

Multiplicative Scatter (or signal) Correction (MSC) was used (Geladi *et al.*, 1985) for spectral data. Both MSC and Standard Normal Variate correction (SNV) were tried for the study, with little difference between the two as far as improving calibrations.

The spectral data were Mean Centred (MC). MC is where the average spectrum of the calibration set is subtracted from every calibration spectrum. MC has the effect of picking out the subtle differences between spectra, thereby improving a model.

### 3.4.3 NIR method and calibration development and validation

In order to ensure the highest standard of validation for NIR development work carried out in this study, the following procedures were used:

- Samples were chosen to cover a representative range of matrices.
- Within each sample type (e.g. soil), samples were chosen to cover a representative range of sub-types (e.g. a range of soils from throughout New Zealand).
- A uniform and reproducible sample preparation and NIR presentation procedure were adopted (Section 3.3).
- Physical and chemical compositions of samples were accurately determined by wet chemistry and classic instrumental methods.
- Reproducibility ($s_r$) of the wet chemical and instrumental methods were determined.
- A robust and accurate calibration model was created. Where used as a working calibration, the model was dynamically maintained and improved.
- Samples were scanned over a period of time to account for seasonal variation.
- The model was validated using separate sample sets.

Generally, it was preferred that at least 200–250 samples were used to obtain a workable calibration. This figure was dependent on a number of factors, and it could occasionally be lower than 200 and higher than 250. These factors include:

- Ability of NIR to detect the analyte signal, i.e. optical activity.
- The analyte tested for, its concentration and matrix.
- Reproducibility of the wet chemistry.

For this study, samples were assigned to either the calibration set or validation set in a systematic way to ensure that both sets were fully representative of the sample range.

Two-thirds of the samples were assigned to the calibration and a third were assigned to the validation set. Standardised residuals were screened and extreme outliers discarded (spectra which were abnormal with respect to others).

The following gave a descriptive list of the mathematical expressions used in this study. The actual mathematical formulae can be found in the Appendix (Chapter 10).

For this study, statistical accuracy of the calibration models was described by the coefficient of determination ($r^2$). $r^2$ was the relative predictive power of a model. $r^2$ was a descriptive measure between 0 and 1, where 1 represents a perfect fit.

The overall error between modelled and reference values was determined using the Root Mean Square Error of Cross Validation (RMSECV) using the leave out procedure. The number of segments and number of factors for the model were also given. The Root Mean Square Error of Prediction (RMSEP) was also quoted, which gave the prediction error on independent validation samples for a calibration. Therefore, the RMSEP gave a measure of the accuracy of an NIR test where the wet chemistry was seen as the 'truth' (or dependent variable). The repeatability of independent validation samples for the test studied using the calibration model was quoted as $s_r$ (test). Repeatability in this study was the difference between results obtained from the same instrument under identical conditions (same operator, identical sample material, in rapid succession). The optimum number of PLS factors for each component was determined by use of the PRESS (Predictive Residual Error Sum of Squares) calculation.

The repeatability or precision of the wet chemistry determinations was also determined and was described as $s_r$(wetchem). Accuracy of the wet chemistry was defined as the error against the defined truth.

The criteria used to choose the 'best' calibration model usually involved the lowest RMSEP/SEP, highest $r^2$, slope closet to 1 and bias closest to zero from the regression between the NIR predicted and the base reference test values.

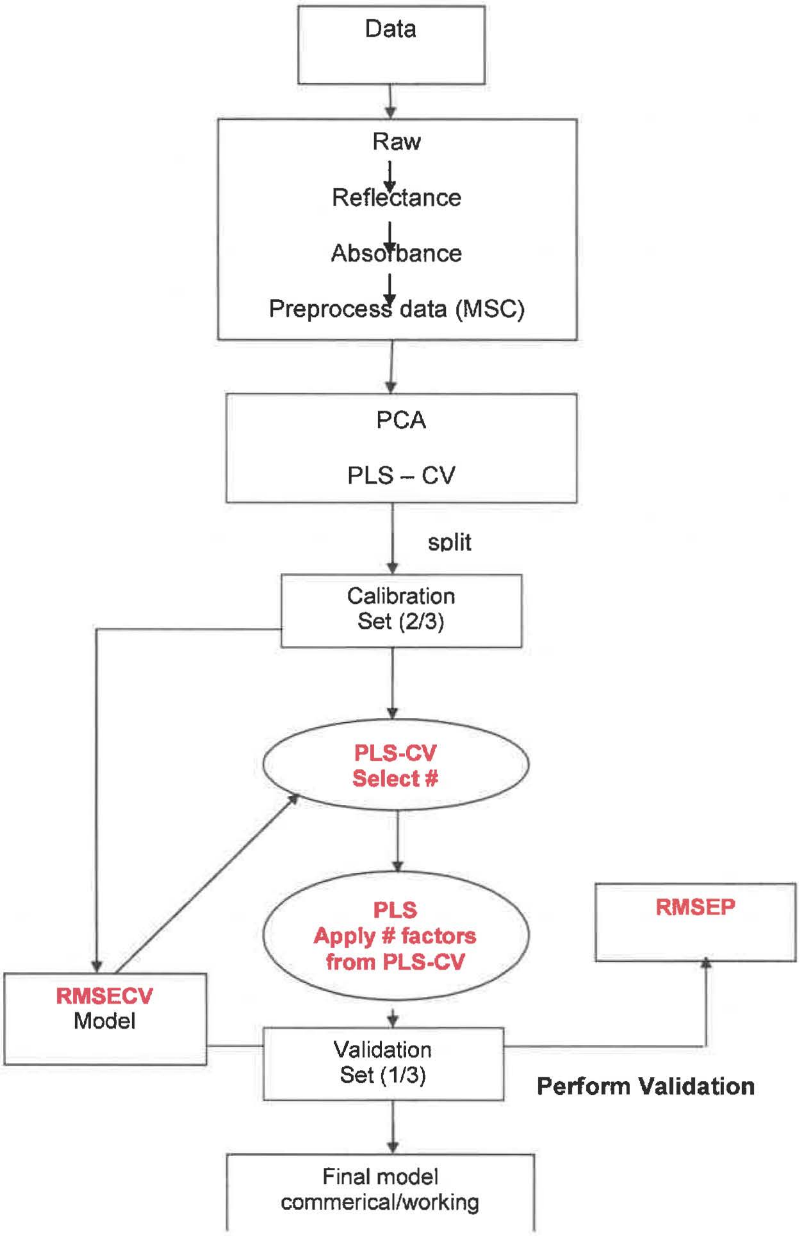

**Figure 3.5:**

Procedure for NIR data preparation, analysis and calibration development. Initially the data undergoes a pre-treatment step, where the raw energy is converted to reflectance and then log-transformed (absorbance). Other pre-treatments of data include MSC and MC and wavelength region selection. PCA is used to eliminate extreme outliers and PLS to create a regression model against the constituent of interest. The sample set is split into a calibration set (2/3) and validation set (1/3). A calibration is developed using PLS, where $R^2$ and RMSECV are quoted. The performance of the calibration is tested against the independent validation set and performance indicators $R^2$ and RMSEP are quoted. Once a robust calibration is achieved, it can then be used as a commercial/working calibration to predict unknown samples.

## 3.5 Method: Plant

### 3.5.1 Overview

Figure 3.6 gives a schematic overview of the procedure used for plant samples. The diagram indicates how samples are normally treated in the lab and how they were treated for this NIR study. Both wet and dry plant material were analysed using the KES NIR.

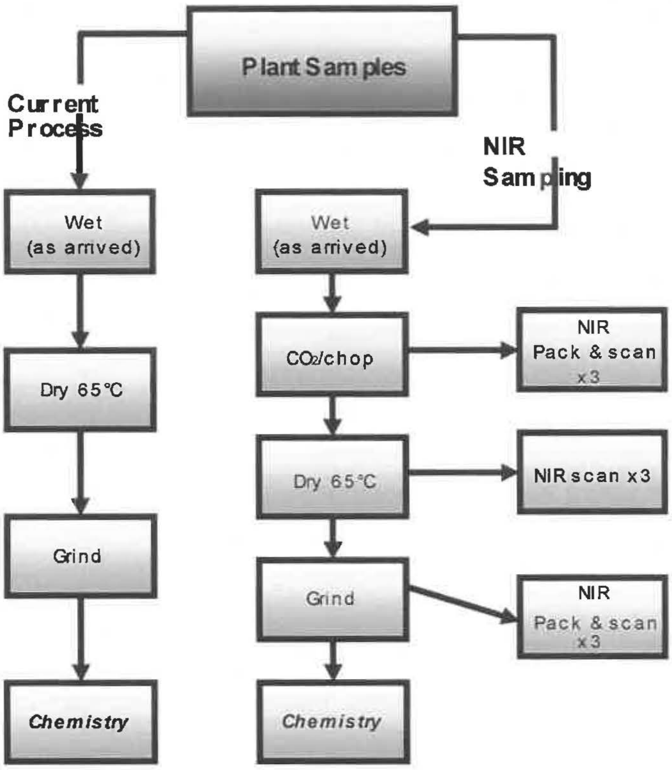

**Figure 3.6:**
Schematic showing the plant procedure used in study.

### 3.5.2 Sample preparation

The NIR scanning of dry plant material is straightforward, because dry samples can be finely ground. The measurement of wet plant material (field moist as received) is more difficult. It is preferred that the sample be small and of consistent size.

A sample preparation procedure for field-moist samples was developed using carbon dioxide ($CO_2$) freezing. This procedure has been patented (Chapter 10: Patents: Compound preparation method). It was found that addition of $CO_2$ did not contaminate the sample with any of the plant analytes being tested for (see Chapter 5). It was also possible to oven-dry the sample within 10 minutes, once chopped up, if required.

An overview of the method is as follows. A slug of $CO_2$ from a cylinder was added to plant samples placed in a food processor with a metal blade attachment. The $CO_2$ was used to make the sample rigid. The lid on the processor was closed and processor started, with the sample being processed for 1 minute. This shattered the sample into small pieces (Figure 3.7). The sample was checked to ensure that it was finely chopped. If not, it was processed for a further minute. The finely chopped sample was poured into a 145 mm diameter Petri dish (Figure 3.8) covered, and left to reach room temperature (20 ± 2 °C). The temperature of plant sample was recorded.

After initial processing, samples were scanned using the KESNIR instrument (Figure 3.9). Immediately after scanning the sample was weighed. In order to determine accuracy, precision, and effect of further processing, plant samples were oven-dried overnight at 65 °C and reweighed (for determination of moisture content) and re-scanned using NIR. Plant samples were then further ground to pass a 2-mm mesh sieve using Thomas-Wiley Mill, Model ED-5 and stored in airtight containers. These ground samples were also scanned using the KESNIR instrument.

Plant samples were scanned over a 15-month period. In total, 274 wet samples were scanned and there were 27 different plant species. The samples were used to build calibrations for the following parameters: moisture, N, P, K, S, Mg, Ca and Na and trace elements (see Chapter 4 for more details). A different sample set was used to build calibrations for nitrate-N (given in more detail in subsections of Chapter 4).

**Figure 3.7:**
Second stage of the carbon dioxide freezing method –frozen sample being shattered in a food processor.

**Figure 3.8:**
Resulting 'shattered' (effectively finely chopped) wet plant sample in a Petri dish.

**Figure 3.9:**
Processed sample about to be presented to the KESNIR series 01 instrument with sample presentation unit 1 (SPU1). Also visible is the calibration tile on the left-hand side of the photo. The sample or calibration tile can be slid into the light path and scans taken as required.

### 3.5.3 Wet chemistry

All wet chemistry was determined in duplicate or triplicate where possible to get an estimate of the repeatability $s_r$(wetchem).

Plant N was determined using a semi micro Kjeldahl method (Bradstreet, 1965) where sulphuric acid digestion with Se as a catalyst converts the nitrogen compounds present to ammonium. The determination of ammonia was based on the modified Berthelot complex reaction (Krom, 1980). The absorption of the formed complex was measured at 660 nm using a Skalar Segmented Flow Analyser (Basson, 1976).

The analysis of P, S, Mg, Ca and K, were determined using a nitric/perchloric ($HNO_3/HClO_4$) acid digestion procedure (Zasoski and Borau, 1977). Plant sample (0.5 g) was digested and diluted to 25 mL with distilled water, with the final matrix 8% $HClO_4$. The above elements, except K, was then determined simultaneously using an ICP-OES (McQuaker, 1979). Table 3.1 outlines the elements tested, the emission lines used, the low and high standard for each elements, the mean concentration of a quality control (solution), the mean concentration of a quality control (plant sample), the detection limit (DL) and the linear range.

Potassium was determined on a 4-channel flame AA Spectrometer using Air/$C_2H_2$. The 8% $HClO_4$ digests are diluted with strontium chloride solution to inhibit the formation of stable ions in the flame (Allen, 1958, Clinton, 1967). The detection limits in K in plant material using the above method is <0.01%.

**Table 3.1:** Gives elements tested, emission lines,concentrations of standards and quality control (QC) and detection limit (DL) for the ICP-OES instrument.

| **Element** | **Ca** | **Mg** | **P** | **S** |
|---|---|---|---|---|
| Emission Line (nm) | 211.2 | 293.6 | 213.5 | 182.0 |
| Unit ('in plant') | % | % | % | % |
| Low Standard (ppm) | 100 | 20 | 20 | 20 |
| High Standard (ppm) | 500 | 100 | 100 | 100 |
| Solution QC (ppm) | 250 | 50 | 50 | 50 |
| Plant QC (in plant) | 1.25 | 0.25 | 0.25 | 0.25 |
| Detection Limit (in plant) | <0.01 | <0.01 | <0.01 | <0.01 |
| Linear Limit (in plant) | 5.00 | 5.00 | 5.00 | 5.00 |

## 3.6 Method: Soil

### 3.6.1 Overview

Figure 3.10 is a schematic overview of the procedure used for soil samples. The diagram indicates how samples are normally treated in the lab and how they were treated for the NIR study. Both wet and dry soil material were analysed using the KES NIR.

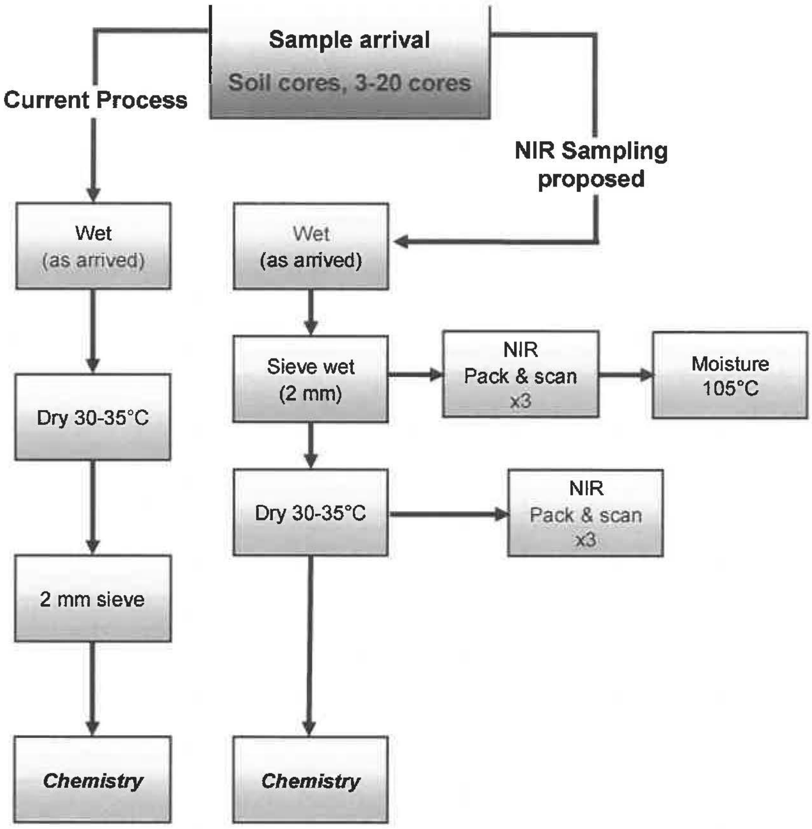

**Figure 3.10:**
Schematic showing the soil procedure used in study.

Soil samples were chosen throughout New Zealand from both the North Island and South Island to cover the range of soil types and natural matrix variation encountered. In order to cover all variations, calibrations for soil testing ensured the inclusion of soils from all 15 New Zealand soil orders and subsoil types, geographical regions and land use. No previous studies have been reported in which NIR spectra have been recorded for a full range of soil orders in a country.

The name by which a soil is known usually corresponds to the subgroup level of classification. Soils are generally named after the locality where they were first discovered and are generally place names, e.g. Te Kowhai soils (or more formally called the Te Kowhai series) were first found in the vicinity of the Te Kowhai settlement. The soils have all formed from the same parent material, are similar in appearance and have the same soil water and soil temperature regimes. These soils occur within a distinct locality and, therefore, all have a similar climatic regime. Soil series, therefore, imply similar soil and climatic features. Each soil series is a grouping of soil types which represent the lowest level of classification. Soil types have the narrowest ranges of characteristics, with relatively uniform appearance (morphology), chemical, physical, climatic and slope features. The soil type may be subdivided into phases if further distinctions are necessary. Table 3.2 gives the number of soil orders, soil groups, soil subgroups, soil series and soil types found in New Zealand.

**Table 3.2:** Number of soil orders, soil group, soil subgroup, soil series and soil type found in New Zealand, with an example of Bruntwood silt loam and its New Zealand soil classification (Hewitt, 1998).

| Soil class | Number | Example: Bruntwood soil |
|---|---|---|
| Soil order | 15 | Allophanic |
| Soil group | 73 | Impeded Allophanic |
| Soil subgroup | 267 | Typic Impeded Allophanic |
| Soil series | 1600 | Bruntwood |
| Soil type | approx 3000* | Bruntwood silt loam |

*A soil series can have 1–3 soils at the soil type level, i.e. silt loam, sandy loam or clay loam, etc.

It would be ideal to have a single calibration for each soil test, with samples down to the soil series or soil type level. But this was beyond the scope of this study since 1600–3000 samples would be required in calibration to comprehensively cover soil variation. Further work is being done by AgResearch to achieve this. A single calibration must encompass all soil types and range of concentrations of analytes studied. Alternative calibrations for individual soil types or soil groups may need to be developed.

Three-hundred-and-seventy field-moist soils were used for this study. These samples consisted of 10–20 cores of 0 (surface)–75 mm in depth and 25 mm in diameter. The sample collection location from the North and South Islands overlain on a soil order map (gross) is illustrated in Figures 3.11 and 3.12 respectively.

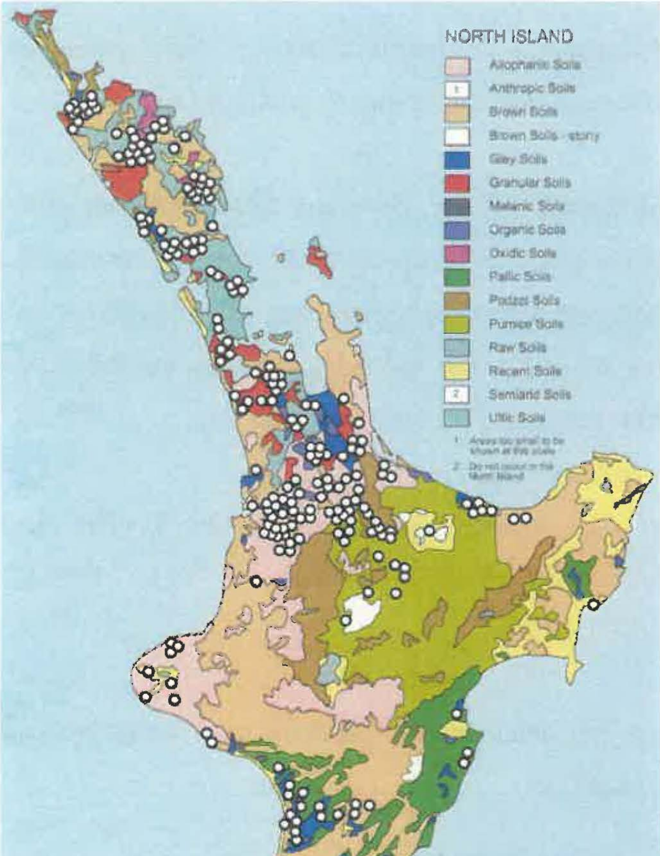

**Figure 3.11:**
North Island collection points.

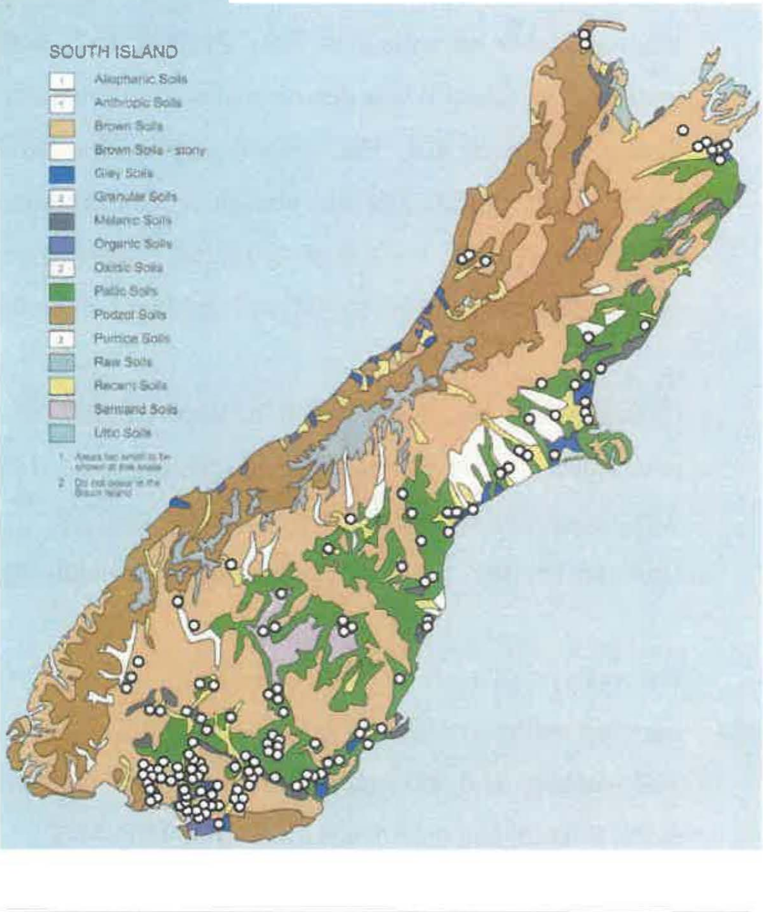

**Figure 3.12:**
South Island collection points.

### 3.6.2 Sample preparation

The difficulty of using NIR for soil analysis is the matrix effect, i.e. many soil types and homogeneity of the samples (this can be overcome by sieving or grinding and mixing).

For this study, soil cores were sieved through a 2 mm sieve and then thoroughly mixed. A Petri dish was then filled with soil and scanned using the KESNIR instrument. Immediately after scanning, a sub-sample of the soil was placed into aluminium foil cups and its weight recorded, then it was placed in an oven at 105 °C. The following morning, the foil cups were removed from the oven and reweighed for moisture content determination.

The remaining soil (2 mm fraction) was air-dried overnight at 30–35 °C. The air-dried samples were scanned in a Petri dish using the KESNIR instrument.

### 3.6.3 Wet chemistry

All wet chemistry or reference methods was determined in duplicate to get an estimate of the repeatability unless otherwise stated $s_r$(RefTest).

Plant-available phosphate in New Zealand soils was determined via a modified Olsen P method. The Olsen P was determined on the 2 mm dry soil fraction and used a volume rather than a weight of soil. The method employed a $NaHCO_3$ extraction method developed by Olsen *et al*., (1954) and the phosphate concentration in the extract was determined by a phospho-molybdate method proposed by Watanabe and Olsen (1965) and Murphy and Riley (1962). Chapter 8 covers the Olsen P method comprehensively.

Exchangeable Mg, Na, Ca and K were determined on the 2 mm dry soil fraction using ammonium acetate soil extracts (Blakemore *et al.,* 1980) by an automated 4-channel Atomic Absorption/Emission Spectrometer using air/$C_2H_2$. The results are expressed in Quick Test Units for advisory purposes (Cornforth and Sinclair, 1984).

For analysis of total S, P, K, Ca, Mg in soil, the 2 mm sieved, dry soil fraction, was sub-sampled using a riffle and ground (using a Teflon-coated ceramic mortar) to a fine powder. Soil samples of 0.500 grams were digested with a mixture of concentrated perchloric/nitric acids, diluted, and then determined using ICP-AES.

Soil N was determined on the finely ground soil using a semi-micro Kjeldahl method (Bradstreet, 1965), where sulphuric acid digestion with Se as a catalyst converts the nitrogen compounds present to ammonium. The determination of ammonia was based on the modified Berthelot complex reaction (Krom, 1980). The absorption of the formed complex was measured at 660 nm using Skalar Segmented Flow Analyser (Basson, 1976).

Available S was measured using High Pressure Ion Chromatography (HPIC) in the extract (Watkinson and Kear, 1994). See Chapter 6 for a comprehensive discussion on current sulphur test methods.

Soil pH was determined using a 1:2.1 (v/v) water slurry left to stand for 16–24 hours at 20°C (Blakemore *et al.,* 1980). A more comprehensive description of the method is given in Chapter 5.

Soil carbon is determined on the finely ground fraction using a carbon analyser (Shimadzu TOC 5000A) via the combustion method (Methods of Soil Analysis (Part 3), 1996). Phosphate retention or Anion Storage Capacity (ASC) is determined on the 2 mm dry soil fraction. The soil sample is shaken with a buffered phosphate solution for 16 hours. The amount of phosphate remaining in solution is determined colorimetrically at 420 nm. The Reserve K test gives an estimate of the amount of fixed K in soil, which is not measured by the exchangeable K test. Reserve K for this study was determined using Carey's, 2003 modified test of Jackson's, 1985 test. The test was measured using 2 mm dry soil fraction. A detailed discussion on the test and method for ASC and reserve K are given in Chapter 5.

## 3.7 Nitrate-N test

High levels of nitrate-N in pasture/feed pose animal health problems and can even lead to stock death. Having a rapid measure of nitrate-N available can minimise this problem. In order to get the range of nitrate-N in pasture samples for a NIR calibration, a randomised block experimental design with 3 replicates was used. Treatments of 0, 50, 100 and 200 kg$^{-1}$ ha$^{-1}$ N, as urea, were applied. The pasture samples were harvested over a 70-day period. The nitrate in the herbage was extracted using acetic acid. The nitrate-N was then determined using the cadmium reduction method on a Tecator 5020 FIAStar Flow Injection Analyser. A detailed discussion on nitrate-N is given in Chapter 4.

## 3.8 N test glasshouse experiment

A total of 52 soils, comprising the major soil groups in New Zealand, were collected for a glasshouse experiment which ran for almost a year. Soils were collected from Northland, Waikato, Bay of Plenty, Central Plateau, King Country, Taranaki and all major districts of the South Island. Ryegrass was grown in pots of soil. Treatments were either N (40 $kg^{-1}$ $ha^{-1}$ N) applied in the form of urea, or nil N. A randomised block experimental design was used with 3 replicates. Herbage cuts were taken during the trial period to measure response to N applied.

The N status of the soil and plants were monitored during the trial. Soil tests which included, total soil N, nitrate-N, ammonium N and mineralisable-N and a range of other soil tests were done. The measurement of total soil N, nitrate-N and mineralisable-N for New Zealand soils using NIR are covered and discussed in Chapter 7.

## 3.9 Sulphur test

The same 43 air-dried soils used by Watkinson and workers of AgResearch to develop the two soil sulphur tests in use by New Zealand laboratories were used (Watkinson and Perrott, 1990) in this study. The soils were from field trials conducted throughout New Zealand to determine pasture yield responses to S fertiliser application. This study outlines the problems associated with the current testing regime and proposes an alternative. This work has a large agronomic component, with a subsection showing the possibility of measuring New Zealand soil S status using NIR. A detailed discussion on the new proposed S test is given in Chapter 6.

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# Chapter 4: Use of NIR Spectroscopy to Determine Major Elements in Wet and Dry Plant Samples.

## 4.1 Abstract

The measurements of major elements in plants were evaluated using a diode array NIR spectrometer. Plant samples were scanned over a 15-month period. In total, 274 samples (which included 27 species) were scanned in a wet state and their dry equivalent. The samples were used to build calibrations for moisture, N, P, K, S, Mg and Ca. Calibrations were also built for the preceding constituents for a 'single species', using 146 pasture samples.

Further calibrations were developed for nitrate-N, using 125 pasture samples in a wet state and their dry equivalent. These samples were collected over a period of 70 days after urea was applied at different rates to the pasture.

The calibrations developed for moisture, N and nitrate-N on both dry and wet plant samples were able to be determined with a high degree of accuracy. A calibration developed for Ca on dry plant showed promise. For elements such as Ca, K, Mg, P and S, NIR was reliant on weak molecular bonds, manifested as subtle differences in the spectra. Therefore, calibration models for these constituents relied on the weak spectral effects, leading to lower accuracy.

## 4.2 Key Words

Plant analysis, NIR, moisture, N, nitrate-N, Ca, K, Mg, P and S.

## 4.3 Introduction

Plant testing in agriculture is used as a means of monitoring nutrient deficiencies and imbalances to enable maximum or sustainable crop/pasture production to be determined. Plant analysis is invariably carried out using wet chemical digestion or extraction techniques, followed by analysis of each specific target element in the digest solution, using the appropriate instrumental method of analysis.

It would be ideal for the New Zealand agricultural industry if a rapid, non-destructive technique such as NIR, could accurately predict the constituents of plant material. Most of the NIR work carried out on plant analysis applications related to feed quality of forages and grains, with numerous studies carried out on these applications. There have been fewer studies on evaluating NIR capability in determining elemental composition of plant materials. Table 4.1 summarises NIR studies in literature (references identified with an * in reference section) on dry plant material for the tests N, Ca, K, Mg, P and S and nitrate-N. Studies on moisture or dry matter are also presented in the table. The number of studies for each test, the concentration range for the test, the reproducibility of the reference method, and Root Mean Square Error of Prediction (RMSEP) range and mean are also given.

Generally, prior to 1995, the NIR studies on calibrations were carried out on scanning instruments with wavelengths 1100–2500 nm, while after 1995, the wavelength range 400–2500 nm has been used to build calibrations. For all studies, dry plant material was ground to a particle size < 1 mm. The $s_r$(ref method), the repeatability of the reference method, has only been presented in a few papers. Since it is an indirect method, the accuracy of the NIR prediction is invariably *not* better than the reference method repeatability.

**Table 4.1:** NIR studies found in literature for moisture and for the tests N, Ca, K, Mg, P, S and nitrate-N on dry plant material (references identified in reference section).

| Test | Studies | Concentration range (%) | $s_r$(ref method) range (%) | No. studies presented RMSEP | RMSEP range (%) | RMSEP mean (%) |
|---|---|---|---|---|---|---|
| Moisture (%) | 3 | 0.8–91.4 | 1.0[c] | 2 | 0.2 –0.9[d] | 0.5 |
| N (%) | 18 | 0.2–7.2 | 0.03–0.034[b] | 12 | 0.07–0.71 | 0.25 |
| Ca (%) | 14 | 0.02–5.19 | 0.13[a] | 8 | 0.03–0.16 | 0.08 |
| K (%) | 15 | 0.3–4.5 | 0.05[a] | 10 | 0.04–0.34 | 0.18 |
| Mg (%) | 15 | 0.03–0.70 | 0.02[a] | 8 | 0.01–0.06 | 0.03 |
| P (%) | 19 | 0.03–1.45 | 0.01–0.03[b] | 12 | 0.01–0.49 | 0.06 |
| S (%) | 5 | 0.04–0.72 | – | 2 | 0.02–0.06 | 0.04 |
| Nitrate-N (%) | 1 | 0.03–0.36 | – | – | – | 0.03[e] |

[a] = data $s_r$(ref method) from one study only; [b] = data $s_r$(ref method) from two studies only; [c] = data $s_r$(ref method) from one study only; [d] = data value 0.9 % is RMSECV not RMSEP; [e] = data value 0.03 % is RMSECV, not RMSEP.

Literature suggests that NIR can indirectly measure the major elements because of their association with organic molecules such as chlorophyll (McClure *et al.*, 2002). This includes the major elements N, P, K, Ca and Mg.

Normally, in a wet-chemistry laboratory, many plant species are analysed via a batch system for the above elements. It would be useful and highly valuable, if a rapid, non-destructive technique, such as NIR, could accurately predict elemental concentrations in individual plant samples. This study evaluates the use of NIR to measure the above elements when many plant species are included in the calibration. It also evaluates the accuracy of a single plant species calibration when compared to a multitude of plant species in the calibration.

## 4.4 Method

### 4.4.1 Sample preparation and presentation

Measurements of major elements in plants were evaluated using a KES diode array NIR Spectrometer (KES Analysis, NY, US). Plant herbage samples were scanned over a 15-month period on one instrument. Each sample was scanned three times. In total, 276 samples comprising 27 species were scanned in a wet state and its dry equivalent (dried at 65 °C). The 27 plant species included asparagus, avocado, barley, brassica, broccoli, calla lily, cereal, chicory, clover, grape (leaves and petioles), grass, kiwifruit, lucerne, maize, mixed pasture, pasja, peony, persimmon, pine (needles), raspberry, red clover, rye grass, swede, turnip, walnut and wheat. These herbage samples are typical of the range of species analysed in New Zealand.

To evaluate the possibility of measuring nitrate-N using NIR, nitrogen was applied in the form of urea to mixed pasture (weeds, ryegrass and clover). In order to get a range of plant nitrate-N concentrations, urea was applied at rates of nil, 50, 100 and 200 kg N ha$^{-1}$ to field trial plots. There were three replicates for each treatment. The 12 plots were sampled at 0, 3, 7, 10, 14, 17, 21, 28, 35, 49 and 70 days after applying urea. Nitrate-N in pasture increases to a maximum level after three weeks on application of urea to pasture. In total, 125 samples were used for this study.

A sample preparation procedure to finely chop field-moist plant samples was developed, using liquid carbon dioxide ($CO_2$) and a food processor (Rajendram and Burling-Claridge, 2004). The sample was placed in a food processor and then frozen using $CO_2$. The frozen sample was then ‘shattered’, using the food processor for approximately 1 minute (Figure 4.1). The ‘shattered’ (effectively, finely chopped) wet plant sample was poured into a 145-mm diameter Petri dish (Figure 4.2) and scanned by the NIR instrument after having reached room temperature, 20 ± 2 °C (Figure 4.3).

**Figure 4.1:**
Carbon dioxide freezing method – frozen sample being shattered in a food processor.

**Figure 4.2:**
Resulting 'shattered' (effectively finely chopped) wet plant sample in a Petri dish.

**Figure 4.3:**
Processed sample presented to the NIR instrument.

Samples were then oven-dried overnight at 65 °C in a fan-forced oven. The samples were placed into a 145-mm diameter Petri dish and scanned in the NIR spectrometer.

To determine if contamination from the $CO_2$ procedure could be an issue, pasture samples collected from the field were mixed thoroughly, divided into two equal portions, and put through the traditional lab method as well as the $CO_2$ procedure. Elements N, P, K, S, Mg, Ca, Na, Cl, nitrate-N and trace elements B, Co, Cu, Fe, Mn and Co were determined in the sample. The results indicated that contamination was not an issue.

## 4.5 Reference Methods

Plant N was determined using a semi micro Kjeldahl method (Bradsheet, 1965, Basson, 1976 and Krom, 1976). The analysis of P, S, Mg, Ca and K, was carried out using a nitric/perchloric ($HNO_3$/$HClO_4$) acid digestion procedure (Zasoski and Borau, 1977). The above elements, except K, were then determined simultaneously, using an ICP-AES (McQuaker *et al.*,1979). Potassium was determined on a 4-channel flame Atomic Absorption Spectrometer using Air/$C_2H_2$ (Allen, 1958 and Clinton, 1967). Plant nitrate-N was extracted from the plant material using acetic acid and then measured on a Tecator flow injection analyser.

The repeatability (or precision) of the wet chemistry and instrumental determinations was also determined, and is described as the pooled standard deviation $s_r$(ref method). Plant N and moisture were determined in duplicate.

The elements P, S, Mg, Ca and K were analysed only once for the 274 samples. To gauge the reproducibility of these elements, twenty determinations of two reference materials (pasture and kiwifruit) were run over a two-month period, in different analytical batches.

## 4.6 Calibration Development

The sample spectra produced were used to build calibrations for moisture, N, P, K, S, Mg and Ca using PLS. Calibrations were also built for moisture and the above elements for 146 pasture samples which were part of the larger (274 number of samples).

For this study, samples were assigned to either the calibration set or validation set in a systematic way to ensure that both sets were fully representative of the sample range.

Two-thirds of the samples were assigned to the calibration, and a third assigned to the validation set. Calibrations were developed selecting the most appropriate pretreatment method, if required, from among SNV, MSC (Geladi *et al.*, 1985), 1st derivative, 1st and 2nd order detrend. The wavelength range was optimized for each individual constituent. Standardised residuals were screened and outliers discarded (spectra which were abnormal with respect to others). In this study, only one outlier was discarded.

The overall error between modeled and reference values for the calibration samples was determined using the Root Mean Square Error of Cross Validation (RMSECV). The number of factors for the model is given. The Root Mean Square Error of Prediction (RMSEP) is quoted – this gives the prediction error on independent validation samples for a calibration. Therefore, the RMSEP gives a measure of the accuracy of an NIR test where the reference method is seen as the 'truth' (or dependent variable). The repeatability of independent validation samples for the test studied using the calibration model is quoted as $s_r$(NIR). Repeatability in this study is the pooled standard deviation for results obtained from the same instrument under identical conditions (same operator, identical sample material, in rapid succession).

## 4.7 Result and Discussion

RMSECV and the RMSEP for the models were very similar, indicating the models were not under- or over-fitted. For this paper, only the RMSEP for the independent validation set is presented.

The precision of the NIR measurements as indicated by $s_r$(NIR), generally, is as good as, and in many cases better than, the precision of the reference method, $s_r$(ref method). This was also found to be true by Shenk *et al.*, 1981 when evaluating NIR for analysis of Ca, P and K in forages of diverse species, growth stages and samples obtained from many locations. The precision of the NIR-determined samples was better than the laboratory wet chemistry error for most of the tests.

Table 4.2a gives the performance of the calibrations for all samples which includes all 27 species for moisture, plant N (in wet and dry state). Table 4.2b gives the performance of the calibrations for only pasture samples for moisture, and plant N (in wet and dry state). Table 4.2c gives the performance of the calibrations for pasture samples for nitrate-N in dry state.

**Table 4.2a:** Calibration statistics for all sample species for moisture, plant N (in wet and dry state).

| Parameter | State | Range | $s_r$(ref method) | No. of factors | RMSEP | $s_r$(NIR) |
|---|---|---|---|---|---|---|
| Moisture (%) | wet | 48.4–90.5 | 0.26 | 17 | 1.3 | 0.5 |
| N (%) | wet | 1.3–6.8[1] | 0.13 | 14 | 0.51 | 0.13 |
| N (%) | dry | 1.4–6.7 | 0.13 | 13 | 0.28 | 0.09 |

[1] = Plant N (%) measured on dry basis.

**Table 4.2b:** Calibration statistics for mixed pasture samples only for moisture and plant N (in wet and dry state).

| Parameter | State | Range | No. of factors | RMSEP | $s_r$(NIR) |
|---|---|---|---|---|---|
| Moisture (%) | wet | 57.6–87.9 | 11 | 1.2 | 0.68 |
| N (%) | wet | 1.94–6.65[1] | 19 | 0.43 | 0.13 |
| N (%) | dry | 1.94–6.65 | 10 | 0.24 | 0.05 |

**Table 4.2c:** Calibration statistics for nitrate-N on pasture samples in wet and dry state.

| **Parameter** | **State** | **Range** | **$s_r$(ref method)** | **No. of factors** | **RMSEP** | **$s_r$(NIR)** |
|---|---|---|---|---|---|---|
| Nitrate-N (%) | wet | 0.00–0.33 | 0.006 | 12 | 0.053 | 0.023 |
| | dry | 0.00–0.33[1] | 0.006 | 18 | 0.038 | 0.014 |

[1] = Plant Nitrate-N (%) measured on dry basis.

Figures 4.4, 4.5 and 4.6 are of the validation sets for moisture and determination of N on dry and wet plant material. Figure 4.7 presents the validation set for nitrate-N on dry pasture samples.

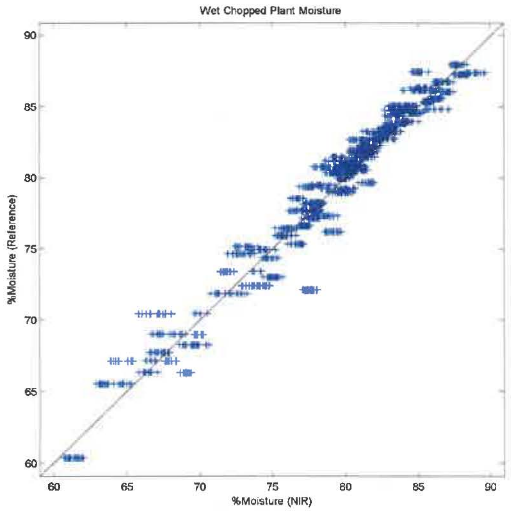

**Figure 4.4:**
Relationship between reference moisture and predicted NIR moisture for the independent validation set for all samples (27 species).

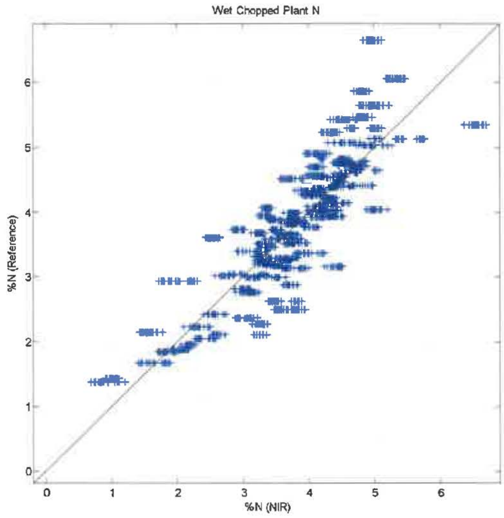

**Figure 4.5:**
Relationship between reference and predicted NIR wet plant N for the independent validation set for all samples (27 species).

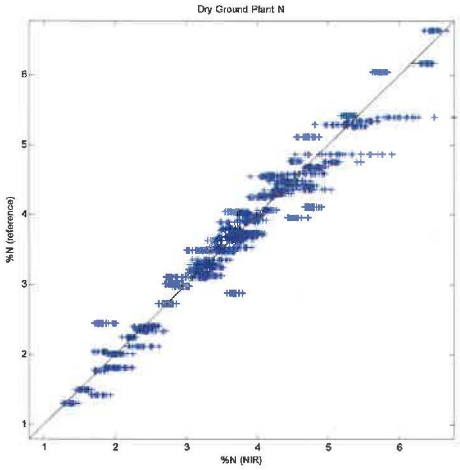

**Figure 4.6:**
Relationship between reference and predicted NIR dry plant N for the independent validation set for all samples (27 species).

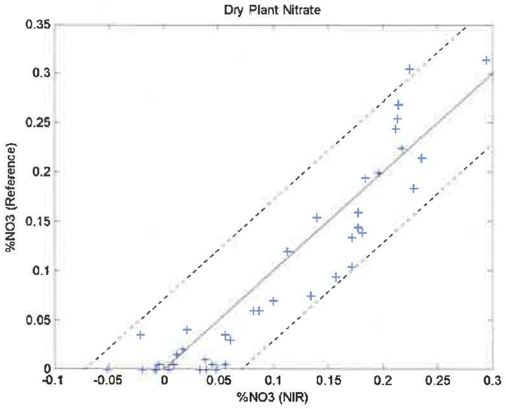

**Figure 4.7:**
Relationship between reference and predicted NIR dry plant nitrate-N for the independent validation set for pasture samples. The dotted lines shows the 95 % confidence limit.

The calibrations developed for moisture and N on dry and wet plant had a high degree of accuracy (low RMSEP). The correlation coefficients for independent validation sets for moisture and N on dry and wet plant were 0.95, 0.95 and 0.75, respectively. The RMSEP for the validation sets for moisture and N on dry and wet plant were 1.3%, 0.28% and 0.51%, in each case. There is a loss in accuracy when N is determined in wet plant, with RMSEP increasing to about four times that of $s_r$(ref method). This is probably due to the absorption of light by the bonds in water molecules and less light back to the detector, masking information and, possibly, also the non-homogeneity of the sample.

There was a slight improvement in accuracy when mixed pasture was compared to all species. RMSEP values for the validation sets for moisture and N on dry and wet plant for mixed pasture were 1.2%, 0.24 % and 0.43% in each case. The concentration range for the pasture study test was slightly narrower.

The results found for this study are comparable to calibration work carried out by (Norris,1998) where RMSEP of 0.17% and 0.42% was achieved for N in wet and dry plant material, respectively. The determination of N in dry and wet (field-moist) grass (Fescue Kentucky 31), using NIR, was studied by McClure *et al.*, 2002. The $r^2$ and SEP for dry and wet grass tissue calibrations were 0.97 (0.29%) and 0.88 (0.97%), respectively. The range of N content for the study was 0.9–6.6%.

The calibrations developed for nitrate-N on dry and wet plant had a high degree of accuracy (Table 4.2c and Figure 4.7). There is a loss in accuracy when nitrate-N is determined in wet plant samples, with an increase in RMSEP. The sample study set is small (125 samples) and nitrate-N may be correlated to the total N content. Nevertheless, the accuracy obtained for this study shows the possibility of measuring nitrate-N rapidly for diagnostic purposes. Study by McClure, 1984 also showed the possibility (RMSECV=0.03%) of measuring nitrate-N in tobacco leaves.

Livestock, particularly cattle, are most commonly poisoned by nitrates in forage. Pasture nitrate concentrations above 0.2% can be harmful to cattle with levels over 0.4% toxic and cause death. Plant species such as oats, wheat and alfalfa are most likely to accumulate toxic concentrations of nitrate.

The calibration performance for all sample species for plant P, K, S, Mg and Ca in wet and dry state is given in Table 4.3a. The calibration performance for mixed pasture samples for P, K, S, Mg and Ca in wet and dry states is given in Table 4.3b. The calibration developed for Ca on dry plant showed promise, with $R^2 = 0.7$ and an RMSEP of 0.31% for a range of 0.17–3.2% Ca in plant material. The relationship between the reference and predicted NIR dry plant Ca for the independent validation set for all samples (27 species) is presented in Figure 4.8. The calibration developed for Ca on wet plant had a lower correlation coefficient and a larger RMSEP value. A study by Vazquez et Aldana *et al.*, 1995 on semi-natural grasslands samples found that Ca and Mg are associated with compounds in the cell wall such as Ca pictate and Mg in chlorophyll, and organic acids are important plant metabolites, and accumulate in grasses in the range of 2–8%. Their study obtained $R^2$ (RMSEP) for Ca and Mg of 0.88 (0.10%) and 0.84 (0.02%), respectively.

**Table 4.3a:** Calibration performance for all samples (27 species) for plant P, K, S, Mg and Ca in wet and dry state.

| Parameter | State | Range | No. of factors | RMSEP | $s_r$ (NIR) |
|---|---|---|---|---|---|
| P (%) | Wet | 0.12–0.73 | 10 | 0.08 | 0.01 |
| | Dry | 0.12–0.73 | 13 | 0.08 | 0.01 |
| K (%) | Wet | 0.96–6.5 | 12 | 0.63 | 0.10 |
| | Dry | 0.96–6.5 | 12 | 0.80 | 0.05 |
| S (%) | Wet | 0.09–1.24 | 9 | 0.15 | 0.02 |
| | Dry | 0.09–1.24 | 14 | 0.12 | 0.01 |
| Mg (%) | Wet | 0.07–0.52 | 9 | 0.07 | 0.01 |
| | Dry | 0.07–0.52 | 7 | 0.06 | < 0.01 |
| Ca (%) | Wet | 0.14–3.20 | 8 | 0.46 | 0.07 |
| | Dry | 0.14–3.20 | 17 | 0.31 | 0.07 |

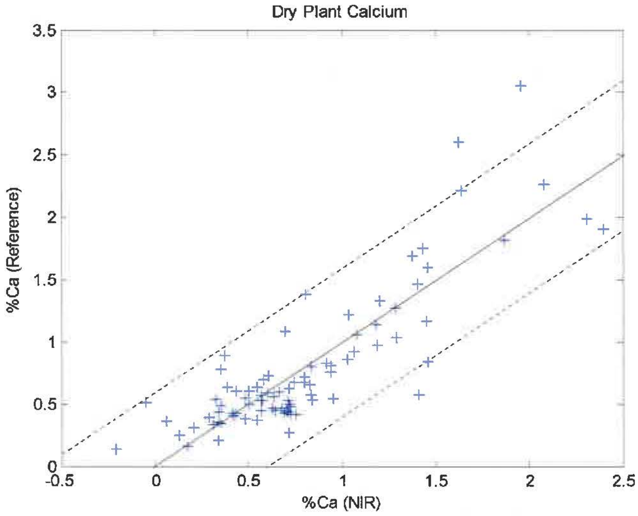

**Figure 4.8:**
Relationship between reference and predicted NIR dry plant Ca for independent validation set for all samples (27 species). The dashed lines denote the 95% confidence limits. Each validation point is the average of three scans.

**Table 4.3b:** Performance of the calibrations for pasture samples only (146 pasture samples) for plant P, K, S, Mg and Ca in wet and dry state.

| Parameter | State | Range | No. of factors | RMSEP | $s_r$ (NIR) |
|---|---|---|---|---|---|
| P (%) | wet | 0.20–0.64 | 12 | 0.08 | 0.02 |
| | dry | 0.20–0.64 | 10 | 0.09 | 0.01 |
| K (%) | wet | 1.06–4.65 | 10 | 0.68 | 0.11 |
| | dry | 1.06–4.65 | 5 | 0.67 | 0.07 |
| S (%) | wet | 0.19–0.53 | 7 | 0.07 | 0.01 |
| | dry | 0.19–0.53 | 6 | 0.06 | < 0.01 |
| Mg (%) | wet | 0.12–0.37 | 4 | 0.04 | < 0.01 |
| | dry | 0.12–0.37 | 10 | 0.04 | < 0.01 |
| Ca (%) | wet | 0.27–1.74 | 14 | 0.23 | 0.04 |
| | dry | 0.27–1.74 | 5 | 0.18 | 0.02 |

**Table 4.4:** Repeatability of P, K, S, Mg and Ca on twenty determinations for two reference materials (pasture and kiwifruit) over two months.

| Species | Element | Mean | $s_r$(ref method) | Coefficient of variation (%) |
|---|---|---|---|---|
| Kiwifruit (leaves) | Ca (%) | 1.91 | 0.08 | 4.2 |
| Pasture | Ca (%) | 0.46 | 0.01 | 2.8 |
| Kiwifruit (leaves) | K (%) | 2.84 | 0.08 | 2.8 |
| Pasture | K (%) | 3.54 | 0.26 | 7.2 |
| Kiwifruit (leaves) | Mg (%) | 0.36 | 0.01 | 3.2 |
| Pasture | Mg (%) | 0.16 | 0.005 | 2.9 |
| Kiwifruit (leaves) | P (%) | 0.23 | 0.01 | 2.7 |
| Pasture | P (%) | 0.39 | 0.01 | 3.1 |
| Kiwifruit (leaves) | S (%) | 0.32 | 0.01 | 3.6 |
| Pasture | S (%) | 0.28 | 0.01 | 4.4 |

Calibrations developed for Mg, S, K and P on dry and wet plant were not satisfactory. The calibrations had $R^2 < 0.5$, and RMSEP for the validation sets obtained were large with respect to $s_r$(ref method). The RMSEP for the above tests would need to be about half of what has been obtained from this study to make NIR a suitable replacement for other methods. The RMSEP were generally very similar but slightly higher for wet than dry. It would be expected that the number of factors used in a calibration would be less for dry plant than wet plant model because of fewer interferences. However, the number of factors required for the calibration models were very similar, with no apparent trend.

It is widely accepted that there are no absorption bands for minerals, ionic forms and salts in the NIR region, but detection of organic complexes and chelates are possible. Studies have shown that, for at least one element or a combination of the elements, Ca, Mg, S, K and P can be determined with a great level of accuracy (Clark *et al.*, 1987, Chen *et al.*, 2002 and Ciavarella, 1998).

The survey of the literature shows that most of the studies had RMSEPs of about 5–10% of the highest concentration value in their study test and calibrations built on tests have been for a single species, on dried and ground samples, and with wavelengths up to 2500 nm.

Studies that built their calibration generally on the wavelength range 400–2500 nm had better success than this study which used a wavelength range of 550-1700 nm to build calibrations. There is possibly more information in the range 1700–2500 nm, which is able to pick up the element-organic molecular vibrations. The measurement of Ca and P, using NIR on 82 samples, consisting of legumes, grasses and legume/grass mixtures, was studied by Redshaw *et al.*, 1986. The study selected certain wavelengths to predict chemical parameters. For Ca, the wavelengths in order of importance were found to be 1958, 2018, 1258, 2458, 1438, 1378 and 2138 nm, respectively. For P, the wavelengths in order of importance were 2098, 1338, 1538, 2258 and 1258 nm, respectively. Calibration statistics of $R^2$ (SEP) for Ca and P of 0.87 (0.15%) and 0.71 (0.02%), respectively, were obtained.

For elements such as Ca, K, Mg, P and S, NIR is reliant on weak molecular bonds, manifested as subtle differences in the spectra. A study by Thygesen *et al.*, 2001 found the

NIR model relied on weak spectral effects and was very sensitive to sample preparations when exploring the ability of NIR to measure P content in potato starch.

The measurement of K in grape petioles, grape leaves, rice shoots and orange leaves by NIR was evaluated by Ciavarella *et al.*, 1998. Correlation coefficients of $r^2 = 0.94–0.99$ and SEP = 0.12–0.18% were achieved on individual calibrations for the four species studied. The regions of the spectrum with the strongest correlations between wavelength and K levels were due to absorption by carbohydrates such as sucrose, starch and cellulose. Potassium in plant tissue exists mainly in its ionic form and, therefore, does not have a NIR signature. Thus, the ability to develop an accurate K calibration must be based on K influencing organic constituents in the plant. Potassium, also being a major element, is found in high concentrations in plants (0.5–6.0%).

## 4.8 Conclusion

A diode array instrument with a useful wavelength range of 550–1700 nm was used to build calibrations of moisture, wet and dry plant N, wet and dry plant nitrate-N and dry plant Ca with considerable accuracy.

Lower accuracies in general were obtained for calibrations for moisture, wet and dry plant N, wet and dry plant nitrate-N and dry plant Ca using the diode array instrument and procedures implemented in this study when compared to other studies in the literature. But the large scan area of the instrument and the ability to measure on wet plant material makes it commercially viable.

The accuracy obtained by the measurement of moisture and total N in plant material indicates that NIR is able to measure these directly as a consequence of O-H and N-H bonds respectively. The accuracy of determination of total N in wet plant is lowered due to the masking effect of water. There is minimal or no loss in accuracy when a large number of plant species is included in the calibration model. This is commercially an important finding because a calibration could include a wide variety of species rather than the need for a single species calibration.

For elements such as Ca, K, Mg, P and S, NIR is reliant on weak molecular bonds manifested as subtle differences in the spectra – therefore calibration models rely on weak spectral effects. NIR does not have the accuracy techniques such as acid digestion/Inductively Coupled Plasma Atomic Emission Spectroscopy or a non-destructive technique such as X-ray Fluorescence possess. These techniques can simultaneously and directly measure the above elements.

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# Chapter 5: NIR Soil Analysis

*Contents*

## 5.1 Abstract

Soil tests TC, TN, TS, ASC, soil type and available N are possible via a direct soil scan. The reference base test for these tests can be time consuming and the NIR offers speed with acceptable accuracies which can be used for agronomic advice. NIR determinations on field moist soil compared to dried soil showed loss in accuracy for the above tests.

Olsen P and K can be measured using rapid extraction, complex formation and presentation to NIR. The accuracy obtained will be acceptable for soil testing purposes. The determination of pH with acceptable accuracy can also be measured by addition of an indictor to the soil:water slurry prior to NIR scanning. Nevertheless, it cannot be compared with the accuracy obtained by measurement using a pH meter.

Soil nutrients analysed in a field moist state and its dry equivalent state were studied in order to see if there were differences. The study indicated that drying of field moist soil show minimal or no change to the test pH, OlsenP, exchangeable Ca, Na and Mg. On average for all soils there is a difference of 3.2 $\mu g\ g^{-1}$ between the measurement of Olsen P determined on field moist and dry soil. This difference is quite small. For exchangeable Ca and Na there were no effects on drying whereas there was a small difference encountered for Mg and larger effects for K. On average, for exchangeable K, a 10% increase was seen on drying the soil.

## 5.2 Key words

Soil, soil analysis, soil moisture, Olsen P, exchangeable K, pH, P retention, total soil S, soil total N (TN), soil total C (TC), available N, soil type, agriculture and New Zealand.

## 5.3 Introduction

Each year in New Zealand, approximately 115,000 soil samples are chemically analysed for their fertility status. Currently, almost all of the soil analyses in New Zealand are carried out using wet chemical extraction techniques, followed by analysis of each specific target element or compound in the extract solution using the appropriate instrumental method of analysis. All wet chemistry is invariably done on dry soil samples and carried out in laboratories.

The use of Near Infrared (NIR) for soil testing is relatively new, with soil testing applications only investigated in the last 2 decades. Literature reviews show that most studies to date have limited themselves to a small number of soil groups or soil types. In practice routine soil testing would need to incorporate factors, such as soil groups.

This study evaluates the use of Near Infrared (NIR) spectroscopy for the analysis of soil in New Zealand on air dried and field moist soils. Soil nutrient determination on air dried soil is historical. Soil nutrient determination on field moist soil has advantage over air dried. The differences between air dried and field moist soils is also evaluated. NIR technology has the potential to make routine soil testing significantly faster, cheaper, and simpler than it is currently. In addition to simplifying current testing programs, the availability of reliable NIR methods is likely to increase the total number of samples that can be analysed. To enable the use of NIR in New Zealand for the purposes of soil testing, calibrations must encompass the wide variety of soil groups found in the country.

Table 5.1a and 5.1b summarises NIR studies in literature presented from tables in chapter 2 on soil tests. Table 5.1a gives an indication of the 'total' element or parameter tested in the soil while Table 5.1b summaries extractable forms. The number of studies for each test, the concentration range for the test, the reproducibility of the base test (reference method) and RMSEP range and mean are also presented. Generally, prior to 1995, the NIR studies on calibrations were carried out on scanning instruments with wavelengths 1100-2500 nm while after 1995, wavelength range 400-2500 nm has been used to build calibrations. For majority of the studies the soil fraction size has all been < 2 mm. The $s_r$(base test) which gives the error in the reference method have only been presented in one or two papers.

**Table 5.1a.** NIR studies found in literature for moisture and for the tests which are an indication of the 'total' element or parameter tested in the soil. A summary from tables found in chapter 2, literature review (Tables 2.1-2.19).

| Test | Studies | Conc. range | $s_r$(Ref test) range | No.studies presented RMSEP | RMSEP range | RMSEP mean |
|---|---|---|---|---|---|---|
| Moisture (%) | 15 | 0.0-70.5 | - | 7 | 0.01-4.9 | 1.7 |
| Clay (%) | 9 | 0-79.0 | 0.26[a] | 4 | 3.8-10.3 | 7.1 |
| Sand (%) | 7 | 1.2-98.3 | 0.28[a] | 3 | 5.9-14.5 | 8.8 |
| Silt(%) | 6 | 0-85.3 | 0.37[a] | 3 | 2.1-9.8 | 5.0 |
| OM (%) | 15 | 0.09-69.3 | - | 10 | 0.2-3.6 | 1.2 |
| OC (%) | 12 | 0.06-14.0 | - | 10 | 0.16-0.74 | 0.3 |
| TC (%) | 18 | 0.05-49.9 | 0.12, 0.35[b] | 12 | 0.08-2.4 | 0.7 |
| TN (%) | 30 | 0.02-2.4 | 0.01, 0.16[b] | 23 | 0.01-0.15 | 0.04 |
| TS (%) | 2 | 0.07-0.28 | 0.01[a] | 2 | 0.02, 0.04[c] | 0.03 |
| TP (%) | 7 | 0.004-0.60 | - | 5 | 0.007-0.04 | 0.02 |
| TK (%) | 5 | 0.07-0.49 | - | 2 | 0.01, 0.3[c] | 0.16 |
| TCa (%) | 8 | 0-29.7 | - | 8 | 0.05-4.6 | 0.9 |
| T Mg (%) | 3 | 0.03-6.1 | - | 2 | 0.21, 0.23[c] | 0.22 |
| TNa (%) | 2 | 0.01-0.19 | - | 2 | 0.002,0.02[c] | 0.01 |

[a] = data $s_r$(base test) from one study only; [b] = data $s_r$(Ref test) from two studies only; [c] = RMSEP data values presented is from two studies.

**Table 5.1b.** NIR studies found in literature for moisture and for the tests which are an indication of the 'extractable' element or parameter tested in the soil. A summary from tables found in chapter 2, literature review (Tables 2.1-2.x).

| Test | Studies | Conc. range | $s_r$(Ref test) range | No.studies presented RMSEP | RMSEP range | RMSEP mean |
|---|---|---|---|---|---|---|
| CEC (c mol kg$^{-1}$) | 10 | 0.4-311.5 | $0.52^a$ | 6 | 2-43 | 10 |
| pH | 12 | 3.5-10.09 | $0.02^a$ | 8 | 0.2-0.46 | 0.36 |
| Available P$^d$ (mg kg$^{-1}$) | 17 | 0.0-912 | - | 14 | 1.0-162 | 49 |
| sulphate-S (mg kg$^{-1}$) | 2 | 4-717 | - | 2 | $70,74^c$ | 72 |
| Exchangeable K (c mol kg$^{-1}$) | 8 | 0.06-36.9 | $0.1^a$ | 5 | 0.19-6.5 | 2.8 |
| Available K (mg kg$^{-1}$) | 6 | 16-1757 | - | 3 | 39-155 | 105 |
| Mineralizeable. N (mg kg$^{-1}$) | 8 | 0-555 | - | 3 | 0.04-23 | 11 |
| Inorganic N$^e$ (mg kg$^{-1}$) | 4 | 0.2-448 | - | 4 | 12.8-44.2 | 28 |
| ammonium-N (mg kg$^{-1}$) | 5 | 0.0-494 | - | 5 | 4.7-86 | 35 |
| nitrate-N (mg kg$^{-1}$) | 6 | 0-394 | - | 6 | 2-38 | 14 |
| Exchangeable Ca (c mol kg$^{-1}$) | 10 | <0.01-98.7 | $0.5^a$ | 5 | 0.6-13.4 | 3.7 |
| Exchangeable Mg (c mol kg$^{-1}$) | 8 | 0.01-94.8 | 0.11 | 5 | 0.35-12.3 | 3.0 |
| Available Mg (mg kg$^{-1}$) | 6 | 17-2886 | - | 4 | 194-248 | 211 |
| Exchangeable Na (c mol kg$^{-1}$) | 3 | 0.1-108.6 | - | 3 | 0.13-14.6 | 5.1 |
| Available Na (mg kg$^{-1}$) | 4 | 16-1330 | - | 4 | 82.9-110 | 96 |

$^a$ = data $s_r$(base test) from one study only; $^b$ = data $s_r$(Ref test) from two studies only; $^c$ = RMSEP data values presented are from two studies; $^d$ = available P in soil solution ext, Olsen P, Colwell P, Bray (I) P, Bray (II) P, Truog P, Melich (III) P; $^e$ = Measurement includes ammonium-N + nitrate-N

The literature suggests that many soil tests are possible particularly with laboratory based NIR instruments. The aim of this study is to evaluate the series KESNIR-01 diode array spectrometer in determining key soil tests used in New Zealand via a direct soil scan. If direct scanning is not possible then use the approach of rapid extracting/complexing of nutrient and then presenting to NIR. This study also evaluates the use of NIR spectroscopy for the analysis of soil on air dried and field moist soils. Therefore the effect of soil drying on soil tests pH, OlsenP, exchangeable Ca, Na, K and Mg.

## 5.4 Method

### 5.4.1 Sample preparation and presentation

Measurements of soils were evaluated using a KES diode array NIR spectrometer with the wavelength rage of 400- 1700 nm. Soil samples were chosen throughout New Zealand from both the North Island and South Island to cover the range of soil types encountered. In order to cover all variations, calibrations for soil testing ensured the inclusion of soils from all 15 New Zealand soil orders and soil subgroup, geographical regions and land use. No previous studies have been reported in which NIR spectra have been recorded for a full range of soil orders in a country. Table 5.2 gives the number of soil orders, soil groups, soil subgroups, soil series and soil types found in New Zealand.

**Table 5.2**: Number of soil orders, soil group, soil subgroup, soil series and soil type found in New Zealand, with an example of Bruntwood silt loam and its New Zealand soil classification (Hewitt, 1998).

| **Soil class** | **Number** | **Example: Bruntwood soil** |
|---|---|---|
| Soil order | 15 | Allophanic |
| Soil group | 73 | Impeded Allophanic |
| Soil subgroup | 267 | Typic Impeded Allophanic |
| Soil series | 1600 | Bruntwood |
| Soil type | approx 3000* | Bruntwood silt loam |

*A soil series can have 1–3 soils at the soil type level, i.e. silt loam, sandy loam or clay loam, etc.

Three-hundred-and-seventy field-moist soils were collected and scanned over a 12 month period (2000-01) on one instrument. The sample collection location from the North and South Islands overlain on a soil order map (gross) is illustrated in Chapter 3, Methods, Figures 3.11 and 3.12 respectively. These samples consisted of 10–20 cores of 0 (surface)–75 mm in depth and 25 mm in width. Soil cores were sifted through a 2 mm sieve and then thoroughly mixed. A 145 mm diameter Petri dish was then filled with soil and scanned using the KES NIR instrument. Each sample was scanned three times.

In order to determine the moisture content of the soil samples a sub-sample of the soil was placed in an oven overnight at 105 °C. A Petri dish of soil of each sample which had been dried between 30-35 °C overnight was also scanned three times.

### 5.4.2 Reference method

The wet chemistry or reference method is a critical step in the procedure in endeavouring to get good NIR calibrations. It is essential to get a good handle of the test, its limitations and factors which influence it. All wet chemistry (reference tests) were determined in duplicate to get an estimate of the repeatability unless otherwise stated $S_r$(Ref test).

Plant-available phosphate in New Zealand soils is determined via a modified Olsen P method. The method employs a $NaHCO_3$ extraction method developed by Olsen *et al.*, 1954 and the phosphate concentration in the extract is determined by a phospho-molybdate method proposed by Watanabe and Olsen (1965) and Murphy and Riley, 1962.

Exchangeable Mg, Na, Ca and K were determined on the 2 mm dry soil fraction using ammonium acetate soil extracts (Blakemore *et al.*, 1980) by an automated 4-channel Atomic Absorption/Emission Spectrophotometer using air/$C_2H_2$. The results are expressed in Quick Test Units for advisory purposes (Cornforth and Sinclair, 1984).

For analysis of total S in soil, the 2 mm sieved, dry soil fraction was sub-sampled using a riffle and ground (using a Teflon-coated ceramic mortar) to a fine powder. Soil samples of 0.500 g were digested with a mixture of concentrated perchloric/nitric acids, diluted, and then determined using ICP-AES (McQuaker *et al.*, 1979).

Soil total N was determined on the finely ground soil using a semi-micro Kjeldahl method (Bradstreet, 1965; Krom, 1980; Basson, 1976).

Soil pH was determined on <2 mm dry soil using a 1:2.1 (v/v) water slurry left to stand for 16–24 hours at 20 °C (Blakemore *et al.*, 1980).

Soil carbon was determined on the finely ground fraction using a carbon analyser (Shimadzu TOC 5000A) via the combustion method (Methods of Soil Analysis, 1996).

Phosphate retention or Anion Storage Capacity (ASC) is determined on the 2 mm dry soil fraction. The soil sample was shaken with a buffered phosphate (1000 ppm) solution for 16 hours. The amount of phosphate remaining in solution was determined colorimetrically at 420 nm (Blakemore *et al.*, 1980).

The Reserve K test gives an estimate of the amount of fixed K in soil, which is not measured by the exchangeable K test. Reserve K for this study was determined using Carey's (2003) modified test of Jackson's (1985) test. The test was measured using 2 mm dry soil fraction.

Available N is used as a measure of N that will become available over the growing season. The test was based on the 7 day anaerobic incubation (Keeney and Bremner, 1966).

### 5.4.3 Calibration Development

The sample spectra produced from direct scanning of soil in Petri dishes were used to build calibrations for soil moisture, Olsen P, Exchangeable K, pH, P retention, total S, total N, total Carbon and available N using PLS. A brief attempt at soil type identification using principle component analysis (PCA) was attempted. Calibrations were developed for both wet and dried soil. If calibrations were not satisfactory for a specific analyte, the approach of "signal boosting" or "complexation" was used.

For this study, samples were assigned to either the calibration set or validation set in a systematic way to ensure that both sets were fully representative of the sample range.
Two-thirds of the samples were assigned to the calibration and a third was assigned to the validation set.

The following pre-treatments were used prior to calibration development. The first 30 detector wavelengths (400–550 nm) were eliminated. Multiplicative Scatter (or signal) Correction (MSC) was used (Geladi *et al.*, 1985) for spectral data. The spectral data were Mean Centred (MC). The overall error between modelled and reference values was determined using the Root Mean Square Error of Cross Validation (RMSECV) using the leave out procedure. The Root Mean Square Error of Prediction (RMSEP) is quoted, which gives the prediction error on independent validation samples for a calibration.

This study endeavoured to answer three key questions which would then enable the measurement of key soil tests to be measured, particularly using field moist soil.

1 Effect of drying

In order to determine soil nutrients in field moist soils using NIR, it was necessary to establish if there was a difference in soil nutrients analysed, when analysed in a field moist state versus its dry equivalent state. This was needed because wet chemistry uses dry sample material. If there is a difference, then how much of a difference is there for the key extractable nutrients Olsen P, pH, QTMg (QT=quick test units), QTK, QTNa and QTCa? There were 85 samples and 3 treatments per sample used for Olsen P QTMg, QTK QTNa and QTCa and 85 samples and 6 treatments for pH to answer the above question. The 85 samples were chosen on the basis of soil type and concentration range in order to see if there was a soil type effect.

1a. The 3 treatments for Olsen P were:

5.0 g dry soil extracted with 100 ml 0.5M $NaHCO_3$ extractant.

Field moist soil equivalent to oven dry 5.0 g soil extracted with 100 ml 0.5M $NaHCO_3$ extractant.

Field moist soil equivalent to oven dry 5.0 g soil extracted with 100 ml 0.5M $NaHCO_3$ extractant – amount $H_2O$ in field moist soil.

1b For the cation determinations (QTMg, QTK QTNa and QTCa) 3 treatments exactly as for Olsen P were used with the exception that the extractant used was 25 ml of 1.0M Na acetate instead of $NaHCO_3$.

1c The 6 treatments for pH were:

20 ml dry soil added to 42 ml distilled $H_2O$.

20 g dry soil added to 42 ml distilled $H_2O$.

20 ml field moist soil added to 42 ml distilled $H_2O$.

20 g field moist soil added to 42 ml distilled $H_2O$.

20 ml (dry equivalent) field moist soil added to 42 ml distilled $H_2O$.

20 g (dry equivalent) field moist soil added to 42 ml distilled $H_2O$.

2. Direct NIR scanning of soil. Is NIR able to determine key nutrients via a direct soil scan? Which of these are we able to predict to a good degree of accuracy?

3. If direct scanning is not possible then use the approach of rapid extracting/complexing of nutrient and then presenting to NIR. One needed to make this step rapid but still

retain the accuracy. i.e. scrubbing with charcoal to get rid of organic matter gave greater accuracy for Olsen P determination but an extra step slowed the procedure.

## 5.5 Results

(1) Effect of drying

For the wet chemistry we needed to establish if there was a difference for soil nutrients analysed in a field moist state and its dry equivalent state. If there was a difference how much of a difference was there for the key extractable nutrients. Table 5.3 gives a summary of the study carried out. The table outlines the soil test, the difference encountered on drying soils and whether the effect is dependent on soil type. The study indicated that drying of field moist soil show minimal or no change to the test pH, OlsenP, Exchangeable Ca, Na and Mg. There was greater change seen for exchangeable K (10%) on average for all soils.

**Table 5.3:** Soil drying effect on soil tests.

| **Parameter** | **Is there a difference** | **How big is the difference on drying** | **Soil type effect** |
|---|---|---|---|
| pH | No | <0.05 pH units | No |
| Olsen P (μg $g^{-1}$) | Yes | +3.2 (μg $g^{-1}$) for all soils | Possibly |
| Exchangeable K (QTK) | Yes | 10 % on average for soils | Yes |
| Exchangeable Mg (QTMg) | Small | log dry= 0.166 + 0.984 log(wet) | No/Yes |
| Exchangeable Ca (QTCa) | No | - | No |
| Exchangeable Na (QTNa) | No | - | No |

No = statistically not significant; Yes = statistically significant; small = just statistically significant

Results for pH indicated that treatment 3 (20 ml field moist soil added to 42 ml distilled $H_2O$) gave the results closest to treatment 1, which is the current reference method in New Zealand (20 ml dry soil added to 42 ml distilled $H_2O$). Average standard error is < 0.05 pH units. The slope in a regression analysis is 1:1 with intercept through zero. Therefore the current test of measuring pH on dry soil (20 ml) can be replaced with measuring it using field moist soil (20 ml). Also further study on 200 soils showed no significant difference if soil pH were measured after10 minutes, 60 minutes or 20 hours on adding distilled $H_2O$ to soil samples.

On average for all soils there is a difference of 3.2 $\mu$g g$^{-1}$ between the measurement of Olsen P determined on field moist and dry soil. This difference is quite small. For exchangeable Ca and Na there were no effects on drying whereas there were small difference encountered for Mg and larger effects for K. On average for exchangeable K a 10% increase was seen on drying the soil.

As part of the above study a procedure and equipment for rapidly drying soil <20 minutes and 35 $^{0}$C was patented (WO 2004/008109, see chapter 10:Patents). The work involved a range of soil types, moisture and Olsen P values. The rapid procedure developed showed no significant difference in results for Olsen P (s.e.d=1.26 Olsen P $\mu$g g$^{-}$1, 30 samples, range:12-54 Olsen P $\mu$g g$^{-1}$) when compared to traditional overnight (30-35 $^{0}$C) drying. There was approximately a 16 % increase on average if samples were dried rapidly at 48 $^{0}$C rather than 35 $^{0}$C.

2. Direct NIR scanning of soil

Direct scanning of soil using KESNIR-01 was only possible for soil moisture, TS, TN, TC, P retention, available N and soil type. These NIR measured tests could be measured to an acceptable degree of accuracy when compared with the reference soil tests. The calibration performance for soil moisture and other tests on dry soil via direct scanning is presented in Table 5.4.

**Table 5.4.** Calibration statistics for moisture and tests carried out on dried soil.

| Parameter | State | Range | $S_r$(Ref test) | RMSECV |
|---|---|---|---|---|
| Moisture (%) | wet | 5-45 | 1.5 | 4.0 |
| Total S (%) | dry | 0.03-0.15 | 0.01 | 0.017 |
| Total N (%) | dry | 0.01-1.62 | 0.03 | 0.14 |
| Total C (%) | dry | 0.5-12.2 | 0.4 | 1.3 |
| P retention (%) | dry | 3.2-97.4 | 0.7 | 6 |
| Available N (mg K g$^{-1}$) | dry | 92-491 | 38 | 47 |

[a] = exchangeable cations K, Ca, Mg and Na measured in quick test units in New Zealand (Cornforth, I. S. and Sinclair, A.G. 1984).

Non linearity of the calibration was observed for soil total carbon with values over 12 %. There was a strong correlation between ASC, C, S and N for the 370 soils studied which indicates there is co-correlation occurring. Table 5.5 shows the correlation between soil tests ASC, C, S and N for the 370 soils. There is a S-H absorption band around 1700 nm. The determination of moisture and P retention take 24 hours to measure using traditional methods. The measurement of available N takes 7 days. Therefore the ability of NIR to measure these within seconds offsets the loss in accuracy. The loss in accuracy in determining the tests using NIR on field moist rather than dry was approximately 15-20%.

**Table 5.5**. Shows the correlation between soil tests ASC, C, S and N for the 370 soils.

| **Test** | **ASC (%)** | **Carbon (%)** | **Nitrogen (%)** |
|---|---|---|---|
| Carbon (%) | 0.54 | | |
| Nitrogen (%) | 0.72 | 0.83 | |
| Sulphur (%) | 0.62 | 0.86 | 0.88 |

One hundred soil samples were used to see if NIR could identify soil types using PCA analysis. Three outliers were found after the PCA analysis was run. It was found that these were not outliers but mislabeling of the soil type. Figure 5.1 shows that pumice soils and volcanic (ash) soils are very similar and overlap.

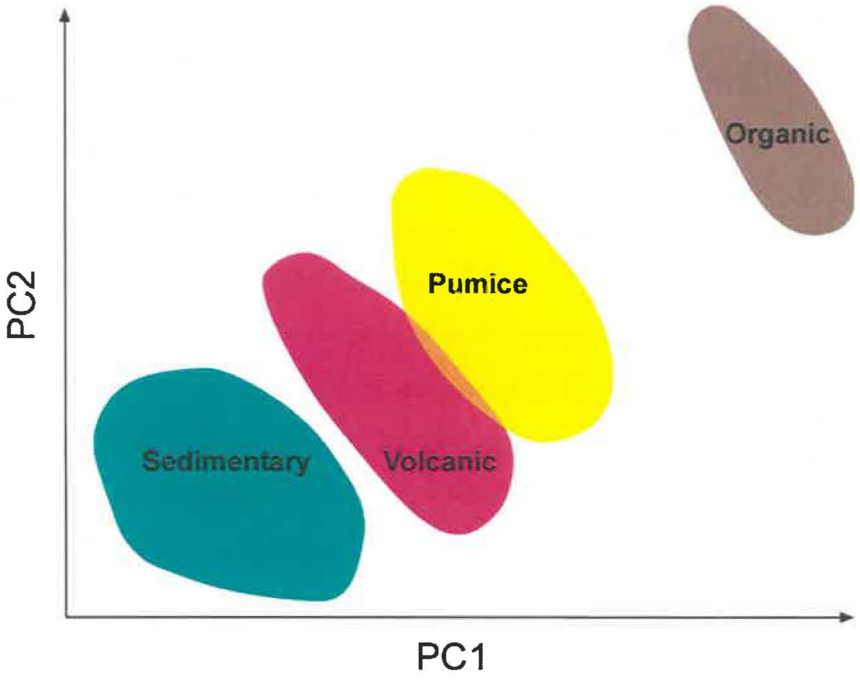

**Figure 5.1:** The 4 distinct soil types was attempted using PCA analysis

3. Rapid extraction/complexing and presentation to NIR for Olsen P, exchangeable K and pH.

   If direct scanning was unsuccessful the approach of rapid extracting/complexing of key nutrients and then presentation to NIR was used (see chapter10: Patents; PCT/NZ2004/000048). Needed to make this step rapid but still retain the accuracy. i.e. scrubbing with charcoal to get rid of organic matter gave greater accuracy but an extra step slowed the procedure.

From a direct scan of soil, soil moisture can be used to determine the amount of oven dried equivalent of field moist soil is required to be used for a rapid extraction procedure. If the soil was dry the appropriate quantity of soil was taken for the test.

**Table 5.6**: Calibration statistics for moisture and tests carried out on dried soil.

| **Parameter** | **State** | **Range** | **$S_r$(Ref test)** | **RMSECV** |
|---|---|---|---|---|
| Olsen P (mg $kg^{-1}$) | dry | 6-100 | 4 | 6 |
| pH | dry | 3.85-7.50 | 0.03 | 0.35 |
| Exchangeable $K^a$ | dry | 1-25 | 1.0 | 3 |

The aim of the work was to determine which step or steps we could eliminate without compromising the accuracy of the Olsen P test. NIR scans were taken at different stages during the measure of Olsen P. One hundred samples were used for this investigation.

The work showed that NIR could not determine P via a direct scan of dry soil in a Petri dish nor filtered soil samples in 0.5M $NaHCO_3$ extract. The work showed that NIR could determine accurately P in soil after addition of the filtered extract to neutralizing & complexing agent (Chapter10: Patents; p266). A brief foray showed that the determination of P is possible where soil in the unfiltered liquor is added to neutralizing & complexing agent is possible using NIR but further work is need to get the desired accuracy acceptable by the agricultural community. Potassium and P measured on the same extract. Very good relationship between K extracted using 1M Na Acetate and 0.5M $NaHCO_3$ ($R^2$=0.96) was found.

For Olsen P, experiments of rapid extraction using a cappuccino maker and a 1 min whisk using a small frothing device were successful and $R^2$>0.95 were obtained when compared to the reference method. But the extraction time which gave best prediction when compared to lab wet reference chemistry was a 10 minute extraction. Use of a soil bag where soil is placed in a 10 micron bag showed no difference when compared to reference method.

## 5.6 Discussion

The results indicate that NIR has, at least, the ability to place New Zealand soils (<2 mm) for the tests TS, TN, TC, P retention and available N into low medium or high category using the KESNIR-01 series spectrometer. If a sample studied contains covalent bonds such as C–H, N–H, S–H or O–H, then it is also very likely to yield accurate results.

Many workers have shown, as is indicated by the number of publications that moisture (15), soil C (27), soil N (30) and mineralizable N (8) in soil can be measured using NIR. Literature suggests (Chang *et al.*, 2001, Moron and Cozzolino, 2002 and McCarty *et al.*, 2002) that direct scanning of soils using NIR for tests such as TC and TN in soil should be possible if calibrations done with soils from throughout the country. Tests such as Olsen P or QTK would be difficult because of the low concentrations ($ug^{-1}$ $g^{-1}$) in soil and the lack of optical activity of ionic species in the NIR region.

There have only been two studies of soil TS (Malley *et al.*, 1999 and Chodak *et al.*, 2002) found in literature. There is an S-H absorption band around 1700 nm and possibly the co-correlation of carbon and nitrogen has enabled TS to be measured. In this study TN correlated well with mineralizeable-N. This is an indication that mineralizeable-N predictions could be influenced by specific information from soil TN.The study by Russell, 2003 also found TN and TC to be strongly correlated with mineralizeable-N.

The fundamental absorbance information found in the Mid-IR region is found in overtones and combination bands in the NIR region. Forrester *et al.*, 2003, showed that Mid-IR could be used to measure (2500-25,000 nm) the P buffering capacity (ASC) of 90 Australian soils. The ASC range was 5-65% and they obtained a RMSECV of 5.2%. This is very similar to the accuracy found in this study. The ASC is the ability of the soil to hold onto P and this is dependent on soil type. This indicates that NIR has the ability to characterize a soil. This is also the finding of this study. NIR is so powerful that it could pick up the outliers which were due to incorrect labeling of the soil type.

It would be ideal to have a single calibration for each soil test, with samples down to the soil series or soil type level, but this was beyond the scope of this study, 1600–3000 samples would have to be calibrated to comprehensively cover soil variation. A single calibration must encompass all soil types and cover the concentration range of the analyte studied. Alternative calibrations for individual soil types or soil groups may need to be developed. Further work has been carried out by AgResearch to fill in the gaps. Currently there are about 700 soil samples in soil calibration for dry and field moist soils.

## 5.7 Conclusions

Soil tests TC, TN, TS, ASC, soil type and available N are possible via a direct scan of dry soil (<2 mm) using a KESNIR-01 series spectrometer. It is expected that accuracies for these tests could be improved using Lab based NIR spectrometers, and fine grinding prior to scanning. This comment is based on findings by other researchers on soil tests using lab based NIR instruments, and the increase of light, and therefore spectral information back to the detector as a result of fine grinding. There is loss in accuracy for the above tests when scans are made on field moist soil.

Olsen P and K can be measured using rapid extraction, complex formation and presentation to NIR with acceptable accuracy for soil testing purposes. Rapid determination of pH (10 minutes) with acceptable accuracy can also be done by addition of an indictor to the soil: water slurry prior to NIR scanning. The accuracy is further improved if measurement is made using a pH meteron the slurry.

Drying of field moist soil show minimal or no change to pH, exchangeable Ca and Na. There was a very small difference noted for Olsen P, and small differences encountered for Mg whereas effects for K were much larger.

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# Chapter 6: Total Soil Sulphur, a Soil Test for the Measurement of the Sulphur Status of New Zealand Pastoral Soils.

*Contetns*

## 6.1 Keywords

Easily mineralisable-S, extractable organic-S, relative yield, organic sulphur, sulphate-S and total soil sulphur.

## 6.2 Abstract

The aim of this study is to determine if the total S pool in soil is a better measure of the sulphur status than *sulphate-S or easily mineralisable organic-S*. Total S accounted for 71% of the variation in Relative yield for 43 field trials, whereas mineralisable-S accounted for 58% and sulphate-S accounted for 59%. Sulphate-S is easily influenced by external sources, such as urine and dung from grazing animals, leaching, fertiliser and atmospheric inputs.

Organic-S accounted on average for 97% of the TS (Total Sulphur) of which phosphate extractable organic S (EOS) consisted of, on average, 3% of TS. The sulphate-S component consists, on average, 3% of the TS. The total sulphur pool, because of its magnitude, is not influenced by external sources to the extent that EOS and sulphate-S, in particular, are. It is, therefore, proposed that total S is a better and more robust measure of the sulphur status for New Zealand pastoral soils.

## 6.3 Introduction

The total sulphur (TS) in New Zealand pastoral topsoils has an approximate range of 0.01–0.25%, of which 90–98% is present as organic sulphur (OS) (Perrott and Sarathchandra, 1987). Generally, the remainder is present as inorganic forms of sulphur. In most well-drained pastoral soils, sulphate-S constitutes 1–2% of TS.

The amount of total organic S in soil is soil-type dependent, and is related to both the level of organic matter and the amounts of S input. As a general rule, soils derived from volcanic ash (Allophanic and Granular soils) have higher organic matter content and organic S levels, relative to soils derived from sedimentary rocks. Sulphur has often been considered a secondary nutrient in respect to the nutrient requirements of plants. However, the importance of S varies around the globe and is dependent on soil type, the plant species grown and the S status of the soil.

Prior to the 1990s, one of the major reasons why so little work was done on S relative to other plant nutrients was the difficulty of measuring S in soils accurately. The development of measuring sulphate-S via ion chromatography and TS via ICP-AES in the last two decades, has led to increased measurement accuracy and therefore spurred further research. Previous to these methods, sulphate-S and S were measured turbid metrically, which did not have the accuracy, precision or detection limits of the current methods in use today.

In the early 1990s, researchers at *AgResearch* developed the two soil sulphur tests used in New Zealand labs today. The test uses 0.02 mol/L $KH_2PO_4$ as the extractant. Four grams of dry soil is extracted with 20 mL of the extractant for 30 minutes, using an end-over end-shaker (Watkinson and Kear, 1996b). One of the sulphur tests measures the *immediately available S* (sulphate-S), using High Pressure Ion chromatography (HPIC) in the extract (Watkinson and Kear, 1994). On the same extract, the total extractable S (TES) – using Inductively Coupled Plasma (ICP) – is measured. The second test, *easily mineralisable component of organic-S*, is determined as the difference between TES and sulphate-S. The mineralisable organic-S is slowly available to pasture over the year and gives an indication of the longer-term sulphur supply of the soil to plants.

Easily mineralised organic-S is approximately 1–5% of the total organic-S in soil. Easily mineralisable organic-S – otherwise known as extractable organic-S (EOS) – ranges from 2–30 mg/kg approximately in New Zealand pastoral soils. Soil sulphate-S in New Zealand pastoral soils has a similar concentration range to EOS if it is not influenced by external sources such as fertilizers. EOS and sulphate-S are related by a quasi-equilibrium relationship (Watkinson and Kear, 1996a).

The EOS test was developed to overcome some of the problems associated with the sulphate-S test. The sulphate-S test values are influenced particularly by fertiliser, dung and urine patches (Kear and Watkinson, 2003) and leaching. Leaching studies showed that sulphate-S concentrations in leachate remained constant at approximately 10 mg $L^{-1}$ over the leaching period from grazed pastures in the Waikato, with leaching losses of 40–70 kg $ha^{-1}$ $yr^{-1}$ S as sulphate-S (Rajendram *et al.*, 1998). Typically, sheep and beef and dairy farms apply S at the range of 30–100 kg $ha^{-1}$ $yr^{-1}$. In the short term, applied S from fertiliser has no effect on EOS, but increases sulphate-S.

Atmospheric inputs of S from annual rainfall were found to be 12 kg ha$^{-1}$ yr$^{-1}$ near the coast and 1 kg ha$^{-1}$ yr$^{-1}$ 99 km inland (Ledgard and Upsdell, 1991). Inputs of 5 and 7 kg ha$^{-1}$ yr$^{-1}$ were found in sites in the Waikato and Taranaki dairy regions, with the sites approximately 35 and 10 km from the coast, respectively (Rajendram *et al.*, 1998). The amount of S deposited via rainfall at a site is dependent on the distance of the site from the nearest coast.

The application rates of sulphur on pastoral soil from urine and dung patches are, on average, 35 and 100 kg/ha respectively. Urine from dairy cows increases the EOS by about 10 mg/kg, but this disappears within a week whereas sulphate-S increases by about 20 mg/kg and disappears within 2 weeks. Dung from cows increases EOS by about 5 mg/kg but persists for up to 2 years. However, sulphate-S increases by about 150 mg/kg initially and introduces an appreciable error in tests measuring soil sulphate levels for over a year (Watkinson and Kear, 1996b and Kear and Watkinson, 2003). Seasonal changes or leaching events generally have no effect on EOS values but can affect sulphate-S values (Ghani *et al.*, 1990). The sulphate-S values are generally higher during the summer periods.

Presently, in New Zealand laboratories, the EOS test complements the sulphate-S test for fertiliser decision- making. It is especially relevant on soils with low anion storage capacity (ASC), e.g. pumice, peat and sedimentary-derived soils.

Trials done throughout New Zealand showed that a single relationship between pasture growth and the two sulphur soil tests could be applied to all soil groups. The EOS and sulphate-S levels, which will sustain near-maximum pasture production, are found to be 15–20 and 10–12 mg/kg, respectively.

Plants uptake sulphur as the anion sulphate-S; annual plant sulphate-S uptake is greater than that measured by sulphate-S in topsoil (0–7.5 cm) at any given time. Therefore, as an example, if pastures produce 12–15 tonne of dry matter per annum and the average concentration of sulphur in the herbage is 0.30% (a level which is not limiting), the uptake by pasture is 36–45 kg ha$^{-1}$ yr$^{-1}$ S. The soil sulphate concentration of 10 mg/kg in the 0–20 cm (average A horizon depth), which gives an adequate sulphate-S and would maintain maximum pasture production, supplies plants with only 18 kg ha$^{-1}$ yr$^{-1}$ S. Therefore, a large proportion of S (> 50%), which is taken up by pasture annually, is the result of mineralisation of organic matter.

If sulphur fertiliser in the form of superphosphate is applied at normal rates for pastoral farming, it will overcome any deficiency for approximately one year. Generally, if soil S levels are below optimum, maximum production can be achieved if maintenance levels of P are applied in the form of a superphosphate or its equivalent – the sulphur requirements are then met. Single super phosphate contains approximately 12.5% sulphur. The amount of S to overcome deficiency for ash, sedimentary and pumice soils is 25, 35 and 45 kg/ha, respectively. Sulphur recommendations are designed to eliminate any sulphur deficiency since it is a very cheap fertiliser, for example, relative to phosphate. Elemental sulphur is also used on sites or soil types where leaching of sulphate-S can be a problem. On dairy farms, typical application rates are in the range of 500–800 kg super phosphate or its equivalent per annum. This is equivalent to 62–100 kg of S per annum. On sheep and beef farms the application rates are in the range of 250–375 kg super phosphate per annum. This is equivalent to 30–47 kg of S per annum.

When it was first developed, the EOS tested was widely adopted and was used to complement sulphate-S, but now, approximately 10% of all soil tests are determined for EOS (*AgResearch* Lab findings). Of the two tests, EOS is a better indicator of the sulphur status of New Zealand soils, but in order to determine EOS, measurements on two different instruments are made with the difference calculated as EOS. There are also problems associated with measuring EOS by difference on a routine basis – both instruments need to be working optimally otherwise accuracy is compromised. The cost of analysing the two tests in New Zealand is approximately $10 each, with the cost of sulphate-S included in the basic soil test and EOS offered as an extra test. This has therefore led to the demise of the EOS test, with the majority opting for the measurement of sulphate-S only, which is not useful.

This study aims to show that the total soil S pool should be a better measure of the sulphur status in pastoral soils. It is a larger pool than the two smaller pools currently tested. The total S pool should not be influenced over a season to the extent of sulphate-S or EOS, because of its relative magnitude. The sulphate-S and EOS are a consequence of the much larger total S pool, because there exists a quasi-equilibrium between the three fractions as proposed by Watkinson and Kear (1996a).

Therefore, this study aims to show that soil total S pool is a better measure of the sulphur status (by the use of relative pasture yield) than *sulphate-S or easily mineralisable organic-S*.

## 6.4 Material and Methods

For this study, the same 43 air-dried soils used by Watkinson and workers of *AgResearch* to develop the two soil sulphur tests in use by New Zealand laboratories were used (Watkinson and Perrott, 1990). The soils were from field trials conducted throughout the country to determine pasture yield responses to S fertiliser application. Sulphur fertiliser had not been applied to the trial sites for at least one year prior to the commencement of the trial. The topsoil was taken to a depth of 7.5 cm from control (untreated) plots. These cores were taken prior to the commencement of the trial. Sulphur in the form of gypsum was applied in excess of that needed to prevent pasture growth deficiency for one year.

The relative yield was calculated as the relative amount of pasture grown over that year on the control plots compared with that on plots applied with S. The relative yield is calculated by the following equation:

$$\text{Relative Yield (R.Y)} = \{100 / (\%\ \text{Response} + 100)\} \times 100.$$

Kear and Watkinson, 1991 showed that long-term storage of air-dried soil samples had little affect on sulphate-S and EOS concentrations.

The measurement of total S was carried out on the sample after being finely ground using a mortar and pestle. Total S was measured by acid digestion, using a mixture of $HNO_3/HClO_4$ followed by determination on ICP, using the 1819.05 with off-line background correction (Perrott *et al.*, 1991). EOS and sulphate-S were determined by difference between ICP measured TES and HPIC sulphate-S. Total S, EOS and sulphate-S were determined in duplicate and the mean result for each soil was used in the comparison. The Anion storage capacity (ASC) was also measured for each soil. Statistical evaluation of relative yield was compared to total soil S, EOS and sulphate-S.

## 6.5 Results and Discussion

A summary of results, which includes Relative Yield (RY), mean concentration and concentration range of TS, EOS and sulphate-S for the 43 soils, is shown in Table 6.1. The proportion of EOS and sulphate-S in relation to TS is also given in Table 6.1.

The range of TS values in this study are similar in range to those found by Perrott and Sarathchandra, 1987, when they looked at nutrient and organic matter levels in New Zealand soils under established pasture.

**Table 6.1:** Relative yield, TS, EOS and sulphte-S for 43 field trial soils..

| | **R.Y (%)** | **TS (%)** | **EOS mg/kg** | **sulphate-S mg/kg** | **EOS of TS (%)** | **sulphate-S of TS (%)** |
|---|---|---|---|---|---|---|
| Mean | 83 | 0.06 | 18 | 17 | 3 | 3 |
| Range | 12–102 | 0.01–0.11 | 5–32 | 2–77 | 2–5.5 | 1–7.5 |

The mean sulphate-S and EOS concentration are very similar for the soils, but there is a greater spread or range for sulphate-S (2–77 mg/kg) in comparison to EOS (5–32 mg/kg). This indicates that, possibly even in a field trial scenario, where the trial site was fenced off prior to commencement of the trial, sulphate-S has been influenced to a large extent by previous urine and dung-affected areas within the site or possibly from previous fertiliser applications. This is possibly true for 4 or 5 sites out of the 43 used in this trial.

The mean percentage of sulphate-S and EOS concentration in relation to TS is similar at 3%.

The relative standard deviation of the samples analysed in duplicate (precision) of the wet chemistry for EOS is 1.1 mg/kg, S-sulphate is 1.6 mg/kg, and for TS is 0.006%.

Sulphate-S accounted for 59% and EOS accounted for 58% of the variation when compared with Relative yield for 43 field trials (Figures 6.1 and 6.2).

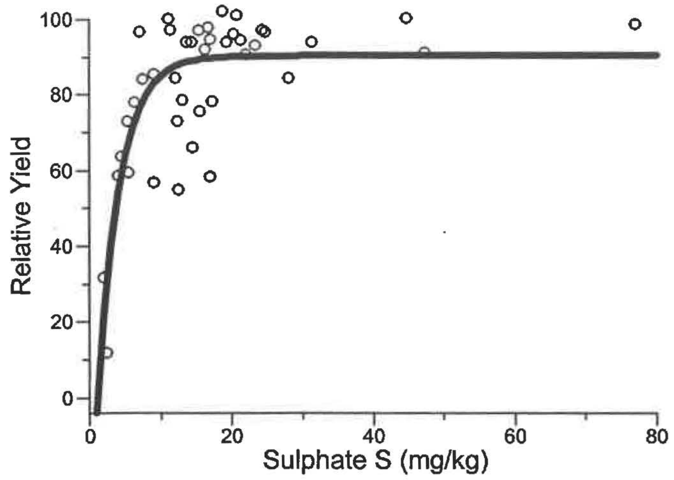

**Figure 6.1:**
Relationship between $SO_4^{2-}$ and Relative yield for 43 field trials.

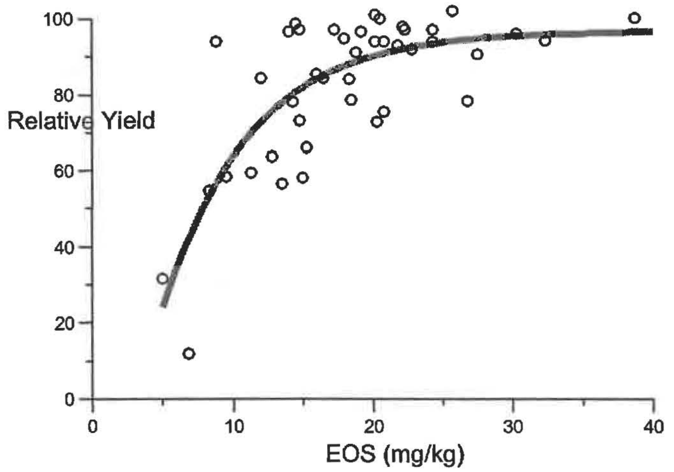

**Figure 6.2:**
Relationship between EOS and Relative yield for 43 field trials.

Total S accounted for 71% of the variation when compared with Relative yield for 43 field trials (Figure 6.3). Multiple regression using TS and ASC did not improve accounted variance.

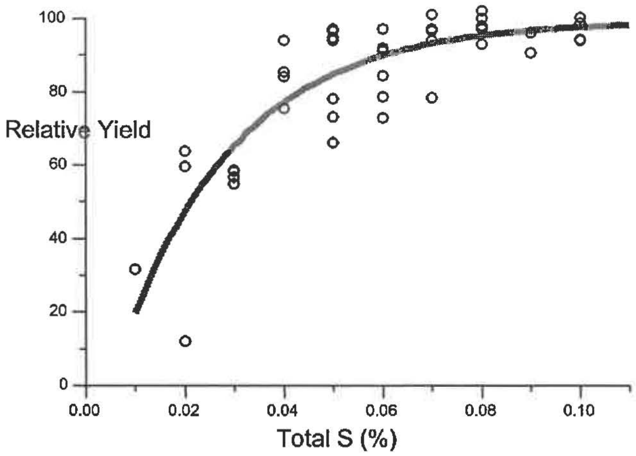

**Figure 6.3:**
Relationship between Total-S and Relative yield for 43 field trials.

Figure 6.4 illustrates the relationship between EOS and Total-S for the 43 field trial soils ($r^2 = 0.74$). Watkinson and Perrott, 1990 also found in their study that there was a good relationship between EOS and TS for the Taupo Series (pumice soils).

It was found that the relationships between TS and S-sulphate was $r^2 = 0.49$, with indications that 4 sites or 5 sites were markedly influenced by dung, urine or past fertiliser applications.

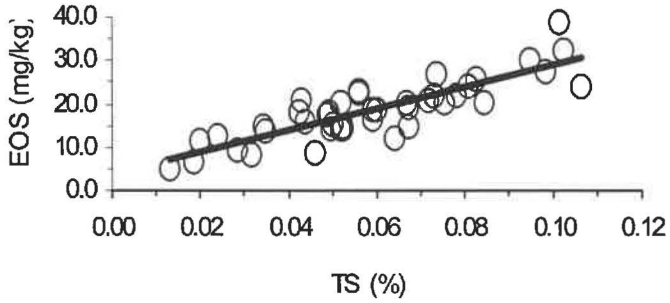

**Figure 6.4:**
Relationship between EOS and Total-S for 43 field trial soils.

Table 6.2 gives the relative ranges of TS, the likelihood of response to S fertiliser application, the expected Relative Yield range, and fertiliser recommendations.

**Table 6.2:** Relative yield, likelihood of response and recommendations.

| TS (%) | Likelihood of Response | R.Y (%) | Recommendation* |
|---|---|---|---|
| <0.04 | High | <75 | Definitely needs sulphur. |
| 0.04 – 0.06 | Medium | 75–90 | Maintenance levels needed.<br>Apply S if non-S fertilizer, i.e. rock phosphate.<br>If sheep or beef farm, this range could be adequate. |
| 0.06 – 0.08 | Low | 90–95 | If dairying, should be in this range; if not, apply S. |
| >0.08 | Nil | >95 | S fertiliser not needed. |

* Recommendations are based on the author's view.

For mineral soils, if TS is < 0.04%, the R.Y will be poor (<75%) and very good responses to sulphur fertiliser will be achieved. Soils with TS levels < 0.04% will critically limit pasture growth.

Soil TS, in the range 0.04–0.06%, will achieve moderate response to S fertiliser application. For sheep or beef farms, TS in this range may be economically feasible, though S is a cheap form of fertiliser relative to phosphate.

Levels between 0.06–0.08% should be okay and small responses to S application will be achieved from the majority of sites in this range. It will be essential in a dairying situation that the TS status be in this range. If not, sulphur should be added to make sure the R.Y is 95% or better because of dairying economics.

Trials done throughout New Zealand showed that a single relationship between pasture growth and soil test could be applied to all soil groups. The EOS and sulphate-S levels, which will sustain near-maximum pasture production, are found to be 15–20 and 10–12 mg/kg respectively. The TS level required to sustain near-maximum pasture production is >0.06%. The single relationship also holds true for the TS test for all mineral soil groups. groups.

TS is an alternative and probably a more robust test than the existing S tests for the measurement of S status of New Zealand pastoral soils. Literature and this work indicate that measurement of sulphate-S alone will be a poor indicator of the S status of pastoral soils.

Studies done by AgResearch on soil testing, (where data from a number of field trials were combined), showed between-year coefficients of variability for hill country and flat to rolling land were 37.4% and 45.8% respectively for sulphate-S. This suggests a flat site considered to have adequate sulphate-S (10 mg/kg) could, the following year, have a test value ranging 1–19 at the 95% confidence limit. A sulphate-S value of <10 would indicate deficiency. The work by AgResearch indicated that sulphate-S was the most variable soil test when compared to other major soil tests. The larger variability found in flat to rolling land, when compared to hill country, can be attributed to greater intensification and sampling regime.

From a practical point of view, when farm advisors/consultants or fertiliser representatives collect samples from farms, they try and 'fit in' with the farmer's rotation. Invariably, soil samples have been collected from a paddock that has been recently grazed. The recommendation is that soil or plant samples are collected just prior to grazing. Practically, however, this is never likely to happen. If a paddock is annually sampled, and stock were in the paddock 1 week prior to sampling, the sample would be invariably collected.. It is very difficult, if not impossible, to distinguish a urine-affected area on recently grazed paddocks i.e. < 3 weeks. Therefore, many of these samples will not give a good indication of the sulphur status if sulphate-S (particularly) or EOS (lesser extent) is determined.

Williams *et al.*, 1988 calculated that on dairy farms, with a stocking rate of 3 cows per hectare, excreta would cover approximately 23% of pasture in 1 year, and the area affected by excreta may be at least twice that covered. Advisory recommendations are that approximately 15–20 cores be taken from a site or paddock. Therefore, it is expected that 4 of these cores will be affected and give an artificially higher S status.

The organic-S component, on average, for these soils, is 97% of the TS, of which EOS consists of, on average, 3%. The sulphate-S component consists, on average, 3% of the TS. The total sulphur pool, because of its magnitude, is not influenced to the extent that EOS and particularly sulphate-S are. Therefore, the TS pool is a better measure of the supply of S to NZ pastures. Pot trial studies (Goh and Pamidi, 2003) showed that soil S taken up by plants after the 8th week period originated directly from the mineralization of soil organic S from S pools other than those present in extractable forms.

This study shows the strong relationship between EOS, TS and Relative yield for pastoral soils in New Zealand and further strengthens the claim that a quasi-equilibrium exists between sulphate-S, EOS and TS.

When Watkinson and colleagues carried out their work to develop a soil sulphur test for New Zealand, they were looking for a quick extractable method that correlated well with field pasture production. The determination of TS via traditional methods is time-consuming and expensive, since it normally employs a digestion procedure. Advances in new measurement technology, such as Total Sulphur Analysers, XRF, Near IR and Mid IR, will enable the measurement of TS to be fast and cheap and therefore better able to accurately predict the sulphur status of New Zealand pastoral soils.

## 6.6 Conclusions

The total sulphur status in New Zealand topsoil is a good indicator of the supply of sulphur to pasture.

Sulphate-S is easily influenced by external sources such as urine and dung from grazing animals, leaching, fertiliser and atmospheric inputs, and is therefore a poor indicator of S in pastoral soils.

This study shows the strong relationship which exists between EOS and TS, and therefore further strengthens the hypothesis of a quasi-equilibrium existing between sulphate-S, easily mineralised-S, and TS.

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# Chapter 7: N status Test

*Contents*

## 7.1 Key Words

Soil, pasture, soil tests, nitrogen (N), N status, soil total N (TN), organic-N, inorganic-N, quazi-equilibrium, mineralization, steady state, anion storage capacity (ASC) response and dry matter yield.

## 7.2 Definition

N status test: Multiple of soil/plant tests which best describes a sites N pool. It gives an indication of the site's ability for pasture/herbage production in the absence of applied N, response to applied N and susceptibility to N leaching.

## 7.3 Abstract

An earlier field trial study in the Waikato over two years, showed soil N status (total soil N (TN) and inorganic-N) influenced pasture growth without N fertiliser and therefore, determined the level of response to N fertiliser.

In order to see if this would hold for all New Zealand soils, and determine whether a N status test or tests could be developed, 52 sites were chosen over a range of fertility levels with total soil N concentrations of 0.2-1.4%. The soils collected were from dairy and sheep/beef farms where N fertiliser had not been applied for at least 3-4 months. The sites were located between Northland to Southland to get a geographical spread and cover the major soil types found in New Zealand. A glasshouse trial was conducted using these soils where moisture and temperature were equivalent for all soils over a seven month period.

The study found that the N status varied greatly across New Zealand and was dependent on soil type and land use. The N status in the soil greatly influences dry matter production. There was invariably a response to N application. The N status in the soil could be determined using inorganic-N and total soil N. There was a very good relationship between inorganic-N and organic-N with the inorganic-N constantly replenished from the organic pool. In soil 99.5% of the TN in the soil, on average, comprised of organic forms of N. The inorganic-N, on average, comprised 0.5% of the total N pool. The inorganic-N is available to plants immediately (days/weeks) and the total soil N which is predominantly soil organic N (months/years) is available over the growing season.

N status in the soil influenced herbage production in the absence of nitrogen fertiliser. The herbage yield from six cuts over seven months was significantly correlated with inorganic-N and TN in soil. Because inorganic-N is taken up by plants, inorganic-N in the soil drives herbage production. Inorganic-N accounted for 77% and TN accounted for 43% of the variation in dry matter yield in absence of N fertiliser. Using multiple regression, 81% of the variation was accounted for when dry matter yield was correlated against inorganic N, TN and ASC for mineral soils. Using multiple regression, TN and ASC accounted for 58% of the variation on this data set.

For initial response (1st cut response), inorganic-N accounted for 57% of the variation. There was no improvement in this relationship by including inorganic-N, Total N, ASC and C:N ratio. The inorganic-N was the best overall predictor of short term responses to N.

A strong relationship existed between grass N concentration and soil inorganic-N concentration and between grass N concentration and soil TN concentration with the grass N maximum corresponding to approximately 5.0%. The corresponding soil inorganic-N and soil TN at this maximum was approximately 30 mg $kg^{-1}$ and 6000 mg $kg^{-1}$ (0.6%) respectively. The concentration of N in grass was a very good indicator of the amount of response achievable on fertiliser N application. The N concentration in grass could also be used to accurately predict N responses to fertiliser application.

This study showed that herbage N, soil inorganic-N and soil TN (which averages 99.5% of soil organic-N) can be used to give a good indication of the N status of soils. These tests can be determined rapidly, accurately and cheaply, using NIR (see Chapter 4 & 5).

## 7.4 Introduction

Nitrogen is the most deficient element in the pastoral system. Therefore, it drives pasture and crop production, yet there is no routine soil N test. Nitrogen (nitrate-N), in excess, can also be environmentally detrimental to the ecosystem. At present, a suite of soil tests known as the basic soil tests in New Zealand consists of pH, Olsen P, sulphate-S and the exchangeable cations Ca, Na, K and Mg.

In the 2004, 340,000 tonnes of N fertiliser were applied to New Zealand agricultural land (Catto W., Ballance Agri-nutrients Ltd. *Pers. Comm.*). The application of N fertiliser has been steadily growing each year. The local regional councils are intending to monitor the use of fertiliser on farms, particularly N, in the future (Lal D.,Environment Waikato. *Pers. Comm.*).

Soil or plant tests may be useful predictive tools for estimating responsiveness to N. Soil tests for N availability have proven difficult to develop, and no single test has been universally adopted. Most of the work done to date in New Zealand has been on field crops, and much of this work was on cereal responses to N application in Canterbury in the 1970's (Ludecke, 1974) and (Steele and Cooper, 1982), estimating nitrogen fertiliser requirements for maize.

The majority of soil N (over 94-98 %) is present in soil organic matter and is not directly available to plants, 1-6 % is fixed in clay minerals ($NH_4^+$), and only 1-2 % of the total N at any one given time, is in the inorganic form ($NO_3^-$, $NH_4^+$ and $NO_2^-$). The release of organic N by mineralization is dependent on a number of soil environment factors such as temperature, moisture, soil nutrient status and C:N ratio (McLaren and Cameron, 1990; Schipper *et al.*, 2004). Mineralization is almost entirely from microbial activity (Whitehead, 1995). Nitrate, a product of mineralization, is susceptible to removal by leaching, denitrification and immobilisation.

Good correlations have been made between one method and another, where chemical soil extractants and biological incubation methods have been used to try and determine the 'potentially mineralizable soil N' (Selvarajah *et al.*, 1987). However, there have not been good correlations between the prediction of mineralizable soil N and the resulting crop response.

The quantitative determination of exchangeable $NO_3^-$ and $NH_4^+$ is easily obtained by 2M KCl extraction. Complications arise due to the extensive spatial variability (Haynes and Williams, 1993) of these ions in field soils. These forms of N are subject to microbial transformations, which can lead to changes in the inorganic content of the soil. It is therefore necessary to analyse the samples as soon as possible after sampling. Soil drying increases inorganic N due to mineralization of organic matter by about four fold (Rajendram *et al.*,1998[1&2]). Accurate soil sampling, with avoidance of urine and dung patches, is an important step in getting meaningful results. This can be achieved by sampling paddocks which have not been grazed for 3-4 weeks and where urine patches are clearly identifiable.

Pasture responses to fertiliser N occur at most times of the year in New Zealand, but the magnitude of the response is variable, particularly in autumn (Cornforth and Sinclair, 1984). For a defined period of pasture growth and N response, soil N availability is determined by inorganic N in soil at the start of the period and that supplied during the period from mineralization of soil organic N.

A wide range of possible tests exist to determine 'potentially mineralizable soil N'including various chemical extractants and biological incubations. However, there are no published studies in New Zealand examining the relationship between pasture N response and some index of soil N availability, apart from Rajendram *et al.*, 1998[1].

Rajendram *et al.*, 1998[1&2] examined the relationship between a range of soil N tests and pasture responses in established Waikato pastures and showed that total soil N was the best overall predictor of short and long-term responses to N. Total soil N accounted for approximately 70% of the variation. Using multiple regression of N response with total soil N, and inorganic N accounted for 75% of the variation, and using a combination of Total N, inorganic N, organic soil Carbon (C) and C: N ratio accounted for 95% of the variation. This preliminary study on 18 Waikato sites under long term dairy pasture indicated:

- Soil N status influenced pasture growth without N fertiliser, and therefore determined the level of response to N fertiliser.
- Total soil N was the best predictor of pasture response to N application.
- Total soil N showed variable but significant correlations with most other tests.
- Soil tests may have a useful role in predicting pasture responsiveness to N fertiliser.

The above work showed that soil testing was useful in predicting pasture responses to N fertiliser in the Waikato district on Ash soils and further work was needed on a wider range of soils. Therefore, this glasshouse trial study is used to further our knowledge on the role of soil N tests over a wide range of soils. A glasshouse trial was chosen in order to keep moisture and temperature conditions the same for all soils.

The aim of the work carried out here and future work to be carried by AgResearch, will produce a suite of tests known as the '*N status tests*' that would endeavour to accurately predict the N status of a site. The test will endeavour to detemine:

- The relative dry matter production, in the absence of applied N, and also predict the response of nitrogen fertiliser application to pasture.
- The supply of available soil N, by determining the inorganic N present in soil at the time of sampling, and the mineralizable N that would become available during the growing season, through mineralization of organic matter.
- Development status of a soil and susceptibility to N leaching. Results from this might then be able to be used in the overseer model.

The '*N status tests*' would be undertaken with the standard tests during regular analysis of farmer's soil samples at analytical laboratories. The soil samples tested would identify whether the farm or parts of each farm have a low, medium or high nitrogen status. The test would need to be quick and reliable and not be cumbersome and time consuming in order to be used by labs. The use of NIR where a combination of tests which can be determined simultaneously, rapidly and also cheaply, would enable this to be a possibility.

## 7.5 Method

Sites were chosen throughout New Zealand on the basis of getting a range of fertility with total soil N concentrations of 0.1-1.5%. The soils collected were from dairy and sheep/beef farms where N fertiliser had not been applied for at least 3-4 months.

In total, 52 sites were sampled from Northland to Southland to get a geographical spread. Soils collected were from Northland, Waikato, Bay of Plenty, Central Plateau, King Country, Taranaki and all major districts of the South Island. A description of the sites is given in the appendix (Table 7a, appendix). The table presents a simplified soil type used by labs for soil testing purposes, separated into ash, sedimentary, pumice, organic and sands. The table also presents a more comprehensive soil type description and the district from which the sample was collected.

Approximately 10-15 kg of soil from the 0-10 cm depth was collected and couriered to Ruakura Research Centre, Hamilton. The sample was placed in the chiller (4 $^0$C) until all the samples were collected.

Each soil was sieved through a 4 mm sieve and mixed thoroughly. A sub-sample was air dried (30-35 °C) and analysed for a range of tests. These tests included ammonium-N, nitrate-N, soil TN, pH, exchangeable Mg, Ca, Na and K, sulphate-S, Olsen P, Organic carbon, total soil S, anion storage capacity (ASC), particle density, allophane reactivity and lab measured bulk density (volume/weight). These tests are presented in Table 7a and 7b (appendix). The reference method to these tests can be found in Blakemore *et al.*,1987.

Each field moist soil was then packed into 7 pots (15 cm diameter) with a bulk density of approximately 0.9 g cm$^{-3}$ and oven dried weight equivalent to 750 grams. One of the pots was used to determine the water holding capacity of the soil. The pots were watered to 80% water holding capacity each day during the period of the trial. Four soils had <750 grams of OD equivalent soil in each pot, due to low bulk densities and high organic matter content.

All pots were leached with 3 pore volumes of distilled water just prior to planting seedlings in order to leach as much of the inorganic-N which would have accumulated during storage and processing of the soils. Twelve seedling of ryegrass were planted in each pot. Calcium carbonate, which was initially applied, and 0.001 M KOH, were applied during the trial to ensure the soils had a pH of approximately 5.8. The essential major and trace elements, required for plant growth (excluding N), were applied to each pot and ensured these were not limiting during the duration of the trial. The pots were placed in the glasshouse randomly and shifted around the glasshouse to overcome glasshouse micro climate effects.

Just prior to N fertiliser application, each pot was sampled using a miniature soil corer (10 mm diameter). The entire depth of potted soil was sampled using the corer. Three corers were taken for each pot. The pooled average for all six pots for a soil were measured for ammonium-N, nitrate-N, inorganic N (ammonium-N + nitrate-N). These results are presented in Table 7a as $NH_4$ (wet soil), $NO_3$ (wet soil) and $NH_4$+$NO_3$ (wet soil).

For each soil, 3 pots were used as control (nil N applied) while the other 3 pots of each soil had N applied at 50 kg N ha$^{-1}$ equivalent. This meant that each N treated pot received 61.6 milligrams of N. The N rate was calculated using the surface area of the pot. The pots were placed on tables within the glasshouse. The position of the pots was re-randomised on a regular basis to overcome glasshouse effects.

The minimum and maximum temperatures were recorded daily during the trial and varied between 1 and 31 °C respectively.

The glasshouse trial was conducted from December 2000 till the end of the 6th cut in August 2001. Herbage cuts were taken 3 cm above the soil surface. The first 2 cuts were treated as conditioning cuts to ensure the plants had been well established in the pots. Herbage growth was monitored for four further cuts until no or small differences were apparent between fertilised and control plots. The dry matter yield was recorded for each pot (Table 7c, appendix). The herbage at each cut from the three control pots and the three N treated pots for each soil was pooled and N content analysed, to estimate N in grass response and N uptake (Table 7d and 7e) respectively. Table 7f summarises all soils, total dry matter yield for pots with nil and N applied, kg of dry matter produced per kg N applied, 1st cut and total response to N fertiliser application, N kg/ha in grass (% response) and N uptake in grass (% response) for the trial.

A problem which happened during the trial was fungal attack on plants which lead to some of the plants dying. Fungicide was sprayed and affected plants replanted. This occurred approximately four months into the trial.

## 7.6 Results and Discussion

The mean, median and range of inorganic-N, TN and inorganic-N as a percentage of TN are presented in table Table 7.1. The inorganic N (ammonium-N + nitrate-N) measured just prior to N fertiliser application ranged from 0-169 mg kg$^{-1}$ soil. The inorganic N median and average were 12 and 28 mg kg$^{-1}$ respectively. The total soil N content in the soils ranged from 0.24-1.4% (2400-14000 mg N kg$^{-1}$) soil with the mean and median approximately 0.52% (5200 mg N kg$^{-1}$). The mean percentage of inorganic N concentration in relation to TN is 0.5%. Therefore, 99.5% on average of the TN in the soil comprised organic-N forms of N. The range for organic forms of N in soil was 97.5-100%. The study by Rajendram *et al.*, 1998[1&2] in Waikato, soils under long term dairy pasture, showed organic N was the main constituent of total soil N, with inorganic N comprising only 0.5-1.3% of total soil N. Therefore, the TN test is a good approximation of the organic-N found in the soils.

**Table 7.1:** The mean, median and range of inorganic-N, TN and inorganic-N as a percentage of TN.

| | **Soil TN (%)** | **Inorganic N mg kg$^{-1}$** | **Inorganic-N as % of TN** |
|---|---|---|---|
| Mean | 0.52 | 28 | 0.5 |
| Median | 0.46 | 12 | 0.3 |
| Range | 0.24-1.4 | 0-169 | 0-2.5 |

The inorganic N range and mean for the glasshouse trial soils was similar when compared to inorganic N measured from pastoral soils (Whitehead, 1995).

The range of TN values in this study is similar to that found by Perrott and Sarathchandra (1987). They looked at nutrient and organic matter levels in 21 New Zealand soils under established pasture which were representative of the major soil groups. The range for TN in mineral soils in their study was 0.22-1.03%. (2200-10,300 mg kg$^{-1}$). The percentage of N 'light fraction' ranged from 16-87% as a percentage of the TN for the soils in Perrott and Sarathchandra (1987) study. The light fraction contains labile organic matter which is important in the mineralization and accumulation in pastoral soils. Greater quantities and larger proportions of the light fraction were found in soils under pasture than in cultivated soils which is consistent with the larger proportion of input of organic material into soil by pasture.

Total soil N was highly correlated ($R^2$=0.80) with soil organic carbon. The average and range for the C:N ratio were 11.4 and 8.5-17.8 respectively for the mineral soils used in this study. A C:N ratio of 10-12 for soils under established pasture suggests that decomposition of organic matter has reached an equilibrium. The soil under a long term pasture system will tend towards a steady state in organic C and N, with organic matter formation and mineralization in balance (Walker *et al*, 1959; Jackman, 1964).

There was also a good relationship between inorganic-N and TN, $R^2$= 0.5 (significant, P<0.001). Figure 7.1 illustrates the relationship between inorganic-N and TN for the 52 soils. There was also an excellent relationship shown between total soil N and inorganic N ($r^2$=0.78) for a two year study by Rajendram *et al.*, 1998[1&2] in Waikato soils under long term dairy pasture.

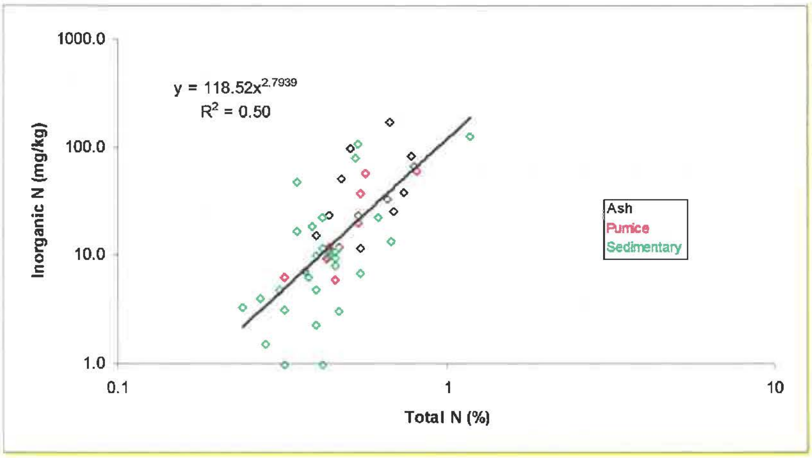

**Figure 7.1:** Relationship between inorganic-N and TN for soils.

A summary of results, which includes the mean and range of total dry matter yield for pots with nil and applied N, kg of dry matter produced per kg applied N, 1st cut and total response to N fertiliser application, N kg/ha in grass (% response) and N uptake in grass (% response), is shown in Table 7.2.

**Table 7.2:** Mean and range of total dry matter yield for pots with nil and applied N, kg of dry matter produced per kg applied N, 1st cut and total response to N fertiliser application, N kg/ha in grass (% response) and N uptake in grass (% response) for the trial.

| | **Total D.M for Control pots kg D.M $ha^{-1}$** | **Total D.M for Nitrogen pots kg D.M $ha^{-1}$** | **kg D.M/kg N applied** | **1st cut Response (%)** | **Total Response (%)** | **N in grass 1st cut Response (%)** | **N in grass all cuts Total Response (%)** | **N uptake in grass 1st cut Response (%)** | **N uptake in grass all cuts Total Response (%)** |
|---|---|---|---|---|---|---|---|---|---|
| Average | 2211 | 2896 | 14 | 39 | 36 | 40 | 14 | 100 | 64 |
| Range | 751 to 5214 | 1331 to 6645 | -1 to 31 | -36 to 202 | -1 to 95 | -12 to 90 | -11 to 39 | -26 to 433 | 4 to161 |

N status in the soil influenced herbage production in the absence of nitrogen fertiliser. The herbage yield was correlated strongly with inorganic-N (Figure 7.2) and TN (Figure 7.3) in soil. Inorganic-N in the soil drives herbage production. Inorganic-N accounted for 77%

(significant, $P<0.001$) and TN accounted for 43% (significant, $P<0.001$) of the variation in dry matter yield in the absence of applied N. The relationship between DM yield and inorganic-N or TN showed the usual exponential (Milscherlich) curve. Taking the square root of inorganic-N or square root of TN and plotting against dry matter yield, showed a straight line relationship (Figures 7.2 and 7.3). Using multiple regression, 81% of the variation was accounted for when dry matter yield was regressed on inorganic N, TN and ASC. The two peat soils were removed when the data were statistically analysed. This was done because there were only two peat soils and they behaved differently when compared to mineral soils. Using multiple regression, TN and ASC accounted for 58% of the variation on this data set. TN is a long term measure but it is able to predict even in the short-term (7 months) reasonably well. The C:N ratio did not add any more information for this data set. The study also showed that soil type has no effect on the relationship between TN or inorganic N and dry matter yield for mineral soils.

The results found from this glasshouse trial confirmed and extended (to cover all soils) the findings of Rajendram *et al.*, 1998[1&2] in Waikato soils under long term dairy pasture for a 2-year study, which found that N status in the soil influenced pasture production without nitrogen fertiliser. Pasture yield was correlated strongly with total N and inorganic-N for both years of the trial. As an example, correlations of pasture yield for the second year of the trial with total N and inorganic-N were $R^2=0.70$ and $R^2=0.69$ respectively.

The length of the glasshouse trial was too short a period for the TN to be a better predictor than inorganic N. In the field trial (Rajendram *et al.*, 1998[1&2]), TN was a better predictor. The glasshouse trial was abandoned after 7 months because many of the ryegrass plants in the pots were attacked by fungus. In this short time period, and for this trial, the small pool (inorganic-N) is a better predictor. It gives a good indication of the uptake by the ryegrass.

There was no apparent effect of soil type influencing inorganic-N when related to yield, but for TN, the peat soils (organic soils) do not conform to the norm like the mineral soils. This is probably due to the mineralization rates for peat being different to mineral soils. Peat soils are developed under anaerobic/reducing conditions. Therefore they have different microbial populations. Peat soils have a low oxidation potential. Much of the organic-N in the peat soils is not available, not easily mineralised by microbes, has different microbe population from that of mineral soils and is proportionally smaller in number in peaty soils (Sparling, 1985).

The peat soils are not freely drained and therefore the environment is non-oxidising. Therefore, peat soils need to be treated differently from mineral soils, which is the case for most soil tests.

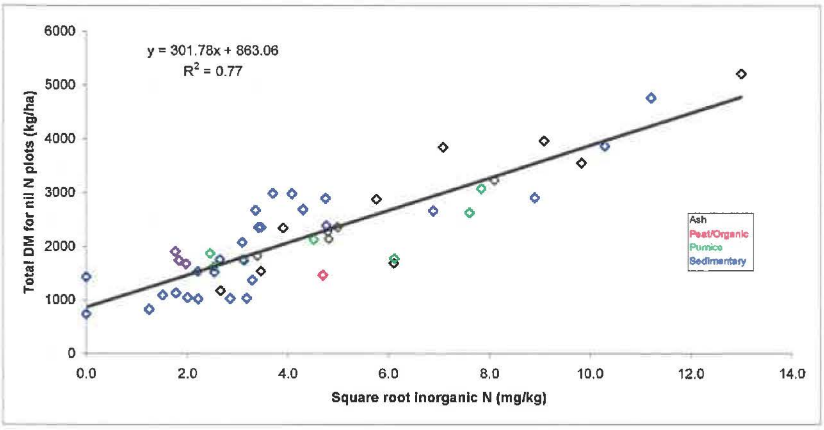

**Figure 7.2:** Relationship between inorganic-N and dry matter yield

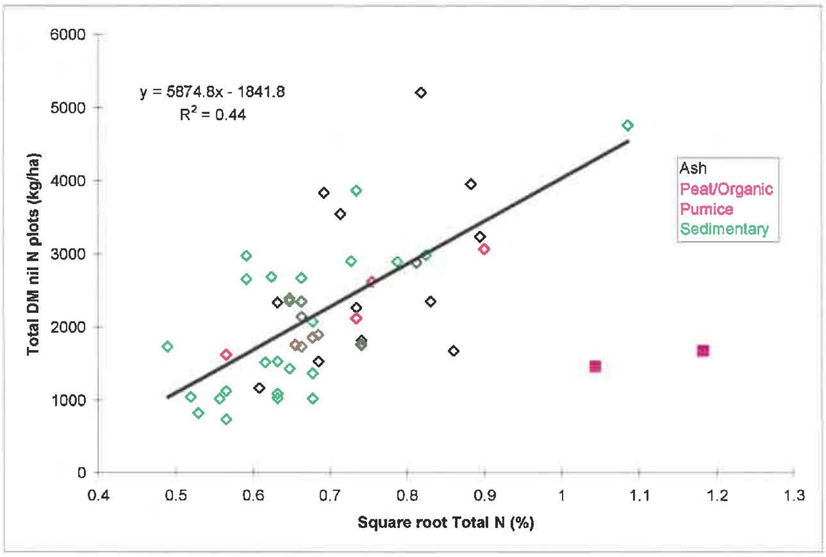

**Figure 7.3:** Relationship between TN and dry matter yield

In the initial response (1st cut response) inorganic-N accounted for 57% of the variation. There was no improvement in this relationship by including inorganic-N, Total N, ASC and C:N ratio (Figures 7.4 and 7.5) in the model. The inorganic-N was the best overall predictor of short term responses to N. The larger the quantity of inorganic-N in soil, the lower the response to N fertiliser application. The relationship was found to be logarithmic. A similar, but weaker trend was also observed for TN and response to N by the ryegrass on application of N. The TN test will be a better indicator in the long term rather than the short term.

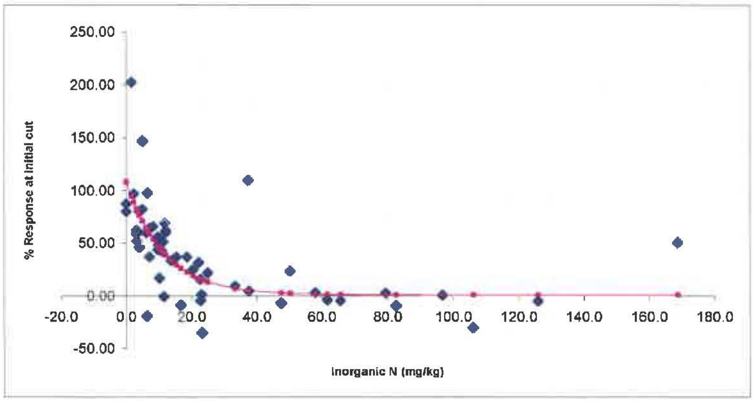

**Figure 7.4:**
Relationship between inorganic-N and initial DM response (first cut response)

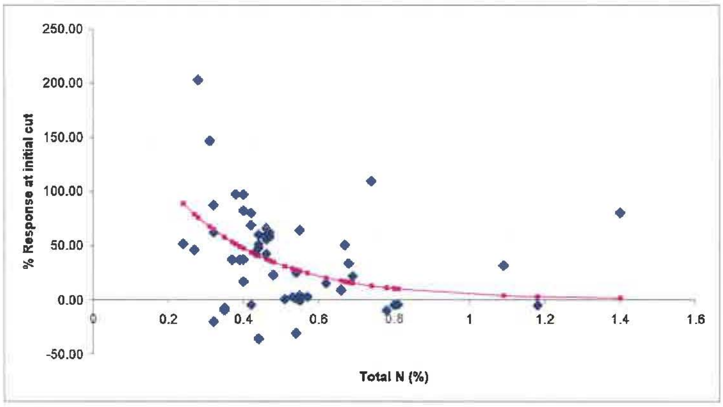

**Figure 7.5:**
Relationship between TN and initial DM response (first cut response)

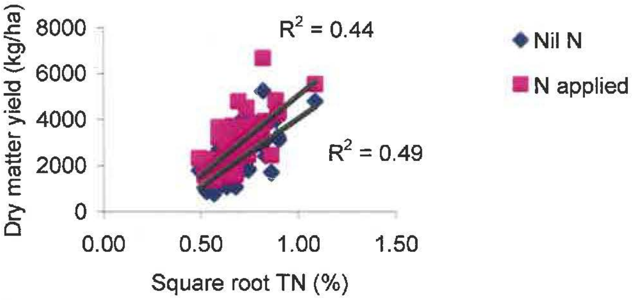

**Figure 7.6:**
Relationship between dry matter yield for nil N applied pots, N applied pots and SQRT TN

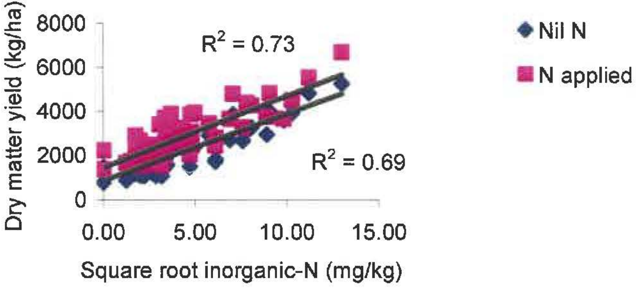

**Figure 7.7:**
Relationship between dry matter yield for nil N applied pots, N applied pots and SQRT inorganic-N

Initial (first harvest) response and total dry matter responses to N, varied between soils, with ranges of -36 to 202 % and -1 to 95% respectively. The average initial (first harvest) response, and total dry matter responses to N, were 39% and 36% respectively.

In the study by Rajendram *et al.*, 1998[1&2] in Waikato soils under long term dairy pasture, total soil N was the best overall predictor of short and long-term responses to N. There was a negative linear relationship between log dry matter response and total soil N ($R^2$=0.72 for 1995 and $R^2$=0.69 for 1996). It was found that there was little or no improvement ($r^2$=0.75) in this relationship by including total soil N and inorganic N in the model. However, 95% of the variability could be accounted for in both years using 5 tests which included total soil N and inorganic N. Using annual N uptake by grass, Hassink, 1995 compared different methods of estimating N supply from mineral grassland soils in the Netherlands. The study found that the test which best estimated N supply was total organic N in soil.

The glasshouse trial is an artificial environment but it gives us a good indication of what is happening. The total N in the field experiment was better at predicting responses to N fertiliser than glasshouse.

Total dry matter responses to N (as % increase over control) varied among soils with only approximately 75% of sites achieving > 10 kg DM/ kg N (Table 7.3).

**Table 7.3.** Total dry matter pasture response ranges, percentage of soils achieving >10 kg DM/kg N for the glasshouse trial.

| Pasture response (%) | Soils which achieved >10 kg DM/ kg N (%) |
|---|---|
| -1 to 95 | 75 |

Pasture production which achieved greater than 10 kilograms dry matter per kilogram of applied nitrogen fertiliser, is used as an indicator by farm advisors of the profitability of applying N to increase feed supply. In the event of a feed shortage, any increase in dry matter production is valuable to the farmer.

### 7.6.1 Herbage test

There was a very good relationship between grass N concentration and inorganic-N (Figure 7.8, $R^2=0.67$, significant: $P<0.001$) and grass N concentration and total soil N (Figure 7.9, $R^2=0.26$, significant: $P<0.001$) with the maximum approximately 5.0%. The corresponding soil inorganic-N and total soil N, at this maximum, are approximately 30 mg $kg^{-1}$ and 0.6% (6000 mg $kg^{-1}$) respectively. The peat soils behaved differently to mineral soils when grass N and TN is compared. The concentration of N in grass is a very good indicator of the amount of response achievable on fertiliser N application. There is a significant relationship between inorganic-N and N uptake in grass, and TN and N uptake in grass, Figure 7.10-7.11.

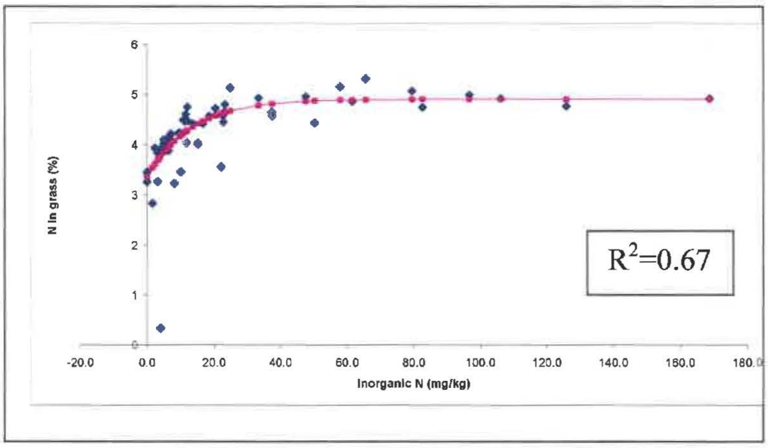

**Figure 7.8:**
Relationship between soil inorganic-N and grass N (%) prior to N application

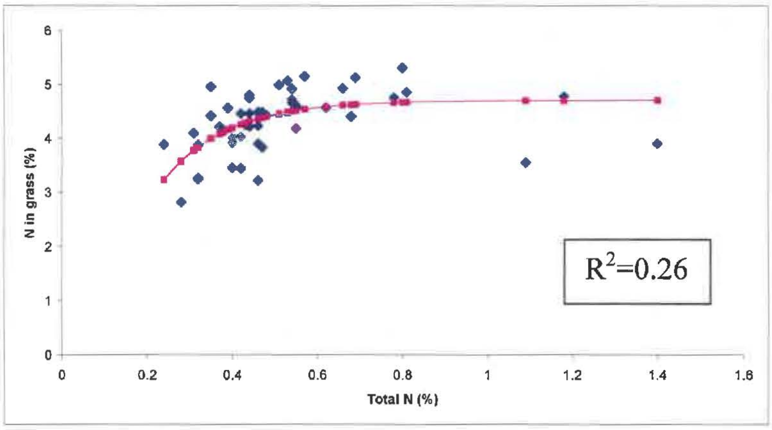

**Figure 7.9:**
Relationship between soil TN and grass N (%) prior to N application

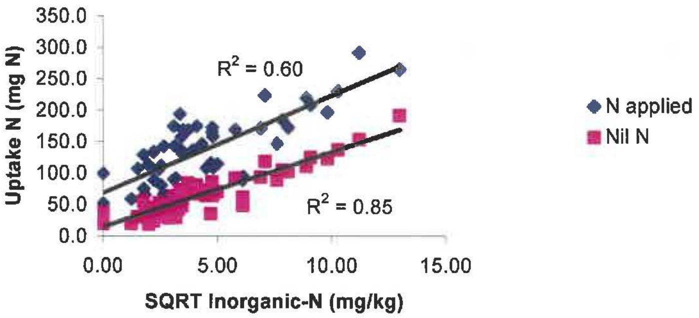

**Figure 7.10:**
Relationship between N uptake in grass for nil N applied pots, N applied pots and SQRT inorganic-N.

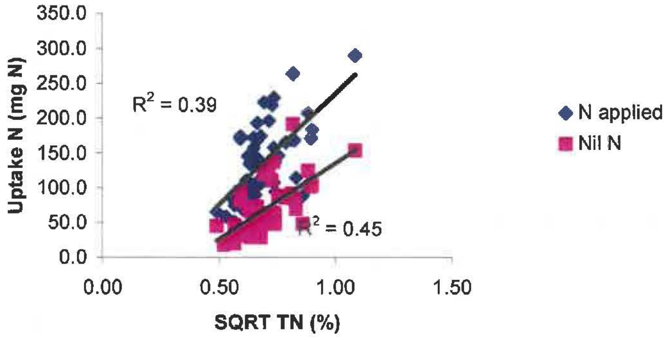

**Figure 7.11:**
Relationship between uptake N in grass for nil N applied pots, N applied pots and SQRT TN

Relationship between inorganic-N and N concentration in grass at the 1st cut response and relationship between TN and N concentration in grass 1st cut response is given in Figures 7.12 and 7.13. The same trends were seen for total response.

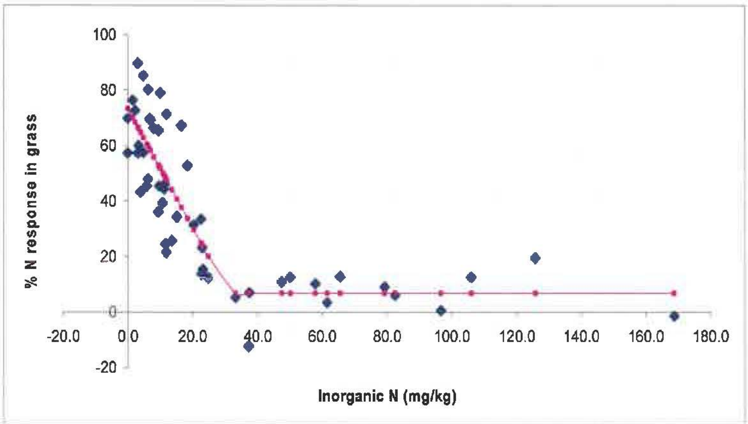

**Figure 7.12:**
Relationship between inorganic-N and N concentration in grass 1st cut response (%)

A spline was fitted to the data and the model used was Y = a+bx where x ≤ knot and Y=a+bk where x > knot (Figure 7.12). The data were fitted using the non-linear procedure of Genstat. The model accounted for 74.3 of the variation (significant, P<0.001). The knot, a, and b were estimated. The knot was estimated to be 31 mg kg$^{-1}$ inorganic N. Multiple regression using inorganic N and TN did not improve the relationship.

Relationship between N concentration in grass prior to N application and N grass yield response (%) at the 1st cut (Figure 7.14). The same relationship is seen for N in grass prior to N application and N in grass total response (%) where $R^2$=0.40.

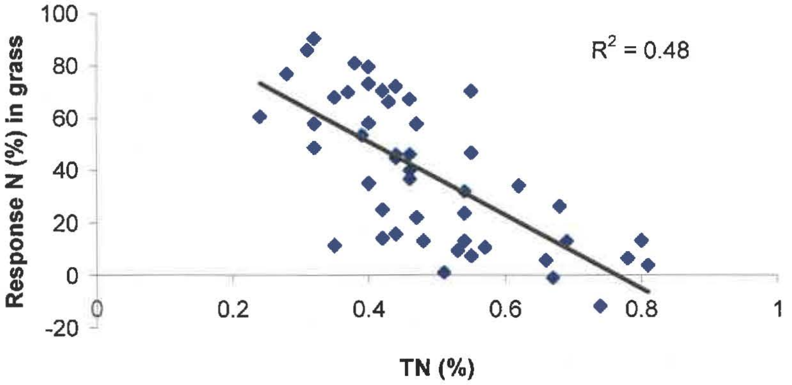

**Figure 7.13:**
Relationship between TN and N concentration in grass at 1st cut Response (%)

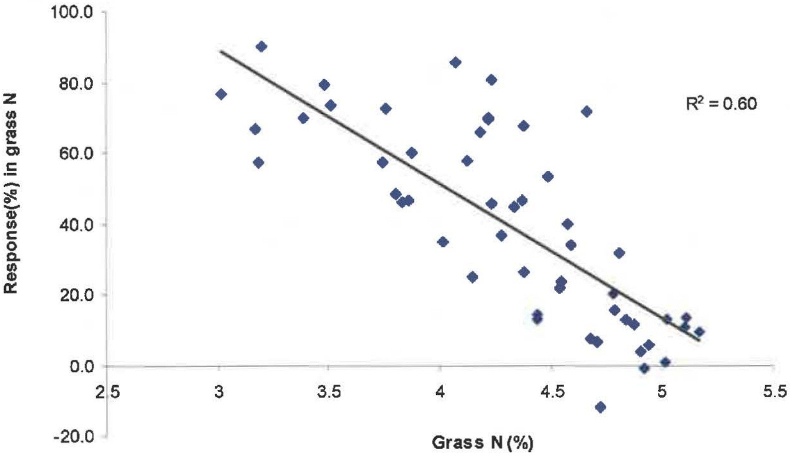

**Figure 7.14:**
Relationship between N concentration in grass prior to N application and N in grass response (%) at 1st cut

The findings from this glasshouse trial and the field trial study (Rajendram *et al.*, 1998 [1&2]) suggest there exists a quazi-equilibrium between inorganic-N and soil organic N (Figure 7.15). This is similar to that postulated by Watkinson and Kear, 1996 for sulphate-S and labile organic-S in New Zealand pastoral soils. The N pool in comparison to the S pool is approximately 10 fold larger. Therefore, the *native* inorganic-N which does not include urine and dung N found in the soil, is a direct measure and is proportional to the soil organic N. Because of the excreta from grazing animals (Haynes and Williams, 1993), the TN would be a more robust test than inorganic-N. Total soil N in the field would be a better predictor than inorganic-N because the pool is 100 times greater and is less influenced by external sources in a pastoral environment. For cropping and horticultural soils, both inorganic-N and organic-N combined may be a better predictor. Nitrogen uptake in a typical dairy pasture is approximately between 450 – 600 kg N $ha^{-1}$ $yr^{-1}$. A proportion of this comes from the N mineralised in the field from organic-N and from excreta N where the same N could have been recycled several times during the year. Measurements by Gill *et al.*, 1995 showed in excess of 300 kg N $ha^{-1}$ $yr^{-1}$ was released by the mineralization of organic N in long term pastoral soils in S.W. England.

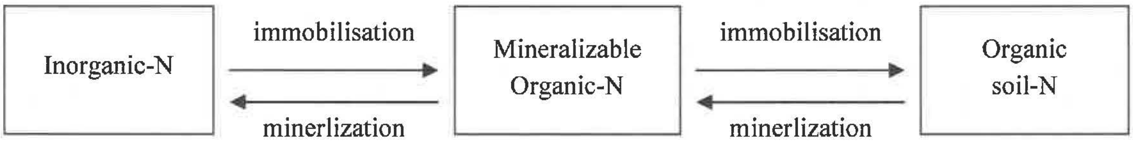

**Figure 7.15:**
Shows a simplified quazi-equilibrium relationship: which exists between inorganic-N and organic-N.

One of the large hurdles that is faced in developing a soil nitrogen test is that it estimates annual mineralization while the key issue for farmers is the degree of response that can be achieved at particular times. Studies suggest that there are long periods of uniform low N mineralization rates with short periods of much greater activity which occur once or twice a year. It is postulated here that both the background rate and the peak rates are related to total N (organic-N) and further work will be carried out to test this. The issue of when peak rates occur (microbial activity) and what controls them remains a challenge but is most likely related to climatic changes (temperature, adequate moisture and substrate).

Generally, soil test suites include only a single test for a nutrient e.g. Olsen P for phosphate fertiliser requirement. For N status both TN and inorganic N could be used, and measured rapidly and cheaply.

### 7.6.2 Proposed procedure for N testing (N status)

Inorganic-N can be measured by a water extract of the soil, complexing the ions in solution and measuring the amount present using NIR. Alternatively inorganic-N can be measured on the extract using an ion selective electrode (ISE). Nitrate-N and ammonium-N can both be measured on the same extract, using a colorimetric/NIR or using (ISE) technique.

### 7.6.3 Steps

Soil from site is placed in a vessel and scanned. Measurements of TN (mineralizable-N) ASC, Carbon, soil texture and soil type are obtained from scan (< 1 minute).

Nitrate-N and ammonium-N measured by a water slurry (same slurry as used for pH measurement), complexing the ions in solution and measuring the amount present using NIR or alternatively measured using ISE (Smith, 1975), (< 5 minutes).

Results from the tests entered into a model, which determines the N status e.g. an index of N responsiveness of a soil, development status of a soil and potential risk to N leaching.

The test could be used to place soils into low producing (highly responsive), medium producing (med responsive) and high producing (low responsive) soils based on their N status.

Selvarajah *et al.*, 1987 evaluated laboratory methods for assessing the availability of nitrogen in agricultural soils. His study showed that 1N $H_2SO_4$ extractable N values could be used to predict the amount of total soil N ($r = 0.993$) without performing Kjeldahl digests. Therefore, as a reference base test for NIR, 1N $H_2SO_4$, extractable N could be used.

## 7.7 Conclusions

Work carried out in a glasshouse trial has shown that herbage N, inorganic-N, TN (mineralizable-N), and ASC give a good picture of the N status of soils. The glasshouse trial confirmed the findings of the previous field trial work carried out in the Waikato. The findings have shown that the tests, inorganic-N and TN, can be extended to all New Zealand mineral soils.

Using multiple regression, 81% of the variation was accounted for when dry matter yield was correlated against inorganic N, TN and ASC. With a rapid measurement technique such as

NIR, herbage-N, total soil N, ASC and Carbon and, therefore, the C: N ratio can be measured rapidly by direct scan of the soil. Soil texture and soil type can also be measured rapidly using NIR by a direct and single scan of the soil. The response to N application was best predicted by inorganic-N.

It is envisaged that the N test suite will be incorporated as part of the basic soil test and could be incorporated into the Overseer model. David Wheeler (AgResearch, Land and Environment Management Group, *Pers. Comm.*) indicated that having an N test will be useful for the Overseer model (Wheeler *et al.*, 2003). The benefit of such a test will help enable the wise use of N fertiliser which will enable optimum production, but also minimise any environment risk.

## 7.8 References

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## 7.9 Appendix

**Table 7a**. Nitrogen test

| Lab Soil Type | Soil Type | District | Fertility status | Bulk density dry soil | NH4 dry soil | NO3 dry soil | NH4+NO3 dry soil ug/g | TN (%) dry soil | NH4 ug/g wet soil | NO3 ug/g wet soil | NH4+NO3 wet soil ug/g | Soil in pot O.D equ (g) | TN in pot ml | NH4 in pot ml | NO3 in pot ml | NH4+NO3 in pot ml |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pumice | Omeheu Sandy Loam | Edgecumbe | High | 0.84 | 12 | 189 | 201 | 0.44 | 3.0 | 9.0 | 12.0 | 750 | 3300 | 2 | 7 | 9 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | Low | 0.84 | 13 | 14 | 27 | 0.32 | 3.5 | 2.9 | 6.4 | 750 | 2400 | 3 | 2 | 5 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | High | 0.74 | 10 | 143 | 153 | 0.57 | 3.8 | 54.1 | 57.9 | 750 | 4275 | 3 | 41 | 43 |
| Pumice | Taupo Sandy Silt | Ngakuru | Med | 0.60 | 11 | 49 | 60 | 0.54 | 5.1 | 15.3 | 20.4 | 750 | 4050 | 4 | 11 | 15 |
| Pumice | Taupo Sandy Silt | Ngakuru | High | 0.54 | 11 | 215 | 226 | 0.81 | 4.6 | 56.9 | 61.5 | 750 | 6075 | 3 | 43 | 46 |
| Pumice | Whenuaroa Sandy Silt | Waikite | Low | 0.57 | 11 | 92 | 103 | 0.55 | 5.2 | 32.2 | 37.5 | 750 | 4125 | 4 | 24 | 28 |
| Pumice | Taupo Sandy Silt | Waikite | Low | 0.59 | 27 | 23 | 50 | 0.46 | 4.0 | 2.0 | 6.0 | 750 | 3450 | 3 | 2 | 5 |
| Sedimentary | Lowland YBE | Alexandra | Low | 0.70 | 25 | 213 | 238 | 0.53 | 5.6 | 73.7 | 79.4 | 750 | 3975 | 4 | 55 | 60 |
| Sedimentary | Lowland YBE, | Alexandra | Low | 0.63 | 8 | 0 | 8 | 0.46 | 10.8 | 0.0 | 10.8 | 750 | 3450 | 8 | 0 | 8 |
| Sedimentary | Te Anau sandy loam | Manapouri | Med | 0.72 | 19 | 135 | 154 | 0.55 | 3.2 | 3.8 | 7.0 | 750 | 4125 | 2 | 3 | 5 |
| Sedimentary | Manewai sandy loam | Manapouri | Low | 0.72 | 31 | 0 | 31 | 0.46 | 8.2 | 0.0 | 8.2 | 750 | 3450 | 6 | 0 | 6 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | Low | 0.81 | 12 | 66 | 78 | 0.4 | 7.3 | 2.8 | 10.1 | 750 | 3000 | 5 | 2 | 8 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | Med | 0.80 | 12 | 129 | 141 | 0.4 | 1.7 | 0.6 | 2.3 | 750 | 3000 | 1 | 0 | 2 |

**Table 7a**. Nitrogen test

| Lab Soil Type | Soil Type | District | Fertility status | Bulk density dry soil | NH4 dry soil | NO3 dry soil | NH4+NO3 dry soil ug/g | TN (%) dry soil | NH4 ug/g wet soil | NO3 ug/g wet soil | NH4+NO3 wet soil ug/g | Soil in pot O.D equ (g) | TN in pot ml | NH4 in pot ml | NO3 in pot ml | NH4+NO3 in pot ml |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Yellow brown Earth (Wehenga) | Hindon | Med | 0.84 | 9 | 131 | 140 | 0.4 | 2.4 | 2.4 | 4.9 | 750 | 3000 | 2 | 2 | 4 |
| Sedimentary | Waitohi silt loam | Makikihi, Timaru | Low-Med | 0.87 | 15 | 55 | 70 | 0.32 | 2.6 | 0.5 | 3.2 | 750 | 2400 | 2 | 0 | 2 |
| Sedimentary | Yellow grey earth | Roxburgh | Med | 0.82 | 7 | 184 | 191 | 0.54 | 3.5 | 102.6 | 106.1 | 750 | 4050 | 3 | 77 | 80 |
| Sedimentary | Yellow grey earth | Native Roxburgh | Med | 0.91 | 6 | 125 | 131 | 0.42 | 3.2 | 8.5 | 11.7 | 750 | 3150 | 2 | 6 | 9 |
| Sedimentary | Waikoikoi silt loam | Chatton, Roxburgh | Med | 0.89 | 6 | 126 | 132 | 0.31 | 0.0 | 4.9 | 4.9 | 750 | 2325 | 0 | 4 | 4 |
| Sedimentary | Yellow grey/ Yellow brown integrate | North Canterbury | Low | 0.89 | 6 | 127 | 133 | 0.38 | 0.0 | 6.4 | 6.4 | 750 | 2850 | 0 | 5 | 5 |
| Sedimentary | Waikoikoi silt loam | Chatton, Mid Canterbury | Med | 0.93 | 5 | 68 | 73 | 0.28 | 0.0 | 1.6 | 1.6 | 750 | 2100 | 0 | 1 | 1 |
| Sedimentary | Yellow Grey Earth | Culverden | Med | 0.73 | 7 | 154 | 161 | 0.39 | 0.0 | 18.5 | 18.5 | 750 | 2925 | 0 | 14 | 14 |
| Ash | Horotiu silt loam | Hamilton | Med | 0.75 | 9 | 97 | 106 | 0.55 | 0.0 | 11.5 | 11.5 | 750 | 4125 | 0 | 9 | 9 |
| Sedimentary | Coastal sands | Awarua,/ greenhills | High | 0.77 | 7 | 164 | 171 | 0.46 | 0.0 | 9.6 | 9.6 | 750 | 3450 | 0 | 7 | 7 |
| Sedimentary | Yellow Brown Earth (lowland) | Reefton, West coast | Med | 0.76 | 34 | 131 | 165 | 0.35 | 2.8 | 44.7 | 47.5 | 750 | 2625 | 2 | 33 | 36 |
| Ash | Gley Soil, Patetonga soil | Tauhei, Waikato | High | 0.76 | 10 | 145 | 155 | 0.48 | 6.5 | 43.7 | 50.2 | 750 | 3600 | 5 | 33 | 38 |
| Sedimentary | Yellow grey earth | Culverden | Low-Med | 0.81 | 8 | 160 | 168 | 0.44 | 0.0 | 11.3 | 11.3 | 750 | 3300 | 0 | 8 | 8 |

**Table 7a**. Nitrogen test

| **Lab Soil Type** | **Soil Type** | **District** | **Fertility status** | **Bulk density dry soil** | **NH4 dry soil** | **NO3 dry soil** | **NH4+NO3 dry soil ug/g** | **TN (%) dry soil** | **NH4 ug/g wet soil** | **NO3 ug/g wet soil** | **NH4+NO3 wet soil ug/g** | **Soil in pot O.D equ (g)** | **TN in pot ml** | **NH4 in pot ml** | **NO3 in pot ml** | **NH4+NO3 in pot ml** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Coastal sands | Awarua,/ Greenhills | Low | 0.72 | 11 | 149 | 160 | 0.44 | 2.4 | 7.3 | 9.8 | 750 | 3300 | 2 | 5 | 7 |
| Sedimentary | Yellow Brown Earth (upland) , Wehenga | Pukerangi, S.I Hill country | Low | 0.80 | 9 | 4 | 13 | 0.24 | 3.4 | 0.0 | 3.4 | 750 | 1800 | 3 | 0 | 3 |
| Sedimentary | Recent, winganui | Taieri plains, Southland | High | 0.84 | 12 | 153 | 165 | 0.42 | 0.0 | 22.8 | 22.8 | 750 | 3150 | 0 | 17 | 17 |
| Sedimentary | Yellow brown earth, Wehenga | Pukerangi, S.I | High | 0.76 | 9 | 134 | 143 | 0.35 | 0.6 | 16.1 | 16.7 | 750 | 2625 | 0 | 12 | 13 |
| Peat/Organic | Organic | Awarua | Med | 0.48 | 24 | 122 | 146 | 1.4 | 3.9 | 0.0 | 3.9 | 428 | 5992 | 2 | 0 | 2 |
| Sedimentary | Recent, winganui | Taieri plains, Southland | Med | 0.64 | 16 | 211 | 227 | 1.18 | 1.5 | 124.3 | 125.8 | 596 | 7033 | 1 | 74 | 75 |
| Ash | Brown granular loam | Morrinsville | Med | 0.66 | 15 | 223 | 238 | 0.78 | 0.0 | 82.6 | 82.6 | 750 | 5850 | 0 | 62 | 62 |
| Peat/Organic | Organic | Awarua,/ Greenhills | High | 0.49 | 17 | 160 | 177 | 1.09 | 0.0 | 22.1 | 22.1 | 428 | 4665 | 0 | 9 | 9 |
| Sedimentary | Recent, Mataura | Tuturau | High | 0.92 | 9 | 49 | 58 | 0.42 | 0.0 | 0.0 | 0.0 | 750 | 3150 | 0 | 0 | 0 |
| Sedimentary | Typic firm Brown, Waikiwi | Gummies bush | High | 0.78 | 17 | 72 | 89 | 0.47 | 0.0 | 3.1 | 3.1 | 750 | 3525 | 0 | 2 | 2 |
| Sedimentary | Brown, Drummond | Oreti | Low | 0.92 | 11 | 35 | 46 | 0.32 | 0.0 | 0.0 | 0.0 | 750 | 2400 | 0 | 0 | 0 |
| Sedimentary | Yellow brown earth | Northland | Med | 0.86 | 14 | 84 | 98 | 0.62 | 0.6 | 22.0 | 22.6 | 750 | 4650 | 0 | 16 | 17 |
| Sedimentary | Yellow brown earth | Northland | Med | 0.84 | 14 | 123 | 137 | 0.68 | 0.0 | 13.7 | 13.7 | 750 | 5100 | 0 | 10 | 10 |

**Table 7a**. Nitrogen test

| Lab Soil Type | Soil Type | District | Fertility status | Bulk density dry soil | NH4 dry soil | NO3 dry soil | NH4+NO3 dry soil ug/g | TN (%) dry soil | NH4 ug/g wet soil | NO3 ug/g wet soil | NH4+NO3 wet soil ug/g | Soil in pot O.D equ (g) | TN in pot ml | NH4 in pot ml | NO3 in pot ml | NH4+NO3 in pot ml |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash | Brown granular loam, Hamilton Clay | Hoe-O-Tainui, Waikato | High | 0.88 | 15 | 98 | 113 | 0.47 | 0.0 | 12.0 | 12.0 | 750 | 3525 | 0 | 9 | 9 |
| Ash | Brown granular loam, Hamilton Clay | Tauhei, Waikato | High | 0.79 | 19 | 131 | 150 | 0.54 | 0.0 | 23.0 | 23.0 | 750 | 4050 | 0 | 17 | 17 |
| Ash | Yellow Brown granular loam, Te Kuiti | Te kuiti hills | High | 0.80 | 14 | 88 | 102 | 0.4 | 1.2 | 14.1 | 15.2 | 750 | 3000 | 1 | 11 | 11 |
| Ash | Yellow Brown loam, Tirau silt loam | Walton | High | 0.79 | 18 | 125 | 143 | 0.66 | 0.0 | 33.3 | 33.3 | 750 | 4950 | 0 | 25 | 25 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | Med | 0.88 | 18 | 100 | 118 | 0.51 | 5.9 | 90.8 | 96.6 | 750 | 3825 | 4 | 68 | 72 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | High | 0.80 | 19 | 130 | 149 | 0.67 | 1.9 | 166.9 | 168.7 | 750 | 5025 | 1 | 125 | 127 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | Low | 0.81 | 16 | 51 | 67 | 0.44 | 1.2 | 22.0 | 23.2 | 750 | 3300 | 1 | 17 | 17 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | Low | 0.94 | 15 | 65 | 80 | 0.37 | 0.0 | 7.1 | 7.1 | 750 | 2775 | 0 | 5 | 5 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | Med | 0.73 | 24 | 161 | 185 | 0.8 | 0.0 | 65.6 | 65.6 | 750 | 6000 | 0 | 49 | 49 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | Med | 0.84 | 12 | 74 | 86 | 0.74 | 0.0 | 37.3 | 37.3 | 750 | 5550 | 0 | 28 | 28 |

Table 7a. Nitrogen test

| Lab Soil Type | Soil Type | District | Fertility status | Bulk density dry soil | NH4 dry soil | NO3 dry soil | NH4+NO3 dry soil ug/g | TN (%) dry soil | NH4 ug/g wet soil | NO3 ug/g wet soil | NH4+NO3 wet soil ug/g | Soil in pot O.D equ (g) | TN in pot ml | NH4 in pot ml | NO3 in pot ml | NH4+NO3 in pot ml |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash | Yellow brown loam, Egmont silt loam | WTARS | Low | 0.85 | 13 | 115 | 128 | 0.69 | 0.6 | 24.2 | 24.9 | 750 | 5175 | 0 | 18 | 19 |
| Pumice | Kaingaroa sand | Matea | Low | 0.62 | 13 | 74 | 87 | 0.43 | 0.0 | 9.6 | 9.6 | 750 | 3225 | 0 | 7 | 7 |
| Sedimentary | Yellow Brown Earth (Dublin upland), Brown | Tarras | Low | 0.89 | 7 | 1 | 8 | 0.27 | 0.0 | 4.0 | 4.0 | 750 | 2025 | 0 | 3 | 3 |

**Table 7b**. Nitrogen Test

| Lab Soil Type | Soil Type | District | allophane reactivity | Particle density | pH dry soil | Ca dry soil (QTU) | K dry soil (QTU) | Mg dry soil (QTU) | Na dry soil (QTU) | OS dry soil ug/g | P dry soil ug/g | SO4 dry soil ug/g | OC (%) dry soil | OM (%) dry soil | Total S (%) dry soil | ASC (%) dry soil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pumice | Omeheu Sandy Loam | Edgecumbe | no reaction | 2.31 | 5.8 | 7 | 22 | 13 | 10 | 6 | 176 | 6 | 4.6 | 7.9 | 0.06 | 12 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | strong | 2.45 | 5.8 | 4 | 5 | 8 | 8 | 4 | 6 | 6 | 3.9 | 6.7 | 0.04 | 46 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | mod/weak | 2.40 | 5.2 | 5 | 8 | 13 | 6 | 4 | 20 | 7 | 5.7 | 9.8 | 0.06 | 42 |
| Pumice | Taupo Sandy Silt | Ngakuru | strong | 2.30 | 5.3 | 2 | 2 | 3 | 9 | 9 | 11 | 47 | 6.4 | 11 | 0.06 | 76 |
| Pumice | Taupo Sandy Silt | Ngakuru | mod/strong | 2.28 | 5.5 | 8 | 6 | 13 | 4 | 19 | 96 | 19 | 9.1 | 15.7 | 0.10 | 54 |
| Pumice | Whenuaroa Sandy Silt | Waikite | strong | 2.22 | 5 | 2 | 3 | 2 | 3 | 9 | 9 | 6 | 6.5 | 11.2 | 0.06 | 61 |
| Pumice | Taupo Sandy Silt | Waikite | strong | 2.25 | 5.5 | 3 | 2 | 5 | 7 | 7 | 9 | 13 | 6.4 | 11 | 0.05 | 51 |
| Sedimentary | Lowland YBE | Alexandra | no reaction | 2.43 | 4.5 | 2 | 5 | 8 | 3 | 10 | 10 | 4 | 7.7 | 13.3 | 0.05 | 51 |
| Sedimentary | Lowland YBE, | Alexandra | no reaction | 2.41 | 4.7 | 1 | 3 | 5 | 3 | 1 | 7 | 7 | 8.2 | 14.1 | 0.05 | 58 |
| Sedimentary | Te Anau sandy loam | Manapouri | strong | 2.51 | 5.4 | 5 | 4 | 10 | 3 | 8 | 17 | 10 | 7.8 | 13.4 | 0.06 | 64 |
| Sedimentary | Manewai sandy loam | Manapouri | mod/strong | 2.50 | 5.6 | 3 | 1 | 2 | 3 | 4 | 8 | 4 | 6.8 | 11.7 | 0.05 | 66 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | no reaction | 2.50 | 5.4 | 4 | 4 | 11 | 3 | 6 | 13 | 3 | 4.9 | 8.4 | 0.04 | 28 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | no reaction | 2.48 | 5.4 | 6 | 6 | 15 | 4 | 7 | 17 | 4 | 4.8 | 8.3 | 0.04 | 28 |
| Sedimentary | Yellow brown Earth (Wehenga) | Hindon | no reaction | 2.52 | 5.6 | 9 | 2 | 14 | 6 | 8 | 14 | 16 | 4.8 | 8.3 | 0.05 | 18 |
| Sedimentary | Waitohi silt loam | Makikihi, Timaru | no reaction | 2.50 | 6 | 9 | 3 | 15 | 10 | 7 | 19 | 4 | 4.1 | 7.1 | 0.04 | 23 |
| Sedimentary | Yellow grey earth | Roxburgh | no reaction | 2.52 | 5 | 7 | 14 | 23 | 3 | 10 | 47 | 17 | 5.5 | 9.5 | 0.06 | 11 |
| Sedimentary | Yellow grey earth | Native Roxburgh | no reaction | 2.57 | 5.6 | 7 | 13 | 31 | 3 | 6 | 26 | 3 | 4.1 | 7.1 | 0.03 | 14 |
| Sedimentary | Waikoikoi silt loam | Chatton, Roxburgh | weak | 2.61 | 5.8 | 9 | 2 | 10 | 6 | 8 | 22 | 20 | 3 | 5.2 | 0.04 | 21 |
| Sedimentary | Yellow grey/Yellow brown integrate | North Canterbury | no reaction | 2.51 | 6.3 | 15 | 10 | 21 | 4 | 7 | 6 | 9 | 3.8 | 6.6 | 0.04 | 17 |

**Table 7b.** Nitrogen Test

| Lab Soil Type | Soil Type | District | allophane reactivity | Particle density | pH dry soil | Ca dry soil (QTU) | K dry soil (QTU) | Mg dry soil (QTU) | Na dry soil (QTU) | OS dry soil ug/g | P dry soil ug/g | SO4 dry soil ug/g | OC (%) dry soil | OM (%) dry soil | Total S (%) dry soil | ASC (%) dry soil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Waikoikoi silt loam | Chatton, Mid Canterbury | weak | 2.64 | 5.8 | 8 | 4 | 9 | 7 | 7 | 32 | 9 | 3.1 | 5.3 | 0.04 | 25 |
| Sedimentary | Yellow Grey Earth | Culverden | no reaction | 2.44 | 5.4 | 5 | 5 | 12 | 5 | 7 | 27 | 17 | 4.3 | 7.4 | 0.05 | 22 |
| Ash | Horotiu silt loam | Hamilton | moderate | 2.35 | 5.4 | 5 | 20 | 11 | 6 | 10 | 22 | 10 | 5.4 | 9.3 | 0.07 | 59 |
| Sedimentary | Coastal sands | Awarua,/greenhills | no reaction | 2.48 | 5.3 | 6 | 6 | 12 | 10 | 10 | 61 | 5 | 5.2 | 9 | 0.07 | 24 |
| Sedimentary | Yellow Brown Earth (lowland) | Reefton, West coast | no reaction | 2.53 | 4.7 | 2 | 2 | 4 | 4 | 6 | 17 | 6 | 3.6 | 6.2 | 0.04 | 23 |
| Ash | Gley Soil, Patetonga soil | Tauhei, Waikato | no reaction | 2.41 | 5.8 | 13 | 8 | 37 | 9 | 10 | 61 | 18 | 4.9 | 8.4 | 0.07 | 28 |
| Sedimentary | Yellow grey earth | Culverden | no reaction | 2.47 | 5.4 | 7 | 6 | 35 | 4 | 7 | 13 | 5 | 4.8 | 8.3 | 0.04 | 22 |
| Sedimentary | Coastal sands | Awarua,/Greenhills | mod/strong | 2.43 | 5.4 | 5 | 5 | 7 | 7 | 9 | 10 | 11 | 7.1 | 12.2 | 0.05 | 43 |
| Sedimentary | Yellow Brown Earth ( upland ) , Wehenga | Pukerangi, S.I Hill country | no reaction | 2.6 | 5.1 | 2 | 3 | 15 | 4 | 2 | 11 | 4 | 2.8 | 4.8 | 0.02 | 19 |
| Sedimentary | Recent, winganui | Taieri plains, Southland | no reaction | 2.50 | 6.2 | 7 | 34 | 30 | 8 | 11 | 63 | 11 | 4.2 | 7.2 | 0.05 | 18 |
| Sedimentary | Yellow brown earth, Wehenga | Pukerangi, S.I | no reaction | 2.50 | 5.2 | 7 | 4 | 20 | 10 | 7 | 26 | 14 | 4.5 | 7.8 | 0.04 | 23 |
| Peat/Organic | Organic | Awarua | no reaction | 1.50 | 4.1 | 3 | 3 | 25 | 8 | 4 | 17 | 17 | 39.9 | 68.8 | 0.47 | 15 |
| Sedimentaary | Recent, winganui | Taieri plains, Southland | no reaction | 2.17 | 5.5 | 10 | 7 | 28 | 10 | 24 | 16 | 53 | 13.8 | 23.8 | 0.19 | 68 |
| Ash | Brown granular loam | Morrinsville | strong | 2.30 | 5.9 | 9 | 3 | 21 | 10 | 14 | 16 | 26 | 7.9 | 13.6 | 0.10 | 78 |
| Peat/Organic | Organic | Awarua,/Greenhills | no reaction | 1.88 | 6.5 | 21 | 8 | 25 | 15 | 22 | 67 | 34 | 22.9 | 39.5 | 0.39 | 68 |
| Sedimentary | Recent, Mataura | Tuturau | no reaction | 2.52 | 6.3 | 10 | 2 | 16 | 8 | 6 | 52 | 6 | 4.7 | 8.1 | 0.05 | 28 |
| Sedimentary | Typic firm Brown, Waikiwi | Gummies bush | no reaction | 2.50 | 5.5 | 4 | 1 | 11 | 7 | 9 | 30 | 5 | 4.9 | 8.4 | 0.05 | 46 |
| Sedimentary | Brown, Drummond | Oreti | no reaction | 2.54 | 6.7 | 11 | 2 | 9 | 5 | 7 | 11 | 6 | 3.4 | 5.9 | 0.04 | 30 |

**Table 7b**. Nitrogen Test

| Lab Soil Type | Soil Type | District | allophane reactivity | Particle density | pH dry soil | Ca dry soil (QTU) | K dry soil (QTU) | Mg dry soil (QTU) | Na dry soil (QTU) | OS dry soil ug/g | P dry soil ug/g | SO4 dry soil ug/g | OC (%) dry soil | OM (%) dry soil | Total S (%) dry soil | ASC (%) dry soil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Yellow brown earth | Northland | no reaction | 2.37 | 5.4 | 7 | 7 | 19 | 7 | 6 | 14 | 4 | 6.7 | 11.6 | 0.07 | 54 |
| Sedimentary | Yellow brown earth | Northland | no reaction | 2.35 | 5.2 | 6 | 8 | 17 | 7 | 8 | 16 | 4 | 7.6 | 13.1 | 0.08 | 53 |
| Ash | Brown granular loam, Hamilton Clay | Hoe-O-Tainui, Waikato | no reaction | 2.42 | 6.8 | 14 | 5 | 16 | 11 | 8 | 42 | 9 | 4.7 | 8.1 | 0.06 | 45 |
| Ash | Brown granular loam, Hamilton Clay | Tauhei, Waikato | no reaction | 2.39 | 6.3 | 10 | 21 | 20 | 5 | 8 | 58 | 15 | 5.3 | 9.1 | 0.07 | 40 |
| Ash | Yellow Brown granular loam, Te Kuiti | Te kuiti hills | weak | 2.48 | 5.2 | 5 | 11 | 16 | 5 | 8 | 42 | 7 | 5 | 8.6 | 0.05 | 41 |
| Ash | Yellow Brown loam, Tirau silt loam | Walton | strong | 2.38 | 4.9 | 5 | 20 | 8 | 5 | 14 | 43 | 29 | 6.7 | 11.6 | 0.07 | 69 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | no reaction | 2.38 | 4.9 | 3 | 8 | 21 | 7 | 8 | 12 | 3 | 5.5 | 9.5 | 0.06 | 39 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | no reaction | 2.33 | 4.9 | 4 | 7 | 19 | 5 | 8 | 90 | 5 | 6.9 | 11.9 | 0.09 | 36 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | no reaction | 2.41 | 5 | 3 | 6 | 17 | 5 | 7 | 8 | 3 | 5.2 | 9 | 0.07 | 38 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | strong | 2.68 | 5.8 | 4 | 2 | 19 | 8 | 9 | 10 | 4 | 3.3 | 5.7 | 0.07 | 78 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | moderate | 2.41 | 5.6 | 6 | 9 | 28 | 12 | 11 | 14 | 8 | 7.4 | 12.8 | 0.12 | 76 |
| Ash | Yellow brown loam, Egmont silt | WTARS | moderate | 2.51 | 5.7 | 4 | 7 | 19 | 6 | 14 | 18 | 31 | 6.3 | 10.9 | 0.12 | 83 |

**Table 7b**. Nitrogen Test

| Lab Soil Type | Soil Type | District | allophane reactivity | Particle density | pH dry soil | Ca dry soil (QTU) | K dry soil (QTU) | Mg dry soil (QTU) | Na dry soil (QTU) | OS dry soil ug/g | P dry soil ug/g | SO4 dry soil ug/g | OC (%) dry soil | OM (%) dry soil | Total S (%) dry soil | ASC (%) dry soil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | loam | | | | | | | | | | | | | | | |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | weak | 2.48 | 5.3 | 5 | 16 | 25 | 8 | 10 | 13 | 9 | 7.1 | 12.2 | 0.11 | 81 |
| Pumice | Kaingaroa sand | Matea | mod/strong | 2.34 | 5.1 | 2 | 2 | 6 | 3 | 10 | 48 | 17 | 5 | 8.6 | 0.05 | 59 |
| Sedimentary | Yellow Brown Earth (Dublinupland), Brown | Tarras | no reaction | 2.65 | 5.9 | 8 | 4 | 16 | 3 | 3 | 10 | 3 | 2.9 | 5 | 0.03 | 17 |

**Table 7c.** Nitrogen Test

| Lab Soil Type | Soil Type | District | D.M cut 0 (1st) 24/01/2001 mean of 6 pots (g) | D.M cut 0 (2nd) 16/02/2001 mean of 6 pots (g) | D.M cut1 19/03/2001 mean control (g) | D.M cut1 19/03/2002 mean N trt (g) | D.M cut 2 mean control (g) | D.M cut 2 mean N trt (g) | D.M cut 3 mean control (g) | D.M cut 3 mean N trt (g) | D.M cut 4 mean control (g) | D.M cut 4 mean N trt (g) | Total D.M including 0 cuts for control pots (g) | Total D.M cuts1+2+3 +4 for Control pots (g) | Total D.M cuts1+2+3 +4 for Nitrogen pots (g) | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pumice | Omeheu Sandy Loam | Edgecumbe | 1.03 | 1.28 | 1.01 | 1.62 | 0.74 | 1.15 | 0.60 | 0.65 | 0.56 | 0.59 | 5.23 | 2.92 | 4.01 | 2371 | 3263 | 17.8 | 37.6 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 0.41 | 0.50 | 0.66 | 0.52 | 0.63 | 1.00 | 0.38 | 0.47 | 0.35 | 0.41 | 2.93 | 2.02 | 2.41 | 1642 | 1957 | 6.3 | 19.1 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 0.39 | 0.74 | 0.92 | 0.94 | 1.14 | 1.54 | 0.56 | 0.71 | 0.62 | 0.76 | 4.37 | 3.24 | 3.95 | 2637 | 3211 | 11.5 | 21.8 |
| Pumice | Taupo Sandy Silt | Ngakuru | 0.29 | 0.62 | 0.75 | 0.94 | 0.74 | 1.14 | 0.57 | 0.62 | 0.57 | 0.54 | 3.55 | 2.63 | 3.24 | 2141 | 2631 | 9.8 | 22.9 |
| Pumice | Taupo Sandy Silt | Ngakuru | 0.66 | 0.97 | 0.89 | 0.85 | 1.34 | 2.00 | 0.79 | 1.47 | 0.78 | 1.01 | 5.43 | 3.80 | 5.32 | 3089 | 4328 | 24.8 | 40.1 |
| Pumice | Whenuaroa Sandy Silt | Waikite | 0.28 | 0.44 | 0.52 | 0.54 | 0.80 | 1.42 | 0.54 | 0.84 | 0.34 | 0.58 | 2.91 | 2.20 | 3.39 | 1786 | 2756 | 19.4 | 54.3 |
| Pumice | Taupo Sandy Silt | Waikite | 0.68 | 0.72 | 0.78 | 1.24 | 0.62 | 0.75 | 0.45 | 0.49 | 0.46 | 0.46 | 3.71 | 2.31 | 2.93 | 1878 | 2382 | 10.1 | 26.8 |
| Sedimentary | Lowland YBE | Alexandra | 0.88 | 1.21 | 1.32 | 1.35 | 1.05 | 1.65 | 0.62 | 0.81 | 0.61 | 0.75 | 5.69 | 3.59 | 4.56 | 2921 | 3710 | 15.8 | 27.0 |
| Sedimentary | Lowland YBE, | Alexandra | 0.06 | 0.31 | 0.79 | 1.12 | 0.37 | 0.65 | 0.25 | 0.36 | 0.29 | 0.23 | 2.07 | 1.70 | 2.35 | 1382 | 1911 | 10.6 | 38.2 |
| Sedimentary | Te Anau sandy loam | Manapouri | 0.93 | 1.29 | 0.81 | 1.32 | 0.44 | 0.70 | 0.49 | 0.50 | 0.44 | 0.46 | 4.40 | 2.18 | 2.98 | 1770 | 2420 | 13.0 | 36.8 |
| Sedimentary | Manewai sandy loam | Manapouri | 0.29 | 0.47 | 0.39 | 0.65 | 0.33 | 0.51 | 0.29 | 0.41 | 0.27 | 0.34 | 2.03 | 1.28 | 1.92 | 1038 | 1558 | 10.4 | 50.1 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 1.05 | 0.75 | 0.46 | 0.53 | 0.33 | 0.48 | 0.26 | 0.48 | 0.23 | 0.35 | 3.08 | 1.28 | 1.85 | 1043 | 1504 | 9.2 | 44.2 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 1.20 | 0.85 | 0.45 | 0.89 | 0.32 | 0.50 | 0.28 | 0.34 | 0.31 | 0.34 | 3.41 | 1.36 | 2.07 | 1103 | 1683 | 11.6 | 52.6 |
| Sedimentary | Yellow brown Earth (Wehenga) | Hindon | 1.31 | 0.99 | 0.65 | 1.17 | 0.52 | 0.54 | 0.42 | 0.44 | 0.32 | 0.32 | 4.21 | 1.90 | 2.48 | 1547 | 2014 | 9.3 | 30.1 |
| Sedimentary | Waitohi silt loam | Makikihi, Timaru | 0.89 | 0.53 | 0.41 | 0.66 | 0.36 | 0.86 | 0.31 | 0.67 | 0.33 | 0.55 | 2.82 | 1.40 | 2.74 | 1141 | 2228 | 21.7 | 95.2 |

Table 7c. Nitrogen Test

| Lab Soil Type | Soil Type | District | D.M cut 0 (1st) 24/01/2001 mean of 6 pots (g) | D.M cut 0 (2nd) 16/02/2001 mean of 6 pots (g) | D.M cut1 19/03/2001 mean control (g) | D.M cut1 19/03/2002 mean N trt (g) | D.M cut 2 mean control (g) | D.M cut 2 mean N trt (g) | D.M cut 3 mean control (g) | D.M cut 3 mean N trt (g) | D.M cut 4 mean control (g) | D.M cut 4 mean N trt (g) | Total D.M including 0 cuts for control pots (g) | Total D.M cuts1+2+3 +4 for Control pots (g) | Total D.M cuts1+2+3 +4 for Nitrogen pots (g) | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Yellow grey earth | Roxburgh | 0.80 | 1.11 | 1.06 | 0.73 | 1.31 | 1.25 | 1.20 | 2.10 | 1.20 | 1.41 | 6.68 | 4.78 | 5.49 | 3883 | 4463 | 11.6 | 14.9 |
| Sedimentary | Yellow grey earth | Native Roxburgh | 1.11 | 1.15 | 0.92 | 1.54 | 0.67 | 0.81 | 0.66 | 0.69 | 0.66 | 0.60 | 5.17 | 2.91 | 3.63 | 2366 | 2954 | 11.8 | 24.9 |
| Sedimentary | Waikoikoi silt loam | Chatton, Roxburgh | 0.91 | 0.68 | 0.44 | 1.07 | 0.31 | 0.51 | 0.25 | 0.25 | 0.27 | 0.27 | 2.86 | 1.27 | 2.11 | 1033 | 1713 | 13.6 | 65.9 |
| Sedimentary | Yellow grey /Yellow brown integrate | North Canterbury | 0.86 | 0.96 | 0.58 | 1.15 | 0.40 | 0.68 | 0.39 | 0.45 | 0.51 | 0.41 | 3.71 | 1.89 | 2.68 | 1534 | 2182 | 13.0 | 42.2 |
| Sedimentary | Waikoikoi silt loam | Chatton, Mid Canterbury | 0.67 | 0.61 | 0.35 | 1.05 | 0.25 | 0.47 | 0.20 | 0.27 | 0.23 | 0.19 | 2.31 | 1.03 | 1.97 | 837 | 1604 | 15.3 | 91.6 |
| Sedimentary | Yellow Grey Earth | Culverden | 1.09 | 0.55 | 1.20 | 1.64 | 0.83 | 0.89 | 0.62 | 0.61 | 0.66 | 0.66 | 4.96 | 3.32 | 3.80 | 2702 | 3089 | 7.8 | 14.3 |
| Ash | Horotiu silt loam | Hamilton | 0.58 | 1.22 | 0.83 | 0.82 | 0.59 | 1.28 | 0.44 | 0.57 | 0.38 | 0.51 | 4.04 | 2.24 | 3.18 | 1824 | 2585 | 15.2 | 41.8 |
| Sedimentary | Coastal sands | Awarua,/ greenhills | 1.06 | 1.55 | 0.85 | 1.32 | 0.62 | 0.98 | 0.45 | 0.85 | 0.65 | 0.97 | 5.17 | 2.56 | 4.12 | 2084 | 3350 | 25.3 | 60.7 |
| Sedimentary | Yellow Brown Earth (lowland ) | Reefton, West coast | 0.56 | 1.01 | 1.05 | 0.97 | 0.98 | 1.73 | 0.59 | 1.11 | 0.67 | 0.63 | 4.86 | 3.29 | 4.44 | 2672 | 3610 | 18.8 | 35.1 |
| Ash | Gley Soil, Patetonga soil | Tauhei, Waikato | 0.97 | 1.38 | 1.36 | 1.67 | 1.28 | 2.16 | 1.01 | 1.12 | 1.07 | 0.89 | 7.08 | 4.72 | 5.84 | 3840 | 4748 | 18.2 | 23.6 |
| Sedimentary | Yellow grey earth | Culverden | 1.10 | 1.68 | 1.25 | 1.89 | 0.88 | 1.23 | 0.58 | 0.70 | 0.59 | 0.68 | 6.08 | 3.30 | 4.50 | 2686 | 3659 | 19.5 | 36.2 |
| Sedimentary | Coastal sands | Awarua,/Greenhills | 0.82 | 1.36 | 0.93 | 1.37 | 0.48 | 0.68 | 0.36 | 0.44 | 0.39 | 0.39 | 4.33 | 2.15 | 2.87 | 1751 | 2336 | 11.7 | 33.4 |
| Sedimentary | Yellow Brown Earth ( upland ) , Wehenga | Pukerangi, S.I Hill country | 0.10 | 0.41 | 0.76 | 1.15 | 0.55 | 0.78 | 0.43 | 0.47 | 0.42 | 0.41 | 2.67 | 2.15 | 2.80 | 1751 | 2279 | 10.6 | 30.2 |

**Table 7c.** Nitrogen Test

| Lab Soil Type | Soil Type | District | D.M cut 0 (1st) 24/01/2001 mean of 6 pots (g) | D.M cut 0 (2nd) 16/02/2001 mean of 6 pots (g) | D.M cut1 19/03/2001 mean control (g) | D.M cut1 19/03/2002 mean N trt (g) | D.M cut 2 mean control (g) | D.M cut 2 mean N trt (g) | D.M cut 3 mean control (g) | D.M cut 3 mean N trt (g) | D.M cut 4 mean control (g) | D.M cut 4 mean N trt (g) | Total D.M including 0 cuts for control pots (g) | Total D.M cuts1+2+3 +4 for Control pots (g) | Total D.M cuts1+2+3 +4 for Nitrogen pots (g) | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Recent, winganui | Taieri plains, Southland | 0.94 | 1.40 | 0.94 | 0.89 | 0.84 | 0.75 | 0.55 | 0.65 | 0.63 | 0.64 | 5.29 | 2.96 | 2.93 | 2407 | 2379 | -0.5 | -1.1 |
| Sedimentary | Yellow brown earth, Wehenga | Pukerangi, S.I | 0.91 | 1.23 | 1.18 | 1.06 | 0.80 | 1.11 | 0.77 | 0.85 | 0.93 | 0.89 | 5.82 | 3.68 | 3.91 | 2992 | 3182 | 3.8 | 6.3 |
| Peat/Organic | Organic | Awarua | 0.89 | 0.88 | 0.70 | 1.26 | 0.43 | 0.82 | 0.33 | 0.50 | 0.61 | 0.64 | 3.85 | 2.08 | 3.23 | 1688 | 2623 | 18.7 | 55.4 |
| Sedimentary | Recent, winganui | Taieri plains, Southland | 1.12 | 1.76 | 1.62 | 1.53 | 1.59 | 2.50 | 1.24 | 1.36 | 1.42 | 1.35 | 8.75 | 5.88 | 6.75 | 4778 | 5485 | 14.1 | 14.8 |
| Ash | Brown granular loam | Morrinsville | 0.65 | 1.10 | 1.14 | 1.02 | 1.57 | 2.54 | 0.97 | 1.13 | 1.19 | 1.21 | 6.62 | 4.87 | 5.89 | 3962 | 4789 | 16.5 | 20.9 |
| Peat/Organic | Organic | Awarua,/Greenhills | 1.14 | 1.17 | 0.59 | 0.78 | 0.40 | 0.64 | 0.38 | 0.54 | 0.45 | 0.50 | 4.13 | 1.82 | 2.46 | 1477 | 2003 | 10.5 | 35.6 |
| Sedimentary | Recent, Mataura | Tuturau | 0.99 | 0.87 | 0.51 | 0.92 | 0.41 | 0.80 | 0.36 | 0.49 | 0.50 | 0.47 | 3.63 | 1.78 | 2.69 | 1447 | 2184 | 14.7 | 50.9 |
| Sedimentary | Typic firm Brown, Waikiwi | Gummies bush | 0.98 | 0.99 | 0.76 | 1.19 | 0.63 | 1.03 | 0.48 | 0.65 | 0.48 | 0.63 | 4.32 | 2.35 | 3.50 | 1913 | 2843 | 18.6 | 48.6 |
| Sedimentary | Brown, Drummond | Oreti | 0.52 | 0.47 | 0.27 | 0.51 | 0.24 | 0.47 | 0.20 | 0.38 | 0.21 | 0.28 | 1.91 | 0.92 | 1.64 | 751 | 1331 | 11.6 | 77.3 |
| Sedimentary | Yellow brown earth | Northland | 0.62 | 1.12 | 1.18 | 1.35 | 1.10 | 1.73 | 0.71 | 0.85 | 0.59 | 0.74 | 5.31 | 3.57 | 4.67 | 2905 | 3799 | 17.9 | 30.8 |
| Sedimentary | Yellow brown earth | Northland | 0.76 | 1.17 | 1.26 | 1.68 | 1.01 | 1.48 | 0.69 | 0.76 | 0.73 | 0.82 | 5.62 | 3.69 | 4.74 | 3000 | 3856 | 17.1 | 28.5 |
| Ash | Brown granular loam, Hamilton Clay | Hoe-O-Tainui, Waikato | 0.85 | 0.97 | 0.41 | 0.67 | 0.52 | 1.03 | 0.50 | 0.74 | 0.46 | 0.47 | 3.71 | 1.89 | 2.92 | 1537 | 2371 | 16.7 | 54.3 |
| Ash | Brown granular loam, Hamilton Clay | Tauhei, Waikato | 1.06 | 1.00 | 0.73 | 0.73 | 0.74 | 0.82 | 0.62 | 1.33 | 0.70 | 0.83 | 4.85 | 2.79 | 3.71 | 2271 | 3019 | 15.0 | 32.9 |

Table 7c. Nitrogen Test

| Lab Soil Type | Soil Type | District | D.M cut 0 (1st) 24/01/2001 mean of 6 pots (g) | D.M cut 0 (2nd) 16/02/2001 mean of 6 pots (g) | D.M cut1 19/03/2001 mean control (g) | D.M cut1 19/03/2002 mean N trt (g) | D.M cut 2 mean control (g) | D.M cut 2 mean N trt (g) | D.M cut 3 mean control (g) | D.M cut 3 mean N trt (g) | D.M cut 4 mean control (g) | D.M cut 4 mean N trt (g) | Total D.M including 0 cuts for control pots (g) | Total D.M cuts1+2+3 +4 for Control pots (g) | Total D.M cuts1+2+3 +4 for Nitrogen pots (g) | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash | Yellow Brown granular loam, Te Kuiti | Te kuiti hills | 0.92 | 0.81 | 0.78 | 1.06 | 0.77 | 0.91 | 0.59 | 0.60 | 0.74 | 0.59 | 4.60 | 2.88 | 3.16 | 2339 | 2572 | 4.7 | 10.0 |
| Ash | Yellow Brown loam, Tirau silt loam | Walton | 0.72 | 0.84 | 0.85 | 0.92 | 0.93 | 1.41 | 0.79 | 0.95 | 0.97 | 0.90 | 5.10 | 3.54 | 4.19 | 2875 | 3404 | 10.6 | 18.4 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 0.68 | 0.79 | 0.89 | 0.89 | 1.69 | 1.88 | 0.92 | 0.97 | 0.87 | 0.70 | 5.83 | 4.37 | 4.44 | 3550 | 3610 | 1.2 | 1.7 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 0.77 | 0.72 | 0.58 | 0.87 | 1.88 | 2.99 | 2.57 | 2.87 | 1.38 | 1.44 | 7.90 | 6.41 | 8.17 | 5214 | 6645 | 28.6 | 27.4 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 0.40 | 0.46 | 0.58 | 0.37 | 0.85 | 1.14 | 0.54 | 0.97 | 0.67 | 0.64 | 3.50 | 2.63 | 3.11 | 2138 | 2531 | 7.9 | 18.4 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 0.31 | 0.53 | 0.48 | 0.65 | 0.39 | 0.62 | 0.26 | 0.37 | 0.31 | 0.29 | 2.28 | 1.44 | 1.93 | 1171 | 1566 | 7.9 | 33.8 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 0.58 | 0.79 | 0.85 | 0.81 | 1.55 | 2.47 | 0.83 | 1.13 | 0.75 | 0.79 | 5.35 | 3.98 | 5.19 | 3238 | 4222 | 19.7 | 30.4 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 0.41 | 0.44 | 0.23 | 0.48 | 0.85 | 1.26 | 0.49 | 0.72 | 0.50 | 0.48 | 2.92 | 2.07 | 2.94 | 1683 | 2390 | 14.1 | 42.0 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 0.36 | 0.52 | 0.56 | 0.68 | 1.02 | 2.26 | 0.71 | 1.15 | 0.61 | 0.69 | 3.78 | 2.90 | 4.78 | 2358 | 3889 | 30.6 | 64.9 |
| Pumice | Kaingaroa sand | Matea | 0.55 | 0.51 | 0.33 | 0.48 | 0.59 | 1.14 | 0.60 | 0.65 | 0.66 | 0.51 | 3.24 | 2.19 | 2.78 | 1778 | 2263 | 9.7 | 27.3 |

**Table 7c.** Nitrogen Test

| Lab Soil Type | Soil Type | District | D.M cut 0 (1st) 24/01/2001 mean of 6 pots (g) | D.M cut 0 (2nd) 16/02/2001 mean of 6 pots (g) | D.M cut1 19/03/2001 mean control (g) | D.M cut1 19/03/2002 mean N trt (g) | D.M cut 2 mean control (g) | D.M cut 2 mean N trt (g) | D.M cut 3 mean control (g) | D.M cut 3 mean N trt (g) | D.M cut 4 mean control (g) | D.M cut 4 mean N trt (g) | Total D.M including 0 cuts for control pots (g) | Total D.M cuts1+2+3 +4 for Control pots (g) | Total D.M cuts1+2+3 +4 for Nitrogen pots (g) | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Yellow Brown Earth (Dublin upland), Brown | Tarras | 0.39 | 0.43 | 0.35 | 0.51 | 0.35 | 0.69 | 0.27 | 0.35 | 0.32 | 0.29 | 2.12 | 1.30 | 1.85 | 1060 | 1501 | 8.8 | 41.7 |

Table 7d.

| Lab Soil Type | Soil Type | district | N (%) in grass Control cut 0 | N(%) in grass N trt cut 0 | N (%) in grass Mean cut 0 | N (%) in grass Control cut 1 | N (%) in grass Nitrogen cut 1 | N in grass 1st cut Response (%) | N (%) in grass Control cut 2 | N (%) in grass Nitrogen cut 2 | N (%) in grass Control cut 3 | N (%) in grass Nitrogen cut 3 | N (%) in grass Control cut 4 | N (%) in grass Nitrogen cut 4 | N (%) in grass sum of control | N (%) in grass Sum N trt | N in grass all cutsTotal Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pumice | Omeheu Sandy Loam | Edgecumbe | 4.58 | 4.74 | 4.66 | 2.2 | 3.78 | 72 | 2.09 | 2.12 | 2.09 | 1.95 | 2.06 | 1.91 | 8.44 | 9.76 | 16 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 3.73 | 3.87 | 3.80 | 3.27 | 4.85 | 48 | 1.98 | 2.4 | 1.93 | 2.03 | 1.72 | 1.74 | 8.9 | 11.02 | 24 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 5.06 | 5.14 | 5.10 | 4.56 | 5.04 | 11 | 2.21 | 2.34 | 2.16 | 2.04 | 1.67 | 1.35 | 10.6 | 10.77 | 2 |
| Pumice | Taupo Sandy Silt | Ngakuru | 4.9 | 4.71 | 4.81 | 3.54 | 4.66 | 32 | 2.2 | 2.11 | 2.07 | 2.19 | 1.7 | 1.77 | 9.51 | 10.73 | 13 |
| Pumice | Taupo Sandy Silt | Ngakuru | 4.95 | 4.85 | 4.90 | 4.86 | 5.04 | 4 | 2.37 | 3.16 | 2.16 | 2.03 | 1.74 | 1.64 | 11.13 | 11.87 | 7 |
| Pumice | Whenuaroa Sandy Silt | Waikite | 4.8 | 4.56 | 4.68 | 4.69 | 5.03 | 7 | 2.62 | 3.33 | 2.13 | 2.1 | 1.63 | 1.65 | 11.07 | 12.11 | 9 |
| Pumice | Taupo Sandy Silt | Waikite | 3.77 | 3.89 | 3.83 | 2.9 | 4.23 | 46 | 2.21 | 2.2 | 2.14 | 2.17 | 1.69 | 1.68 | 8.94 | 10.28 | 15 |
| Sedimentary | Lowland YBE | Alexandra | 5.27 | 5.06 | 5.17 | 4.81 | 5.26 | 9 | 2.32 | 2.88 | 2.08 | 2.25 | 1.83 | 1.87 | 11.04 | 12.26 | 11 |
| Sedimentary | Lowland YBE, | Alexandra | 4.67 | 4.48 | 4.58 | 3.02 | 4.22 | 40 | 2.25 | 2.23 | 2.28 | 2.33 | 1.66 | 1.75 | 9.21 | 10.53 | 14 |
| Sedimentary | Te Anau sandy loam | Manapouri | 4.26 | 4.18 | 4.22 | 2.34 | 3.98 | 70 | 2.3 | 2.12 | 2.43 | 2.37 | 1.93 | 1.84 | 9 | 10.31 | 15 |
| Sedimentary | Manewai sandy loam | Manapouri | 3.12 | 3.22 | 3.17 | 2.41 | 4.02 | 67 | 2.53 | 2.83 | 2.46 | 2.37 | 1.8 | 1.69 | 9.2 | 10.91 | 19 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 3.51 | 3.45 | 3.48 | 2.62 | 4.7 | 79 | 2.43 | 3.99 | 2.27 | 2.18 | 1.74 | 1.73 | 9.06 | 12.6 | 39 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 3.6 | 3.92 | 3.76 | 2.61 | 4.51 | 73 | 2.36 | 2.58 | 2.22 | 2.14 | 1.74 | 1.65 | 8.93 | 10.88 | 22 |

**Table 7d.**

| Lab Soil Type | Soil Type | district | N (%) in grass Control cut 0 | N(%) in grass N trt cut 0 | N (%) in grass Mean cut 0 | N (%) in grass Control cut 1 | N (%) in grass Nitrogen cut 1 | N in grass 1st cut Response (%) | N (%) in grass Control cut 2 | N (%) in grass Nitrogen cut 2 | N (%) in grass Control cut 3 | N (%) in grass Nitrogen cut 3 | N (%) in grass Control cut 4 | N (%) in grass Nitrogen cut 4 | N (%) in grass sum of control | N (%) in grass Sum N trt | N in grass all cutsTotal Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Yellow brown Earth (Wehenga) | Hindon | 4.24 | 4.01 | 4.13 | 2.15 | 3.39 | 58 | 2.2 | 1.93 | 2.25 | 2.24 | 1.52 | 1.87 | 8.12 | 9.43 | 16 |
| Sedimentary | Waitohi silt loam | Makikihi, Timaru | 3.14 | 3.26 | 3.20 | 2.62 | 4.98 | 90 | 2.09 | 2.35 | 2.2 | 2.16 | 1.63 | 1.92 | 8.54 | 11.41 | 34 |
| Sedimentary | Yellow grey earth | Roxburgh | 4.77 | 4.91 | 4.84 | 4.39 | 4.96 | 13 | 3.17 | 4.28 | 2.31 | 2.63 | 1.86 | 1.71 | 11.73 | 13.58 | 16 |
| Sedimentary | Yellow grey earth | Native Roxburgh | 4.26 | 4.03 | 4.15 | 2.81 | 3.51 | 25 | 2.18 | 2.1 | 2.1 | 2.14 | 1.57 | 1.7 | 8.66 | 9.45 | 9 |
| Sedimentary | Waikoikoi silt loam | Chatton, Roxburgh | 4.05 | 4.09 | 4.07 | 2.24 | 4.16 | 86 | 1.99 | 1.86 | 1.93 | 2.12 | 1.53 | 1.64 | 7.69 | 9.78 | 27 |
| Sedimentary | Yellow grey/Yellow brown integrate | North Canterbury | 4.34 | 4.12 | 4.23 | 2.17 | 3.92 | 81 | 1.91 | 1.58 | 1.91 | 1.88 | 1.34 | 1.16 | 7.33 | 8.54 | 17 |
| Sedimentary | Waikoikoi silt loam | Chatton, Mid Canterbury | 3.23 | 2.81 | 3.02 | 1.97 | 3.48 | 77 | 2.08 | 1.89 | 2.16 | 1.95 | 1.79 | 1.6 | 8 | 8.92 | 12 |
| Sedimentary | Yellow Grey Earth | Culverden | 4.42 | 4.56 | 4.49 | 2.35 | 3.6 | 53 | 2.18 | 1.86 | 2.24 | 2.23 | 1.96 | 1.66 | 8.73 | 9.35 | 7 |
| Ash | Horotiu silt loam | Hamilton | 4.14 | 4.6 | 4.37 | 3.3 | 4.83 | 46 | 2.47 | 2.65 | 2.36 | 2.14 | 1.69 | 1.56 | 9.82 | 11.18 | 14 |
| Sedimentary | Coastal sands | Awarua,/greenhills | 4.33 | 4.22 | 4.28 | 2.91 | 3.97 | 36 | 2.41 | 2.46 | 2.53 | 2.44 | 2.04 | 1.84 | 9.89 | 10.71 | 8 |
| Sedimentary | Yellow Brown Earth ( lowland ) | Reefton, West coast | 4.8 | 4.95 | 4.88 | 4.44 | 4.94 | 11 | 2.48 | 3.55 | 2.21 | 2.14 | 1.62 | 1.65 | 10.75 | 12.28 | 14 |
| Ash | Gley Soil, Patetonga soil | Tauhei, Waikato | 4.45 | 4.42 | 4.44 | 3.77 | 4.26 | 13 | 2.37 | 2.46 | 2.13 | 1.93 | 1.51 | 1.5 | 9.78 | 10.15 | 4 |
| Sedimentary | Yellow grey earth | Culverden | 4.22 | 4.45 | 4.34 | 2.65 | 3.83 | 45 | 2.06 | 2.1 | 2.17 | 2.29 | 1.7 | 1.69 | 8.58 | 9.91 | 16 |

Table 7d.

| Lab Soil Type | Soil Type | district | N (%) in grass Control cut 0 | N(%) in grass N trt cut 0 | N (%) in grass Mean cut 0 | N (%) in grass Control cut 1 | N (%) in grass Nitrogen cut 1 | N in grass 1st cut Response (%) | N (%) in grass Control cut 2 | N (%) in grass Nitrogen cut 2 | N (%) in grass Control cut 3 | N (%) in grass Nitrogen cut 3 | N (%) in grass Control cut 4 | N (%) in grass Nitrogen cut 4 | N (%) in grass sum of control | N (%) in grass Sum N trt | N in grass all cutsTotal Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Coastal sands | Awarua,/Greenhills | 4.25 | 4.21 | 4.23 | 2.71 | 3.95 | 46 | 2.2 | 2.22 | 2.46 | 2.25 | 1.87 | 1.8 | 9.24 | 10.22 | 11 |
| Sedimentary | Yellow Brown Earth ( upland ) , Wehenga | Pukerangi, S.I Hill country | 3.87 | 3.88 | 3.88 | 2.74 | 4.39 | 60 | 1.94 | 1.93 | 2.14 | 2.07 | 1.38 | 1.7 | 8.2 | 10.09 | 23 |
| Sedimentary | Recent, winganui | Taieri plains, Southland | 4.43 | 4.44 | 4.44 | 3.35 | 3.82 | 14 | 2.15 | 3 | 2 | 2.07 | 1.46 | 1.41 | 8.96 | 10.3 | 15 |
| Sedimentary | Yellow brown earth, Wehenga | Pukerangi, S.I | 4.35 | 4.41 | 4.38 | 2.75 | 4.61 | 68 | 2.22 | 2.33 | 2.27 | 2.14 | 1.51 | 1.55 | 8.75 | 10.63 | 21 |
| Peat/Organic | Organic | Awarua | 3.83 | 3.9 | 3.87 | 2.57 | 3.77 | 47 | 2.14 | 2.13 | 2.37 | 2.22 | 1.65 | 1.73 | 8.73 | 9.85 | 13 |
| Sedimentaary | Recent, winganui | Taieri plains, Southland | 4.8 | 4.76 | 4.78 | 3.91 | 4.69 | 20 | 2.42 | 2.8 | 2.34 | 2.16 | 1.66 | 1.61 | 10.33 | 11.26 | 9 |
| Ash | Brown granular loam | Morrinsville | 4.67 | 4.74 | 4.71 | 4.24 | 4.51 | 6 | 2.42 | 2.62 | 2.16 | 1.96 | 1.59 | 1.6 | 10.41 | 10.69 | 3 |
| Peat/Organic | Organic | Awarua,/Greenhills | 3.47 | 3.55 | 3.51 | 2.32 | 4.03 | 74 | 2.05 | 2.62 | 2.05 | 2.1 | 1.42 | 1.47 | 7.84 | 10.22 | 30 |
| Sedimentary | Recent, Mataura | Tuturau | 3.33 | 3.44 | 3.39 | 2.71 | 4.61 | 70 | 2.28 | 2.17 | 2.11 | 1.99 | 1.32 | 1.25 | 8.42 | 10.02 | 19 |
| Sedimentary | Typic firm Brown, Waikiwi | Gummies bush | 3.67 | 3.82 | 3.75 | 2.8 | 4.41 | 58 | 2.43 | 2.58 | 2.31 | 2.18 | 1.74 | 1.55 | 9.28 | 10.72 | 16 |
| Sedimentary | Brown, Drummond | Oreti | 3.13 | 3.24 | 3.19 | 2.8 | 4.41 | 58 | 2.5 | 3.28 | 2.07 | 1.99 | 1.36 | 1.34 | 8.73 | 11.02 | 26 |
| Sedimentary | Yellow brown earth | Northland | 4.62 | 4.56 | 4.59 | 3.29 | 4.4 | 34 | 2.18 | 2.3 | 2.06 | 1.97 | 1.6 | 1.48 | 9.13 | 10.15 | 11 |
| Sedimentary | Yellow brown earth | Northland | 4.36 | 4.4 | 4.38 | 3.25 | 4.1 | 26 | 1.88 | 2.07 | 2.09 | 2.09 | 1.47 | 1.59 | 8.69 | 9.85 | 13 |

**Table 7d.**

| Lab Soil Type | Soil Type | district | N (%) in grass Control cut 0 | N(%) in grass N trt cut 0 | N (%) in grass Mean cut 0 | N (%) in grass Control cut 1 | N (%) in grass Nitrogen cut 1 | N in grass 1st cut Response (%) | N (%) in grass Control cut 2 | N (%) in grass Nitrogen cut 2 | N (%) in grass Control cut 3 | N (%) in grass Nitrogen cut 3 | N (%) in grass Control cut 4 | N (%) in grass Nitrogen cut 4 | N (%) in grass sum of control | N (%) in grass Sum N trt | N in grass all cutsTotal Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash | Brown granular loam, Hamilton Clay | Hoe-O-Tainui, Waikato | 4.61 | 4.47 | 4.54 | 3.88 | 4.73 | 22 | 2.98 | 3.12 | 2.11 | 1.88 | 1.39 | 1.46 | 10.36 | 11.19 | 8 |
| Ash | Brown granular loam, Hamilton Clay | Tauhei, Waikato | 4.45 | 4.64 | 4.55 | 3.58 | 4.42 | 23 | 2.25 | 4.03 | 2.03 | 2.44 | 1.43 | 1.33 | 9.29 | 12.22 | 32 |
| Ash | Yellow Brown granular loam, Te Kuiti | Te kuiti hills | 4.02 | 4.01 | 4.02 | 3.37 | 4.54 | 35 | 2.07 | 2.21 | 2.34 | 2.16 | 1.59 | 1.64 | 9.37 | 10.55 | 13 |
| Ash | Yellow Brown loam, Tirau silt loam | Walton | 4.96 | 4.92 | 4.94 | 4.15 | 4.38 | 6 | 2.66 | 3.09 | 2.2 | 2.05 | 1.6 | 1.57 | 10.61 | 11.09 | 5 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 5.05 | 4.98 | 5.02 | 4.77 | 4.81 | 1 | 2.8 | 2.91 | 2.11 | 2.03 | 1.67 | 1.56 | 11.35 | 11.31 | 0 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 4.92 | 4.91 | 4.92 | 4.91 | 4.85 | -1 | 4.58 | 4.09 | 2.16 | 1.49 | 1.62 | 1.44 | 13.27 | 11.87 | -11 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 4.79 | 4.79 | 4.79 | 4.23 | 4.89 | 16 | 2.37 | 3.39 | 2.33 | 2.11 | 1.64 | 1.67 | 10.57 | 12.06 | 14 |

**Table 7d.**

| Lab Soil Type | Soil Type | district | N (%) in grass Control cut 0 | N(%) in grass N trt cut 0 | N (%) in grass Mean cut 0 | N (%) in grass Control cut 1 | N (%) in grass Nitrogen cut 1 | N in grass 1st cut Response (%) | N (%) in grass Control cut 2 | N (%) in grass Nitrogen cut 2 | N (%) in grass Control cut 3 | N (%) in grass Nitrogen cut 3 | N (%) in grass Control cut 4 | N (%) in grass Nitrogen cut 4 | N (%) in grass sum of control | N (%) in grass Sum N trt | N in grass all cutsTotal Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 4.23 | 4.21 | 4.22 | 2.89 | 4.9 | 70 | 1.92 | 2.23 | 2.31 | 2.03 | 1.58 | 1.5 | 8.7 | 10.66 | 23 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 4.91 | 5.3 | 5.11 | 4.54 | 5.14 | 13 | 2.47 | 2.74 | 1.89 | 1.93 | 1.41 | 1.49 | 10.31 | 11.3 | 10 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 4.81 | 4.63 | 4.72 | 5.12 | 4.51 | -12 | 2.34 | 2.99 | 1.98 | 1.88 | 1.63 | 1.68 | 11.07 | 11.06 | 0 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 4.92 | 5.12 | 5.02 | 4.32 | 4.87 | 13 | 2.45 | 2.72 | 1.76 | 1.6 | 1.51 | 1.53 | 10.04 | 10.72 | 7 |
| Pumice | Kaingaroa sand | Matea | 4.14 | 4.23 | 4.19 | 2.40 | 3.98 | 66 | 2.59 | 2.54 | 2.01 | 1.95 | 1.68 | 1.6 | 6.6 | 6.55 | -1 |
| Sedimentary | Yellow Brown Earth (Dublin upland), Brown | Tarras | 0.37 | 0.33 | 0.35 | 0.32 | 0.46 | 44 | 2.01 | 2.11 | 2.24 | 2.11 | 1.57 | 1.56 | 8.22 | 9.76 | 19 |

| Table 7e. | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Lab Soil Type** | **Soil Type** | **district** | **N uptake in grass Mean cut 0 (ml N)** | **N uptake in grass Control cut 1 (ml N)** | **N uptake in grass Nitrogen cut 1 (ml N)** | **N uptake in grass 1st cut Response (%)** | **N uptake in grass Control cut 2 (ml N)** | **N uptake in grass Nitrogen cut 2 (ml N)** | **N uptake in grass Control cut 3 (ml N)** | **N uptake in grass Nitrogen cut 3 (ml N)** | **N uptake in grass Control cut 4 (ml N)** | **N uptake in grass Nitrogen cut 4 (ml N)** | **N uptake in grass sum of control cut 0+1+2+3+4 (ml N)** | **N uptake in grass sum of control cut 1+2+3+4 (ml N)** | **N uptake in grass Sum N trt cut 1+2+3+4 (ml N)** | **N uptake in grass all cuts Total Response (%)** |
| Pumice | Omeheu Sandy Loam | Edgecumbe | 107.7 | 22.3 | 61.1 | 174 | 15.5 | 24.5 | 12.6 | 12.7 | 11.5 | 11.3 | 169.6 | 61.9 | 109.6 | 77.0 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 34.4 | 21.5 | 25.4 | 18 | 12.5 | 24.1 | 7.4 | 9.6 | 6.0 | 7.1 | 81.8 | 47.4 | 66.1 | 39.6 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 57.6 | 42.1 | 47.5 | 13 | 25.1 | 36.0 | 12.1 | 14.6 | 10.4 | 10.2 | 147.3 | 89.7 | 108.3 | 20.7 |
| Pumice | Taupo Sandy Silt | Ngakuru | 44.0 | 26.7 | 43.6 | 64 | 16.4 | 24.1 | 11.7 | 13.6 | 9.7 | 9.5 | 108.5 | 64.4 | 90.9 | 41.0 |
| Pumice | Taupo Sandy Silt | Ngakuru | 79.8 | 43.4 | 42.8 | -1 | 31.8 | 63.1 | 17.1 | 29.8 | 13.5 | 16.5 | 185.5 | 105.8 | 152.3 | 44.0 |
| Pumice | Whenuaroa Sandy Silt | Waikite | 33.3 | 24.5 | 27.3 | 11 | 21.0 | 47.4 | 11.4 | 17.6 | 5.5 | 9.6 | 95.7 | 62.4 | 102.0 | 63.4 |
| Pumice | Taupo Sandy Silt | Waikite | 53.6 | 22.5 | 52.3 | 132 | 13.8 | 16.4 | 9.6 | 10.6 | 7.8 | 7.7 | 107.3 | 53.7 | 87.0 | 62.1 |
| Sedimentary | Lowland YBE | Alexandra | 108.2 | 63.5 | 70.8 | 12 | 24.3 | 47.5 | 12.9 | 18.3 | 11.1 | 14.1 | 220.0 | 111.8 | 150.7 | 34.9 |
| Sedimentary | Lowland YBE, | Alexandra | 16.9 | 23.9 | 47.3 | 98 | 8.4 | 14.4 | 5.7 | 8.3 | 4.8 | 4.0 | 59.6 | 42.7 | 74.0 | 73.1 |
| Sedimentary | Te Anau sandy loam | Manapouri | 93.7 | 19.0 | 52.7 | 178 | 10.0 | 14.8 | 11.8 | 11.8 | 8.6 | 8.4 | 143.1 | 49.4 | 87.7 | 77.6 |
| Sedimentary | Manewai sandy loam | Manapouri | 24.0 | 9.5 | 26.1 | 176 | 8.3 | 14.5 | 7.1 | 9.8 | 4.8 | 5.7 | 53.7 | 29.7 | 56.2 | 89.4 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 62.6 | 12.0 | 24.9 | 108 | 8.1 | 19.3 | 6.0 | 10.5 | 4.0 | 6.1 | 92.7 | 30.0 | 60.8 | 102.5 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 77.1 | 11.8 | 40.1 | 239 | 7.5 | 12.9 | 6.2 | 7.3 | 5.3 | 5.6 | 108.0 | 30.9 | 65.9 | 113.6 |
| Sedimentary | Yellow brown Earth (Wehenga) | Hindon | 95.0 | 13.9 | 39.8 | 186 | 11.4 | 10.4 | 9.4 | 9.9 | 4.9 | 6.0 | 134.5 | 39.6 | 66.1 | 67.1 |
| Sedimentary | Waitohi silt loam | Makikihi, Timaru | 45.4 | 10.7 | 32.7 | 207 | 7.5 | 20.3 | 6.7 | 14.5 | 5.4 | 10.6 | 75.7 | 30.3 | 78.0 | 157.6 |
| Sedimentary | Yellow grey earth | Roxburgh | 92.0 | 46.5 | 36.2 | -22 | 41.6 | 53.5 | 27.7 | 55.2 | 22.4 | 24.1 | 230.3 | 138.3 | 169.0 | 22.3 |

Table 7e.

| Lab Soil Type | Soil Type | district | N uptake in grass Mean cut 0 (ml N) | N uptake in grass Control cut 1 (ml N) | N uptake in grass Nitrogen cut 1 (ml N) | N uptake in grass 1st cut Response (%) | N uptake in grass Control cut 2 (ml N) | N uptake in grass Nitrogen cut 2 (ml N) | N uptake in grass Control cut 3 (ml N) | N uptake in grass Nitrogen cut 3 (ml N) | N uptake in grass Control cut 4 (ml N) | N uptake in grass Nitrogen cut 4 (ml N) | N uptake in grass sum of control cut 0+1+2+3+4 (ml N) | N uptake in grass sum of control cut 1+2+3+4 (ml N) | N uptake in grass Sum N trt cut 1+2+3+4 (ml N) | N uptake in grass all cuts Total Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Yellow grey earth | Native Roxburgh | 93.6 | 25.8 | 54.1 | 110 | 14.6 | 17.0 | 13.9 | 14.7 | 10.4 | 10.1 | 158.2 | 64.6 | 95.9 | 48.4 |
| Sedimentary | Waikoikoi silt loam | Chatton, Roxburgh | 64.5 | 9.8 | 44.7 | 356 | 6.2 | 9.5 | 4.8 | 5.4 | 4.1 | 4.4 | 89.5 | 25.0 | 63.9 | 156.1 |
| Sedimentary | Yellow grey/Yellow brown integrate | North Canterbury | 77.0 | 12.7 | 44.9 | 255 | 7.6 | 10.7 | 7.4 | 8.5 | 6.9 | 4.8 | 111.6 | 34.6 | 68.9 | 98.9 |
| Sedimentary | Waikoikoi silt loam | Chatton, Mid Canterbury | 38.6 | 6.8 | 36.4 | 433 | 5.3 | 8.9 | 4.4 | 5.3 | 4.1 | 3.0 | 59.2 | 20.5 | 53.6 | 160.7 |
| Sedimentary | Yellow Grey Earth | Culverden | 73.3 | 28.3 | 58.9 | 108 | 18.2 | 16.6 | 14.0 | 13.6 | 13.0 | 11.0 | 146.7 | 73.4 | 100.1 | 36.3 |
| Ash | Horotiu silt loam | Hamilton | 78.6 | 27.5 | 39.6 | 44 | 14.5 | 33.9 | 10.4 | 12.1 | 6.5 | 8.0 | 137.4 | 58.9 | 93.7 | 59.1 |
| Sedimentary | Coastal sands | Awarua,/greenhills | 111.3 | 24.7 | 52.4 | 112 | 14.9 | 24.2 | 11.3 | 20.7 | 13.2 | 17.8 | 175.5 | 64.2 | 115.1 | 79.4 |
| Sedimentary | Yellow Brown Earth (lowland ) | Reefton, West coast | 76.6 | 46.8 | 47.9 | 2 | 24.2 | 61.3 | 13.0 | 23.8 | 10.8 | 10.5 | 171.4 | 94.8 | 143.4 | 51.2 |
| Ash | Gley Soil, Patetonga soil | Tauhei, Waikato | 104.4 | 51.4 | 71.0 | 38 | 30.4 | 53.2 | 21.5 | 21.7 | 16.1 | 13.3 | 223.9 | 119.4 | 159.2 | 33.3 |
| Sedimentary | Yellow grey earth | Culverden | 120.5 | 33.2 | 72.3 | 118 | 18.2 | 25.9 | 12.6 | 16.0 | 10.0 | 11.5 | 194.5 | 74.0 | 125.7 | 69.9 |
| Sedimentary | Coastal sands | Awarua,/Greenhills | 92.2 | 25.1 | 54.0 | 115 | 10.5 | 15.0 | 8.9 | 10.0 | 7.3 | 7.0 | 144.0 | 51.7 | 85.9 | 66.1 |
| Sedimentary | Yellow Brown Earth (upland) , Wehenga | Pukerangi, S.I Hill country | 19.8 | 20.8 | 50.3 | 142 | 10.6 | 15.1 | 9.2 | 9.7 | 5.8 | 7.0 | 66.2 | 46.4 | 82.0 | 76.8 |
| Sedimentary | Recent, winganui | Taieri plains, Southland | 103.5 | 31.5 | 34.0 | 8 | 18.1 | 22.4 | 11.0 | 13.5 | 9.1 | 9.0 | 173.3 | 69.8 | 78.9 | 13.1 |
| Sedimentary | Yellow brown earth, Wehenga | Pukerangi, S.I | 93.5 | 32.4 | 48.9 | 51 | 17.8 | 25.9 | 17.6 | 18.3 | 14.0 | 13.7 | 175.3 | 81.7 | 106.8 | 30.7 |
| Peat/Organic | Organic | Awarua | 68.5 | 18.1 | 47.6 | 163 | 9.3 | 17.5 | 7.8 | 11.0 | 10.1 | 11.1 | 113.7 | 45.2 | 87.3 | 93.0 |

Table 7e.

| Lab Soil Type | Soil Type | district | N uptake in grass Mean cut 0 (ml N) | N uptake in grass Control cut 1 (ml N) | N uptake in grass Nitrogen cut 1 (ml N) | N uptake in grass 1st cut Response (%) | N uptake in grass Control cut 2 (ml N) | N uptake in grass Nitrogen cut 2 (ml N) | N uptake in grass Control cut 3 (ml N) | N uptake in grass Nitrogen cut 3 (ml N) | N uptake in grass Control cut 4 (ml N) | N uptake in grass Nitrogen cut 4 (ml N) | N uptake in grass sum of control cut 0+1+2+3+4 (ml N) | N uptake in grass sum of control cut 1+2+3+4 (ml N) | N uptake in grass Sum N trt cut 1+2+3+4 (ml N) | N uptake in grass all cuts Total Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentaary | Recent, winganui | Taieri plains, Southland | 137.5 | 63.3 | 71.8 | 13 | 38.5 | 70.0 | 29.1 | 29.4 | 23.6 | 21.8 | 292.0 | 154.5 | 193.0 | 24.9 |
| Ash | Brown granular loam | Morrinsville | 82.3 | 48.2 | 45.9 | -5 | 38.0 | 66.5 | 21.0 | 22.1 | 19.0 | 19.3 | 208.5 | 126.2 | 153.8 | 21.9 |
| Peat/Organic | Organic | Awarua,/Greenhills | 81.1 | 13.8 | 31.3 | 127 | 8.2 | 16.9 | 7.7 | 11.3 | 6.3 | 7.4 | 117.1 | 36.0 | 66.9 | 85.7 |
| Sedimentary | Recent, Mataura | Tuturau | 62.7 | 13.9 | 42.4 | 205 | 9.3 | 17.4 | 7.7 | 9.8 | 6.6 | 5.9 | 100.1 | 37.4 | 75.5 | 101.9 |
| Sedimentary | Typic firm Brown, Waikiwi | Gummies bush | 73.5 | 21.2 | 52.6 | 148 | 15.4 | 26.5 | 11.2 | 14.2 | 8.4 | 9.7 | 129.6 | 56.1 | 103.0 | 83.6 |
| Sedimentary | Brown, Drummond | Oreti | 31.5 | 7.7 | 22.5 | 194 | 6.1 | 15.3 | 4.1 | 7.6 | 2.8 | 3.7 | 52.2 | 20.7 | 49.1 | 137.5 |
| Sedimentary | Yellow brown earth | Northland | 79.6 | 38.7 | 59.4 | 53 | 24.0 | 39.8 | 14.6 | 16.8 | 9.4 | 11.0 | 166.3 | 86.7 | 127.0 | 46.4 |
| Sedimentary | Yellow brown earth | Northland | 84.3 | 41.1 | 68.7 | 67 | 18.9 | 30.7 | 14.4 | 16.0 | 10.7 | 13.0 | 169.5 | 85.1 | 128.4 | 50.9 |
| Ash | Brown granular loam, Hamilton Clay | Hoe-O-Tainui, Waikato | 82.6 | 16.0 | 31.5 | 97 | 15.4 | 32.2 | 10.6 | 14.0 | 6.4 | 6.9 | 131.0 | 48.4 | 84.7 | 75.0 |
| Ash | Brown granular loam, Hamilton Clay | Tauhei, Waikato | 93.6 | 26.0 | 32.3 | 24 | 16.7 | 32.9 | 12.7 | 32.5 | 10.1 | 11.1 | 158.9 | 65.4 | 108.8 | 66.4 |
| Ash | Yellow Brown granular loam, Te Kuiti | Te kuiti hills | 69.3 | 26.3 | 48.3 | 84 | 15.9 | 20.1 | 13.8 | 13.0 | 11.7 | 9.7 | 137.0 | 67.7 | 91.0 | 34.4 |
| Ash | Yellow Brown loam, Tirau silt loam | Walton | 77.0 | 35.3 | 40.4 | 15 | 24.6 | 43.7 | 17.4 | 19.5 | 15.5 | 14.1 | 169.8 | 92.8 | 117.7 | 26.8 |

Table 7e.

| Lab Soil Type | Soil Type | district | N uptake in grass Mean cut 0 (ml N) | N uptake in grass Control cut 1 (ml N) | N uptake in grass Nitrogen cut 1 (ml N) | N uptake in grass 1st cut Response (%) | N uptake in grass Control cut 2 (ml N) | N uptake in grass Nitrogen cut 2 (ml N) | N uptake in grass Control cut 3 (ml N) | N uptake in grass Nitrogen cut 3 (ml N) | N uptake in grass Control cut 4 (ml N) | N uptake in grass Nitrogen cut 4 (ml N) | N uptake in grass sum of control cut 0+1+2+3+4 (ml N) | N uptake in grass sum of control cut 1+2+3+4 (ml N) | N uptake in grass Sum N trt cut 1+2+3+4 (ml N) | N uptake in grass all cuts Total Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 73.4 | 42.6 | 43.0 | 1 | 47.3 | 54.6 | 19.3 | 19.6 | 14.5 | 11.0 | 197.1 | 123.7 | 128.2 | 3.6 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 73.2 | 28.6 | 42.4 | 48 | 86.1 | 122.4 | 55.5 | 42.7 | 22.4 | 20.7 | 265.8 | 192.6 | 228.2 | 18.5 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 41.4 | 24.5 | 18.1 | -26 | 20.1 | 38.5 | 12.5 | 20.4 | 10.9 | 10.7 | 109.5 | 68.0 | 87.7 | 28.9 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 35.5 | 13.8 | 31.9 | 131 | 7.6 | 13.8 | 6.1 | 7.4 | 4.8 | 4.4 | 67.8 | 32.3 | 57.4 | 78.1 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 69.9 | 38.7 | 41.5 | 7 | 38.2 | 67.7 | 15.7 | 21.7 | 10.6 | 11.8 | 173.1 | 103.3 | 142.7 | 38.2 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 40.0 | 11.8 | 21.6 | 84 | 20.0 | 37.8 | 9.6 | 13.5 | 8.2 | 8.0 | 89.6 | 49.5 | 81.0 | 63.5 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 44.3 | 24.3 | 33.3 | 37 | 25.0 | 61.6 | 12.5 | 18.4 | 9.2 | 10.5 | 115.3 | 71.0 | 123.7 | 74.3 |
| Pumice | Kaingaroa sand | Matea | 44.1 | 8.0 | 19.0 | 137 | 15.3 | 29.0 | 12.1 | 12.7 | 11.1 | 8.2 | 90.6 | 46.5 | 68.9 | 48.2 |
| Sedimentary | Yellow Brown Earth (Dublin upland), Brown | Tarras | 2.9 | 1.1 | 2.4 | 109 | 7.1 | 14.6 | 6.1 | 7.5 | 5.1 | 4.5 | 22.3 | 19.4 | 28.9 | 48.8 |

| Table 7f. | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Lab Soil Type** | **Soil Type** | **District** | **Total D.M for Control pots kg D.M/ha** | **Total D.M for Nitrogen pots kg D.M/ha** | **kg D.M/kg N applied** | **Response (%)** | **N in grass 1st cut Response (%)** | **N in grass all cuts Total Response (%)** | **N uptake in grass 1st cut Response (%)** | **N uptake in grass all cuts Total Response (%)** |
| Pumice | Omeheu Sandy Loam | Edgecumbe | 2371 | 3263 | 17.8 | 37.6 | 72 | 16 | 174 | 77.0 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 1642 | 1957 | 6.3 | 19.1 | 48 | 24 | 18 | 39.6 |
| Pumice | Rotoiti Sandy Loam | Te Ngae, Rotorua | 2637 | 3211 | 11.5 | 21.8 | 11 | 2 | 13 | 20.7 |
| Pumice | Taupo Sandy Silt | Ngakuru | 2141 | 2631 | 9.8 | 22.9 | 32 | 13 | 64 | 41.0 |
| Pumice | Taupo Sandy Silt | Ngakuru | 3089 | 4328 | 24.8 | 40.1 | 4 | 7 | -1 | 44.0 |
| Pumice | Whenuaroa Sandy Silt | Waikite | 1786 | 2756 | 19.4 | 54.3 | 7 | 9 | 11 | 63.4 |
| Pumice | Taupo Sandy Silt | Waikite | 1878 | 2382 | 10.1 | 26.8 | 46 | 15 | 132 | 62.1 |
| Sedimentary | Lowland YBE | Alexandra | 2921 | 3710 | 15.8 | 27.0 | 9 | 11 | 12 | 34.9 |
| Sedimentary | Lowland YBE, | Alexandra | 1382 | 1911 | 10.6 | 38.2 | 40 | 14 | 98 | 73.1 |
| Sedimentary | Te Anau sandy loam | Manapouri | 1770 | 2420 | 13.0 | 36.8 | 70 | 15 | 178 | 77.6 |
| Sedimentary | Manewai sandy loam | Manapouri | 1038 | 1558 | 10.4 | 50.1 | 67 | 19 | 176 | 89.4 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 1043 | 1504 | 9.2 | 44.2 | 79 | 39 | 108 | 102.5 |
| Sedimentary | Ruapuna stoney silt-loam | Anama, Mid Canterbury | 1103 | 1683 | 11.6 | 52.6 | 73 | 22 | 239 | 113.6 |
| Sedimentary | Yellow brown Earth (Wehenga) | Hindon | 1547 | 2014 | 9.3 | 30.1 | 58 | 16 | 186 | 67.1 |
| Sedimentary | Waitohi silt loam | Makikihi, Timaru | 1141 | 2228 | 21.7 | 95.2 | 90 | 34 | 207 | 157.6 |
| Sedimentary | Yellow grey earth | Roxburgh | 3883 | 4463 | 11.6 | 14.9 | 13 | 16 | -22 | 22.3 |
| Sedimentary | Yellow grey earth | Native Roxburgh | 2366 | 2954 | 11.8 | 24.9 | 25 | 9 | 110 | 48.4 |
| Sedimentary | Waikoikoi silt loam | Chatton, Roxburgh | 1033 | 1713 | 13.6 | 65.9 | 86 | 27 | 356 | 156.1 |

Table 7f.

| Lab Soil Type | Soil Type | District | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) | N in grass 1st cut Response (%) | N in grass all cuts Total Response (%) | N uptake in grass 1st cut Response (%) | N uptake in grass all cuts Total Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Sedimentary | Yellow grey/Yellow brown integrate | North Canterbury | 1534 | 2182 | 13.0 | 42.2 | 81 | 17 | 255 | 98.9 |
| Sedimentary | Waikoikoi silt loam | Chatton,<br>Mid Canterbury | 837 | 1604 | 15.3 | 91.6 | 77 | 12 | 433 | 160.7 |
| Sedimentary | Yellow Grey Earth | Culverden | 2702 | 3089 | 7.8 | 14.3 | 53 | 7 | 108 | 36.3 |
| Ash | Horotiu silt loam | Hamilton | 1824 | 2585 | 15.2 | 41.8 | 46 | 14 | 44 | 59.1 |
| Sedimentary | Coastal sands | Awarua,/greenhills | 2084 | 3350 | 25.3 | 60.7 | 36 | 8 | 112 | 79.4 |
| Sedimentary | Yellow Brown Earth ( lowland ) | Reefton, West coast | 2672 | 3610 | 18.8 | 35.1 | 11 | 14 | 2 | 51.2 |
| Ash | Gley Soil, Patetonga soil | Tauhei, Waikato | 3840 | 4748 | 18.2 | 23.6 | 13 | 4 | 38 | 33.3 |
| Sedimentary | Yellow grey earth | Culverden | 2686 | 3659 | 19.5 | 36.2 | 45 | 16 | 118 | 69.9 |
| Sedimentary | Coastal sands | Awarua,/Greenhills | 1751 | 2336 | 11.7 | 33.4 | 46 | 11 | 115 | 66.1 |
| Sedimentary | Yellow Brown Earth ( upland ) , Wehenga | Pukerangi, S.I Hill country | 1751 | 2279 | 10.6 | 30.2 | 60 | 23 | 142 | 76.8 |
| Sedimentary | Recent, winganui | Taieri plains, Southland | 2407 | 2379 | -0.5 | -1.1 | 14 | 15 | 8 | 13.1 |
| Sedimentary | Yellow brown earth, Wehenga | Pukerangi, S.I | 2992 | 3182 | 3.8 | 6.3 | 68 | 21 | 51 | 30.7 |
| Peat/Organic | Organic | Awarua | 1688 | 2623 | 18.7 | 55.4 | 47 | 13 | 163 | 93.0 |
| Sedimentaary | Recent, winganui | Taieri plains, Southland | 4778 | 5485 | 14.1 | 14.8 | 20 | 9 | 13 | 24.9 |
| Ash | Brown granular loam | Morrinsville | 3962 | 4789 | 16.5 | 20.9 | 6 | 3 | -5 | 21.9 |

Table 7f.

| Lab Soil Type | Soil Type | District | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) | N in grass 1st cut Response (%) | N in grass all cuts Total Response (%) | N uptake in grass 1st cut Response (%) | N uptake in grass all cuts Total Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Peat/Organic | Organic | Awarua,/Greenhills | 1477 | 2003 | 10.5 | 35.6 | 74 | 30 | 127 | 85.7 |
| Sedimentary | Recent, Mataura | Tuturau | 1447 | 2184 | 14.7 | 50.9 | 70 | 19 | 205 | 101.9 |
| Sedimentary | Typic firm Brown, Waikiwi | Gummies bush | 1913 | 2843 | 18.6 | 48.6 | 58 | 16 | 148 | 83.6 |
| Sedimentary | Brown, Drummond | Oreti | 751 | 1331 | 11.6 | 77.3 | 58 | 26 | 194 | 137.5 |
| Sedimentary | Yellow brown earth | Northland | 2905 | 3799 | 17.9 | 30.8 | 34 | 11 | 53 | 46.4 |
| Sedimentary | Yellow brown earth | Northland | 3000 | 3856 | 17.1 | 28.5 | 26 | 13 | 67 | 50.9 |
| Ash | Brown granular loam, Hamilton Clay | Hoe-O-Tainui, Waikato | 1537 | 2371 | 16.7 | 54.3 | 22 | 8 | 97 | 75.0 |
| Ash | Brown granular loam, Hamilton Clay | Tauhei, Waikato | 2271 | 3019 | 15.0 | 32.9 | 23 | 32 | 24 | 66.4 |
| Ash | Yellow Brown granular loam, Te Kuiti | Te kuiti hills | 2339 | 2572 | 4.7 | 10.0 | 35 | 13 | 84 | 34.4 |
| Ash | Yellow Brown loam, Tirau silt loam | Walton | 2875 | 3404 | 10.6 | 18.4 | 6 | 5 | 15 | 26.8 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 3550 | 3610 | 1.2 | 1.7 | 1 | 0 | 1 | 3.6 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 5214 | 6645 | 28.6 | 27.4 | -1 | -11 | 48 | 18.5 |
| Ash | Brown granular loam, Naike clay loam | Whatawhata | 2138 | 2531 | 7.9 | 18.4 | 16 | 14 | -26 | 28.9 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 1171 | 1566 | 7.9 | 33.8 | 70 | 23 | 131 | 78.1 |

**Table 7f.**

| Lab Soil Type | Soil Type | District | Total D.M for Control pots kg D.M/ha | Total D.M for Nitrogen pots kg D.M/ha | kg D.M/kg N applied | Response (%) | N in grass 1st cut Response (%) | N in grass all cuts Total Response (%) | N uptake in grass 1st cut Response (%) | N uptake in grass all cuts Total Response (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 3238 | 4222 | 19.7 | 30.4 | 13 | 10 | 7 | 38.2 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 1683 | 2390 | 14.1 | 42.0 | -12 | 0 | 84 | 63.5 |
| Ash | Yellow brown loam, Egmont silt loam | WTARS | 2358 | 3889 | 30.6 | 64.9 | 13 | 7 | 37 | 74.3 |
| Pumice | Kaingaroa sand | Matea | 1778 | 2263 | 9.7 | 27.3 | 66 | -1 | 137 | 48.2 |
| Sedimentary | Yellow Brown Earth (Dublin upland), Brown | Tarras | 1060 | 1501 | 8.8 | 41.7 | 44 | 19 | 109 | 48.8 |

# Chapter 8: The Olsen P Test:

# Should it be on a volume or weight basis ?

*Contents*

## 8.1 Abstract

Olsen P is not a defined or fixed fraction; the test is based on an equilibrium. The ratio of soil to solution and the buffering capacity of the soil are critical to the amount of P released. This study shows that Olsen P increases with decreasing soil-to-solution ratio (decreasing B.D). The current 'Quick Test' Olsen P method for recommendation purposes assumes a bulk density or weight/volume of 0.9, which is not the case for many soils. The range of weight/volume for the 100 soils studied were 0.46–1.63. This is equivalent to 2.3–8.2 grams of soil extracted with 100 mL of 0.5M $NaHCO_3$. These soils are typical of commercial samples sent for routine soil testing.

The current practice is that commercial laboratories determine Olsen P by volume, whereas research laboratories determine Olsen P by weight. There is an increasing and appreciable difference between the two methods as divergence occurs from weight/volume of 1.0.

## 8.2 Introduction

The phosphate status in New Zealand agricultural soils was determined by the Truog P test until June 1976, when it was replaced by the Olsen P test (Parfitt and Davin, 1985). Both tests calculated P concentration on a soil volume basis. The Truog method used a 2.2 mL spoonful of soil, while the Olsen P test was measured using a 4 mL scoop of soil (*Pers. comm.* Oomen; Oomen, 1978 and Grigg, 1975).

The initial Olsen P trial studies were carried out on a small number of sites where comparison between weight and volume were investigated. These trials were carried out on seven soil types, with soils derived mainly from ash and sedimentary material. On these trials Olsen P was determined on both volume and weight basis and compared to pasture yield. The weight and volume methods for Olsen P performed similarly in predicting pasture responses to phosphate fertiliser application. These trials were conducted around late 1960 to the early 1970s for 4 years (Saunders *et. al.*, 1987). The experiments were on commercial farms and managed under a system of occasional cuts to measure pasture response.

Based on this initial trial work, it was decided, for convenience, that commercial laboratories measure Olsen P on a volume rather than a weight basis. This was also justified by the claim that a volume basis gives a better idea of plant P availability, because plants uptake P from a volume of soil, rather than a weight. As a consequence, in field trials conducted by MAF, the resulting Olsen P measurements in collected soil samples analysed by the Soil Fertility Service, were measured on a soil volume basis.

Based on the volume method, MAF field experiments produced different relationships between Olsen P and pasture production for the various major soil groups. This is reflected in the recommendations for fertiliser P application. It is proposed that there may be a single relationship for all New Zealand soils for fertiliser recommendation purposes if a weight of soil, rather than a volume, is used in the Olsen P test.

The current practice is that commercial laboratories determine Olsen P by volume, whereas research laboratories determine Olsen P by a weight basis. There is also confusion or unawareness of which method is used in a particular study. Consequently, the results are sometimes reported incorrectly. The determination of Olsen P by volume and weight of soil are considered.

The aim of the work carried out in this chapter is to get a better understanding of the Olsen P test. Olsen P is a critical soil test for New Zealand agriculture. The knowledge gained from this chapter was used to standardise a 'base reference Olsen P method for NIR' in Chapter 5. The accuracy of NIR calibrations is directly related to the base reference method i.e. the NIR test can only be as good as the reference method.

## 8.3 Method

One hundred soil samples were used in the study. Soil samples derived from volcanic ash (30), sediments (51), pumice (13), and peat (6), were used. The samples were selected to represent a range of Olsen P values. Samples were selected from throughout the country, ensuring that a wide variety of soil types were included.

The Olsen P method determines the levels of plant available phosphate in New Zealand soils. The method employs a $NaHCO_3$ extraction method developed by Olsen *et al.*, 1954, where the phosphate concentration in the extract is determined by a phospho-molybdate method proposed by Watanabe and Olsen, 1965 and Murphy and Riley, 1962.

For this study, Olsen P was determined for the 100 soils on a weight basis, as proposed by Olsen *et al.*, 1954. This method is used by research laboratories. Five grams of air dried soil is extracted with 100 mL of 0.5M $NaHCO_3$ and reported as µg P extracted per gram of soil (µg/g).

Olsen P was measured for 100 soils using a modified method (Soil Fertility Service Lab method). This method is used by commercial labs where Olsen P is determined on a volume basis. 5 mL of soil, using a scoop, is extracted with 100 mL of 0.5M $NaHCO_3$ and reported as µg/ml.

Four soils from ash, sedimentary, pumice and peat were chosen with a range of Olsen P values. The four soils were chosen on the basis of having Olsen P obtained by commercial Labs of values of approximately 10, 20, 30 and 40 µg/ml respectively. These were chosen to determine if similar trends were seen for the differing Olsen P ranges when different weights were taken. Olsen P was determined for the 16 soils using weights of 2.5, 4.0, 5.0, 7.5 and 10.0 grams of each soil extracted with 100 mL 0.5 M NaHCO3. These weights would correspond to volume to weight ratios (bulk densities) of 0.5, 0.8, 1.0, 1.5 and 2.0 respectively.

The P retention or anion storage capacities (ASC) of the soils were also measured.

## 8.4 Results and Discussion

The current 'Quick Test' Olsen P method (which is based on a soil volume) for recommendation purposes, assumes a bulk density or weight/volume ratio of 0.9, which is not true for many soils (Table 8.1).

The current commercial method does not take into account the actual dilution factors involved. The concentration of phosphate extracted is multiplied by 20, irrespective of the amount of soil in the 5 mL scoop. For example, a peat and pumice soil with weight/volume ratios of 0.5 and 0.7 should, in practice, have dilution factors of 40 and 29 respectively.

The range of weight/volume for the 100 soils studied was 0.46–1.63. This is equivalent to 2.3–8.2 grams of soil extracted with 100 mL of 0.5M $NaHCO_3$. These soils are typical of commercial samples sent in for routine soil testing. It is expected that, for New Zealand soils, the weight/volume would be even greater than reported in this paper.

**Table 8.1:** Number of soils, weight/volume range and median weight/volume value for each major soil category.

| Soil group | Number | Weight/volume (range) | Weight/volume (median) |
|---|---|---|---|
| Peat | 6 | 0.46–0.75 | 0.58 |
| Pumice | 12 | 0.65–0.93 | 0.70 |
| Sedimentary | 50 | 0.75–1.63 | 0.84 |
| Ash | 32 | 0.50–0.93 | 0.67 |

Extraction of P from soil by 0.5 M $NaHCO_3$ at pH 8.5 is considered to be a two-stage process. During stage one, hydroxide and bicarbonate desorbs phosphate from soil particles, and in stage two, there is competition between P, bicarbonate and $OH^-$ for secondary adsorption (Barrow & Shaw$^{I}$, 1976).

Figures 8.1 (a) (Ash), 1 (b) (peat), 1 (c) (pumice) and 1 (d) (sedimentary) show the relationship between Olsen P values obtained and weight of soil for the four soils of each major category. The graphs show that Olsen P is influenced by soil weight and therefore, bulk density. This was also the finding of (Barrow & Shaw$^{II}$, 1976*)*. They found that the soil:solution ratio was very important, and that secondary absorption played a major role in the amount of P extracted into solution. At small soil:solution ratios, the effect on displacement was dominant, and the net effect was an increase in the amount of phosphate in extract. At large soil:solution ratios, secondary adsorption eventually predominated and caused a decrease in the amount of phosphate in the extract. Olsen P is not a defined or fixed pool, as it is dependent on conditions of measurement. Olsen P increases with decreasing soil to solution ratio (decreasing B.D). The ratio of soil to solution and the buffering capacity of the soil are critical to the amount of P extracted.

Barrow and Shaw$^{I}$, 1976 developed a mathematical model which estimated the amount of phosphate initially displaced and the amount which underwent secondary adsorption onto the soil. They found that the secondary adsorption was dependent on the soil: solution ratio and the type of soil. The soil:solution ratio effect appeared to arise because of the adsorption of bicarbonate. As a result, at high soil:solution ratios, the bicarbonate concentration in solution is lower and competition for adsorption of the phosphate is less effective. The P buffering capacity of soils in 0.5 M $NaHCO_3$ extracts and the number of potential P adsorption sites present on the soil is highly correlated with the availability of P to plants, because it directly affects the rate of diffusion (Barlow and Shaw$^{III}$, 1976).

It thus becomes very important that all soils are treated the same, i.e. an exact weight should be used. In using a volume of soil, the soil:solution ratio varies, depending on the soil type. This has probably led to the differing relationships obtained in the MAF field trials.

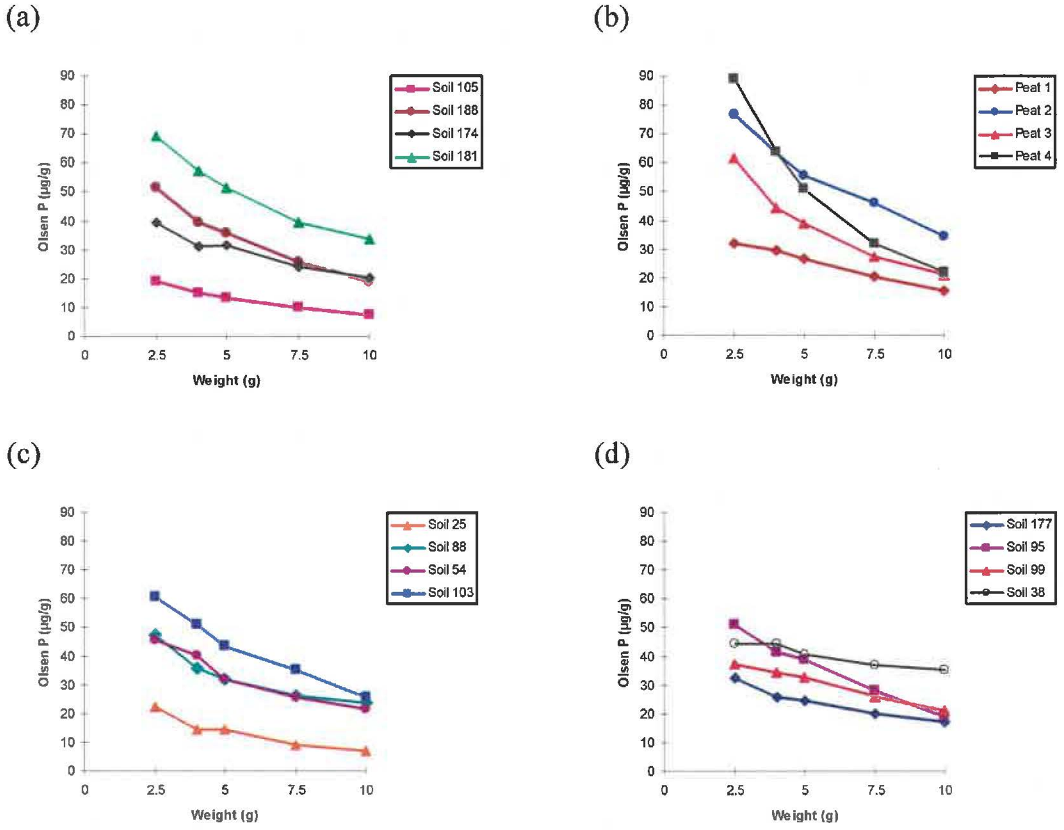

**Figure 8.1:**
Olsen P(µg/g) obtained for four soils: (a) Ash soils; (b) Peat soils; (c) Pumice soils and (d) Sedimentary soils.

Table 8.2 shows the Olsen P target levels for agronomic advice which will maintain near-maximum pasture production (Roberts and Morton, 1999). These levels are based on field trials and Olsen P determined via the volume method.

**Table 8.2:** Olsen P target levels for agronomic advice which will maintain near-maximum pasture production.

| Soil group | Target Olsen P |
|---|---|
| Peat | 35–45* |
| Pumice | 35–45 |
| Sedimentary | 20–30 |
| Ash | 22–30 |

* Based on interim research results.

Lower bulk density soils (such as peat and pumice) have less soil in the extracting vessel. Therefore, more P is extracted into solution for these soils, compared to higher bulk density sedimentary soils. This has probably lead to higher Olsen P target levels than needed being suggested to maintain maximum pasture production.

Table 8.3 and Figure 8.2 show the relationship between Olsen P for one of the ash soils determined on a volume and weight basis. The principle or trend shown is found for all soils irrespective of soil type (Figure 8.3).

**Table 8.3.** The relationship between Olsen P for one of the ash soils determined on a volume and weight basis.

| Weight (g) | Olsen P volume (μg/mL) | Olsen P weight (μg/g) | Bulk density |
|---|---|---|---|
| 2.5 | 26 | 52 | 0.5 |
| 4.0 | 32 | 40 | 0.8 |
| 5.0 | 36 | 36 | 1.0 |
| 7.5 | 39 | 26 | 1.5 |
| 10.0 | 39 | 19 | 2.0 |

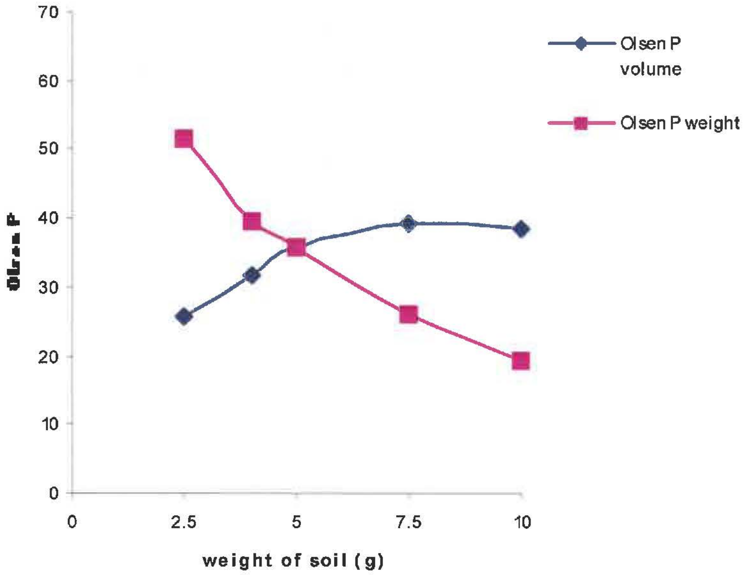

**Figure 8.2:** The relationship between Olsen P for one of the ash soils determined on a volume and weight basis.

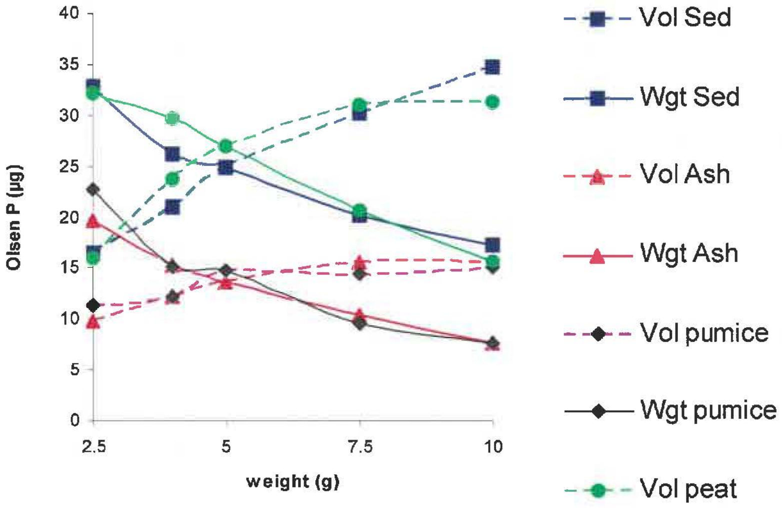

**Figure 8.3:** The graph shows the relationship between soil weight and soil volume to Olsen P determined for the four soil categories.

The conversion of Olsen P (determined by volume) to Olsen P (determined by weight) is not straightforward, because the measurement is dependent on an equilibrium. It is, nevertheless, possible to establish a relationship where 96% of the variation was accounted for. The relationship is $\log_e(\text{Pvol}) = -1.69 + 1.13 \log_e(\text{Pwt}) + 0.0057\ \text{ASC} + 0.895\ \text{B.D.}$

Figure 8.4 shows the relationship between Olsen P determined by volume (standard quick test procedure) and by weight.

The three peat soils which did not conform to the relationship have low bulk densities and low ASC values, whereas, the three that fitted the relationship well, were the more mineralised peats, which had higher bulk density and ASC values.

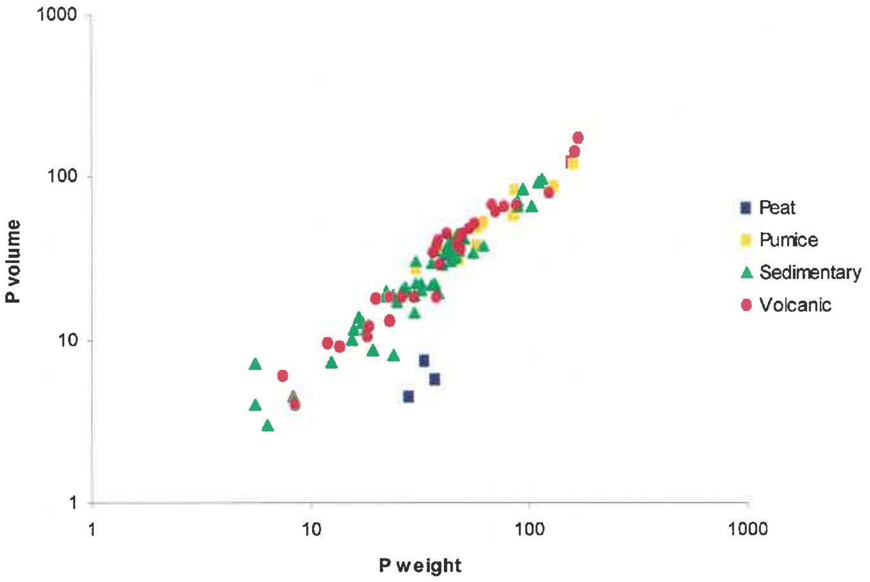

**Figure 8.4:**
The relationship between Olsen P determined by volume (standard quick test procedure) and by weight.

The initial work by Saunders *et al*., 1987, comprising weight and volume, was run on seven soil types. Three of these were yellow-brown loams (ash), two were yellow-brown pumice soils (pumice), and the remaining two were yellow-grey earths (sedimentary). The experiments were on commercial farms and managed under a system of occasional cuts, to measure pasture responses to P fertiliser. The Olsen P test using weight and volume performed similarly, even though it was concluded that volume was better. The volume determination of Olsen P in Saunders *et al*., 1987 study was done only on samples collected in late summer. Values, on a volume basis, for the early spring samples, were calculated by regression, obtained between volume and weight values, for the late summer samples. As a consequence the Olsen volume method using 0–75 mm depth samples was chosen (MAF soil testing service); all subsequent research trial samples were measured using the volume method.

One single relationship may hold for ash, sedimentary and pumice soils if a weight of soil is used. It may also hold true for the more mineralised peats.

## 8.5 Conclusions

Currently, soils are not represented by Olsen P in such a way that their P values are truly representative of their actual P status.

Olsen P values are influenced by soil weight. The ratio of soil to solution, and the buffering capacity of the soil, are critical to the amount of P extracted. Olsen P is not a defined or fixed pool. Its size depends on conditions of measurement. Olsen P increases with decreasing soil to solution ratio (decreasing B.D).

The need for different relationships for different soil groups (in the recommendations for Olsen P by volume) suggests the assumption that P availability is related to volume (rather than weight) of soil may be wrong.

Recommendations traditionally offered by agronomists may be simplified and not be soil group dependent for mineral soils.

## 8.6 References

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# Chapter 9:  Transportable NIR Calibrations

*Contents*

## 9.1 Abstract

Three NIR instruments were used to develop three independent calibrations for estimation of nitrogen (%N) in dried ground plant material. These calibrations were applied to each of three instruments.

Samples measured on the two instruments, other than the one used to build the calibration, were predicted with a similar root mean square error of prediction (RMSEP = 0.22–0.35%) to those measured on the same instrument (RMSEP = 0.18–0.24%). The repeatability ($S_r$) for the estimation of %N by the Kjeldahl method is 0.13%.

This demonstrates, that with little or no loss in accuracy, it is feasible to apply a calibration generated on one instrument to other instruments for the purpose of estimating %N in plant material. A bias was observed for the prediction from the instruments and with a bias correction the prediction results can be further improved.

The methodology used to develop transportable calibrations can be applied to other analytes. This is of commercial importance, as it enables instruments to be sold without the need to develop a machine-specific calibration for every analyte of interest.

## 9.2 Introduction

One of the major obstacles to the uptake of NIR technology by industry has been the need to calibrate every NIR instrument individually for each analyte of interest. In the past, the use of a calibration developed on another instrument has proved far from adequate. The transferability of calibrations between instruments has been difficult. The major NIR manufacturers see this as a problem and are currently addressing this (Brimmer, 2004). The NIR diode array instruments used in this work uses a new approach to obtain spectra, which shows promise over other instruments.

In this work, the following terms will be used:

- **Transportable calibration:** A calibration developed on an instrument, which can then be immediately used on other instruments to predict samples.

- **Transferable calibration:** A calibration developed on an instrument which needs linear transformation on the predicted parameter to be used on other instruments to predict samples.

This study compares the calibration performance of three KS-NIR 01 instruments for the prediction of total N in plant material. The performance of each calibration was evaluated for the prediction of spectra recorded from the other two instruments. A bias correction was applied to the transferred calibrations to observe if this improved performance.

## 9.3 Method

### 9.3.1 NIR Instruments

Three diode array KES-NIR 01 series instruments were fitted to separate mounts, which enabled samples to be scanned within a petri dish. The instruments were operated in an air-conditioned laboratory, but no attempt was made to protect them from dust (aside from maintenance at regular intervals).

### 9.3.2 Samples

166 samples of plant material were obtained from samples which came into AgResearch commercial Lab (Celentis Analytical). These had been submitted for routine analysis over a period of 5 months. After drying and grinding, three sub-samples were removed for analysis. The remainder was scanned once by each of the three NIR instruments over a period of two days. Sub-samples were analysed total N, using the Kjeldahl method over three separate runs.

### 9.3.3 Unit Characterisation

The NIR instruments were initially characterised using absolute reference (Spectralon) tiles. During operation, a more physically robust calibration tile was measured for every sample to correct for instrumental drift. Calibration tiles were used to tie the sample spectra to the absolute reference tile and thereby, to the virtual reference spectrum, employing the Spectrum Toolbox V7.04 (not commercially available). This software was developed by the AgResearch NIR team.

### 9.3.4 Data Analysis

Samples were assigned to either the calibration set or validation set in a systematic way. The sets were chosen randomly but ensured that both sets were fully representative of the sample range.

A calibration for each instrument was obtained using Grams PLS™. Standardised residuals were screened and extreme outliers discarded.

The calibration obtained from each instrument was applied in turn to spectra of validation samples generated by each of the three instruments. For each instrument, the root mean standard error of prediction (RMSEP) was calculated for each of the three calibrations applied. The standard error of prediction (SEP) was also calculated. The following gives a list of the mathematical expressions used in this study.

**RMSEP** = $\sqrt{(\Sigma e_i^2/n)}$, where $e_i$ = prediction errors
**SEP** = $\sqrt{[\Sigma(e_i - \text{bias})^2/(n-1)]}$
**Bias** = $\Sigma e_i/n$
**$S_r$ (Repeatability)** = $\sqrt{[\Sigma(a_{j,i} - \bar{a}_j)^2/(n-1)]}$, where $a_{j,i}$ is the result of the i'th replicate of the j'th sample and $\bar{a}$ j is the average

## 9.4 Results and Discussion

The calibration set comprised 108 samples after five extreme outliers had been discarded, with N concentration ranging from 1.4% to 5.5% with a mean of 3.6%.

The validation set comprised 51 samples with N concentrations ranging from 2.0% to 5.2%, with a mean of 3.5%. Both of these sets represented a range of plant types typical of samples submitted to *Celentis Analytical* (Table 9.1). Two samples (grape and peony) were omitted, as they were not adequately represented in the calibration set and seemed atypical when compared with other plant types.

**Table 9.1.** Distribution of plant types within the calibration and validation sets.

| **Plant type** | **No. of samples** | |
|---|---|---|
| | **Calibration** | **Validation** |
| Asparagus | 3 | 1 |
| Avocado | 1 | |
| Barley | 1 | 1 |
| Brassica | 2 | 1 |
| Calla lily | 1 | |
| Cereal | | 1 |
| Chicory | 1 | |
| Clover | 3 | |
| Grape | 1 | |
| Grass | 9 | 7 |
| Kiwifruit | 6 | 4 |
| Lucerne | 2 | |
| Mixed pasture | 71 | 30 |
| Red clover | 1 | |
| Ryegrass | 2 | 1 |
| Walnut | 1 | |
| Wheat | 3 | 5 |
| Total samples | 108 | 51 |

For the validation samples, the $S_r$ (repeatability) of %N by the Kjeldahl method was 0.13%. You would therefore expect the accuracy of the NIR predictions to be no better than 0.13%.

Calibrations obtained on all three machines performed consistently, giving a standard error of cross validation (SECV) of 0.20%. As a rule of thumb, in NIR the SECVs are at best, approximately twice that of wet chemistry ($S_r$).

Presented in Table 9.2 are RMSEPs for each instrument used to measure validation samples. Validation samples measured on the two instruments, other than the one used to build the calibration, show only slightly-increased RMSEP, compared to samples measured on the same instrument. The bias corrected results (SEP) is presented in Table 9.3. It shows marked improvement for some results. This indicates that there is a bias difference between instruments.

It is thus possible to apply a calibration generated on one instrument to another for the purpose of estimating %N in plant material, keeping accuracy within acceptable limits. This can be further improved if a bias is applied. This methodology could be applied to other analytes measurable using NIR. In particular, it can be applied to analyses that are expensive or require a large number of samples to be taken.

**Table 9.2** Root mean standard errors of prediction (RMSEP) for the calibrations

| **Calibration Built on:** | **Samples measured on:** | | |
|---|---|---|---|
| | **KES01** | **KES02** | **KES03** |
| KES01 | 0.24 | 0.27 | 0.35 |
| KES02 | 0.22 | 0.24 | 0.24 |
| KES03 | 0.24 | 0.35 | 0.18 |

**Table 9.3.** Standard errors of prediction (SEP) for the calibration with bias correction.

| Calibration Built on: | **Samples measured on:** | | |
|---|---|---|---|
| | **KES01** | **KES02** | **KES03** |
| KES01 | 0.24 | 0.22 | 0.23 |
| KES02 | 0.27 | 0.24 | 0.26 |
| KES03 | 0.25 | 0.25 | 0.19 |

## 9.5 Conclusions and Implications

The results demonstrate proof of transportable calibration for the chosen NIR instrument. With a bias correction the accuracy of the predictions can be further improved (transferable calibration).

The Plant N calibration is transferable and it is likely this would apply to other calibration models for other constituents.

## 9.6 References

Brimmer, P. 2004. Global trends in process technologies. Proceedings: Foss Directions, Perth, Australia. 21-23 April.

# Chapter 10: Thesis Conclusion & Appendix

*Contents*

## 10.1 Thesis Conclusion and Further Research

### Conclusion

This study found that NIR could not determine pH, Olsen P, sulphate-S, available K, Mg, Ca and Na and nitrate-N from a direct soil scan for New Zealand soils. A rapid sample preparation method/complexing ('signal enhancement') of field-moist or dried soils for the measurement of Olsen P and available K prior to presenting to the NIR could enable accurate measurements. The study also found that pH could be rapidly and accurately measured after a 10-minute extraction on field-moist or dried soils using a pH meter. The accuracy of pH mesurements using NIR was improved when compared to direct soil scans when the soil solution was complexed by an indicator and presented to the NIR. The 'signal enhancement' method was patented.

This study showed that plant moisture, N, nitrate-N and Ca in dry and wet plant material could be measured with a high degree of accuracy by NIR. NIR did not have the desired accuracy for the other major elements P, S, Mg and K. In order to carry out tests on wet plant material a patented procedure using $CO_2$ to determine parameters in wet plant was developed. This study also showed that transfereable calibrations was possible with the KESNIR instruments for the measurement of plant N.

Also as part of this thesis a study using soils from throughout New Zealand was used to develop a soil nitrogen test for New Zealand pastoral soils. The study found that inorganic-N in the soil drives pasture production, N content in grass can be used to accurately predict N responses to fertiliser application and there is always a response to N application. Using multivariate analysis, 81% of the variation was accounted for when dry matter yield was correlated against inorganic-N soil TN, and Anion Storage Capacity (ASC). Soil TN, ASC and plant N can be accurately and rapidly measured using NIR.

The sulphur status of New Zealand pastoral soils is currently determined by measuring sulphate-S or easily mineralisable organic-S. This study outlines the problems associated with the current S tests and shows that soil TS may be a more robust measure of the S status of New Zealand pastoral soils.

### Further Research

This study has shown that transfereable NIR calibrations for plant N using the KES diode array instrument is possible but further work is necessary to determine if transfereable calibration is also possible for other tests.

Another area of research that can be further investigated is a routine soil N test. This thesis has shown that using a glass house trial a routine soil nitrogen test may be possible. In order for a routine test to be accepted it must be field calibrated. Therefore field trials around NZ will need to be conducted.

The sulphate-S test has been shown to be variable when sampled anually. The total soil S test has shown to be a good indicator of pasture response to S applications and more robust than the sulphate test. A measure of the total soil S variability in the field will need to be established for NZ soils.

## 10.2 Glossary

| | |
|---|---|
| **Accuracy** | Refers to how close an average measurement is to the accepted value of the sample. In the case of NIR, how close is the NIR result relative to the wet chemistry (the reference test) for the measured analyte. |
| **Chemometrics** | Performing calculations on measurements of chemical data, primarily spectra. |
| **Coefficient of Variation** | A relative measure of dispersion found by expressing the standard deviation as a percentage of the arithmetic mean. |
| **Monochromator** | Is used to transfer nominal regions of wavelengths out of the continuous light source. |
| **Multiplicate Scatter Correction (MSC)** | Attempts to remove the effects of scattering by linearizing each spectrum to an 'ideal' spectrum. It does this by averaging all spectrum in the calibration set to get the ideal spectrum |
| **Neural networks** | Is a modelling technique (software, uses Fuzzy logic). Data sets with known results are presented to neural networks, which learns from experience and builds on this. Neural network is then able to predict unknowns. |

| | |
|---|---|
| **Precision** | Refers to the repeatability of many measurements on the same sample. How close are the values in relation to each other if measured a number of times? A measurement device can have excellent precision but poor accuracy and vice versa. ***The ideal measurement device will have both good accuracy and precision.*** |
| **Transferable calibration** | A calibration developed on an instrument which needs linear transformation on the predicted parameter to be used on other instruments to predict samples. |
| **Transportable calibration** | A calibration developed on an instrument, which can then be immediately used on other instruments to predict samples. |
| **Repeatability** | Mean standard deviation of multiple measurements using the same instrumentation, operator and conditions. |
| **Robust Calibration** | The robust calibration is the ultimate goal of a chemometrian. A calibration which covers all variation for the analtye in the sample matrix studied. The calibration should not be sensitive to season, subtle temp or methodology change. |
| **R-squared ($R^2$)** | Referred to as the proportion of explained variation, is a useful summary for any linear model. R squared is the relative predictive power of a model. R squared is a descriptive measure between 0 and 1. The closer it is to one, the better your model is |

### 10.2.1 List of Abbreviations and Symbols

| | |
|---|---|
| **CLS** | Classical least squares |
| **FT** | Fourier transform |
| **IR** | Infrared |
| **MSC** | Multiplicative scatter (or signal) correction |
| **NIR** | Near infrared |
| **PCA** | Principal component analysis |
| **PCR** | Principal component regression |
| **$r^2$** | Coefficient of determination |

| | |
|---|---|
| **RMSEP** | Root mean square error of prediction |
| **RMSECV** | Root mean square error of cross validation |
| **SEC** | Standard error of calibration |
| **SEP** | Standard error of prediction |
| **S/N** | Signal-to-noise ratio |
| **SNV** | Standard normal variate |
| **Sr** | Repeatability |
| **SSE** | Sum of squared errors |
| **UV/VIS** | Ultraviolet/visible |

## Equations

***Yk*** = the known concentration
***Yp*** = predicted concentration
***n*** = the number of samples in the training/validation set
***f*** = the number of factors in the model.

Bias

$$Bias = \frac{\sum_{i=1}^{n} (Yk_i - Yp_i)}{n}$$

**PRESS** – Prediction Residual Error Sum of Squares

$$PRESS = \sum_{i=1}^{n} (Yk_i \ Yp_i)^2$$

**RMSD** – Root Mean Squared Deviation

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n} (Yk_i - Yp_i)^2}{n}}$$

**RMSEP/RMSECV** – Standard Error of Prediction/Standard Error of Cross Validation

$$SECV = SEP = \sqrt{\frac{\sum_{i=1}^{n} (Yk_i - Yp_i)^2}{n}}$$

**SEC/SEE** – Standard Error of Calibration

$$SEC = \sqrt{\frac{\sum_{i=1}^{n} (Yk_i - Yp_i)^2}{n}}$$

**$S_r$ (Repeatability)** = $\sqrt{[\Sigma(a_{j,i} - \bar{a}_j)^2/(n-1)]}$, where $a_{j,i}$ is the result of the i'th replicate of the j'th sample and $\bar{a}$ j is the average

## 10.3 Poster Paper

### Evaluation of Soil analysis using Near Infrared for New Zealand

Gordon Rajendram, Geoff Mercer, Kevin Taukiri, Robert Burlingh-Claridge and Per Hansen

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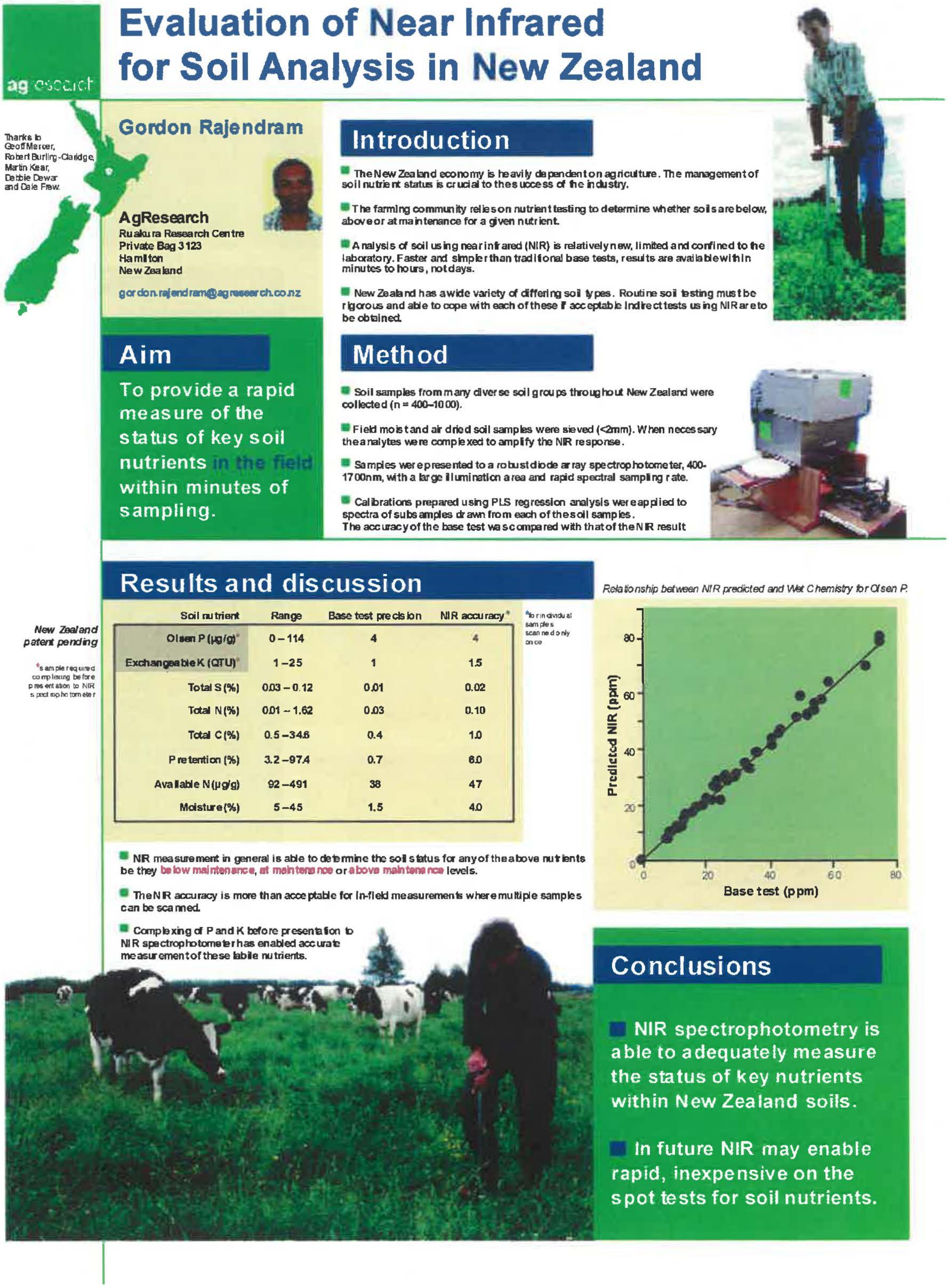
The use of Near Infrared (NIR) for soil testing is relatively new, with soil testing applications only investigated in the last 2 decades. Literature reviews show that most studies to date have limited themselves to a limited number of soil groups or soil types. Many of these studies used only a small number of samples in the calibrations.

Due to these limitations better correlations have been reported than would be achieved in practice for routine soil testing. In practice routine soil testing would need to incorporate factors, such as soil groups, to ensure that the appropriate calibration is used for a particular soil test.

NIR technology has the potential to make routine soil testing significantly faster, cheaper, and simpler than it is currently. In addition to simplifying current testing programs, the availability of reliable NIR methods is likely to increase the total number of samples that can be analysed.

AgResearch is New Zealand's largest crown research institute, concentrating on pastoral and agricultural areas of research. AgResearch has developed NIR calibrations and test methodologies for measuring feed quality. These tests are now offered commercially. AgResearch is now investigating the use of NIR for soil testing purposes. To enable the use of NIR in New Zealand for the purposes of soil testing calibrations must encompass the wide variety of soil groups found in the country.

NIR measurements must at least be able to determine the soil status for key nutrients, be they below maintenance, at maintenance or above maintenance levels. Initial work showed that NIR spectroscopy is able to adequately measure the status of key nutrients within New Zealand soils. Ongoing work has enabled robust calibrations with NIR accuracy similar to that obtained with wet chemistry.



# Evaluation of Near Infrared for Soil Analysis in New Zealand

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Thanks to
Geoff Mercer,
Robert Burling-Claridge,
Martin Kear,
Debbie Dewar
and Dale Frew.

## Aim

To provide a rapid measure of the status of key soil nutrients in the field within minutes of sampling.

## Introduction

- The New Zealand economy is heavily dependent on agriculture. The management of soil nutrient status is crucial to the success of the industry.
- The farming community relies on nutrient testing to determine whether soils are below, above or at maintenance for a given nutrient.
- Analysis of soil using near infrared (NIR) is relatively new, limited and confined to the laboratory. Faster and simpler than traditional base tests, results are available within minutes to hours, not days.
- New Zealand has a wide variety of differing soil types. Routine soil testing must be rigorous and able to cope with each of these if acceptable indirect tests using NIR are to be obtained.

## Method

- Soil samples from many diverse soil groups throughout New Zealand were collected (n = 400–1000).
- Field moist and air dried soil samples were sieved (<2mm). When necessary the analytes were complexed to amplify the NIR response.
- Samples were presented to a robust diode array spectrophotometer, 400-1700nm, with a large illumination area and rapid spectral sampling rate.
- Calibrations prepared using PLS regression analysis were applied to spectra of subsamples drawn from each of the soil samples.
The accuracy of the base test was compared with that of the NIR result

## Results and discussion

*New Zealand patent pending*

| Soil nutrient | Range | Base test precision | NIR accuracy* |
|---|---|---|---|
| Olsen P (µg/g)* | 0 – 114 | 4 | 4 |
| Exchangeable K (QTU)* | 1 – 25 | 1 | 1.5 |
| Total S (%) | 0.03 – 0.12 | 0.01 | 0.02 |
| Total N (%) | 0.01 – 1.62 | 0.03 | 0.10 |
| Total C (%) | 0.5 – 34.6 | 0.4 | 1.0 |
| P retention (%) | 3.2 – 97.4 | 0.7 | 6.0 |
| Available N (µg/g) | 92 – 491 | 38 | 47 |
| Moisture (%) | 5 – 45 | 1.5 | 4.0 |

*sample required complexing before presentation to NIR spectrophotometer

*for individual samples scanned only once

- NIR measurement in general is able to determine the soil status for any of the above nutrients be they below maintenance, at maintenance or above maintenance levels.
- The NIR accuracy is more than acceptable for in-field measurements where multiple samples can be scanned.
- Complexing of P and K before presentation to NIR spectrophotometer has enabled accurate measurement of these labile nutrients.

*Relationship between NIR predicted and Wet Chemistry for Olsen P.*

## Conclusions

- NIR spectrophotometry is able to adequately measure the status of key nutrients within New Zealand soils.
- In future NIR may enable rapid, inexpensive on the spot tests for soil nutrients.

agresearch

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# The Olsen P test: should it be on a volume or weight basis?

## Aim

Currently Olsen P is determined by soil volume rather than weight.

To compare results for Olsen P determined by both volume and weight.

## Introduction

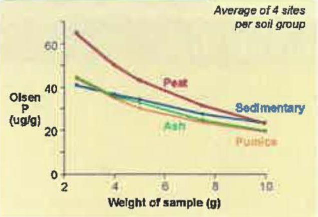
- For convenience, commercial laboratories measure Olsen P on a volume rather than a weight basis. This was justified by the claim that it gives a better idea of plant availability because plants take up P from a volume of soil, rather than a weight.
- This decision was based on a small number of trial sites. These trials were mainly carried out on soils derived from ash and sedimentary material.
- As a consequence in field trials conducted by MAF, the corresponding Olsen P measurements made by the Soil Fertility Service were measured on a volume basis.
- However, field experiments produced different relationships between Olsen P and pasture production for the major soil groups. This is reflected in the recommendations.

## Method

- Soil samples derived from volcanic ash, sediments, pumice and peat were used for this study.
- Olsen P was determined on a weight (µg/g; 5 g:100 ml) and volume basis (µg/ml; 5 ml:100 ml) for 100 soil samples with a range of Olsen P values.
- Olsen P was determined for 16 soils using weights of 2.5, 4.0, 5.0, 7.5 and 10.0 grams of each soil extracted with 100 ml 0.5 M $NaHCO_3$.

## Results and discussion

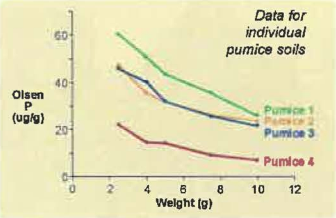
- Olsen P values influenced by soil weight.
- This effect differs with soil group.
- The ratio of soil to solution and the buffering capacity of the soil are critical to the amount of P extracted.
- Olsen P is not a defined or fixed pool. Its size depends on conditions of measurement.


*Average of 4 sites per soil group*

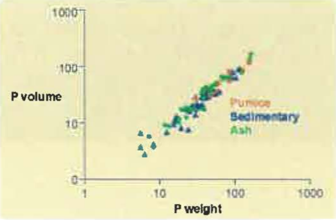
- The current method does not take into account the real dilution factor. The current "Quick Test" Olsen P method for recommendation purposes assumes a bulk density or weight/volume of 0.9, which is not the case for many soils.

| Soil group | Number | Weight/volume (range) | Weight/volume (median) |
|---|---|---|---|
| Peat | 6 | 0.46 – 0.75 | 0.58 |
| Pumice | 12 | 0.65 – 0.93 | 0.70 |
| Sedimentary | 50 | 0.75 – 1.63 | 0.84 |
| Ash | 32 | 0.50 – 0.93 | 0.67 |

- Olsen P increases with decreasing soil to solution ratio (decreasing B.D.).


*Data for individual pumice soils*

- Relationship between Olsen P determined volume (standard quick test procedure) and by weight.
- The relationship: $\log_e(\text{Pvol}) = -1.7 + \log_e(\text{Pwt}) + 0.0057\ \text{ASC} + 0.895\ \text{B.D.}$ accounts for 96% of the variation.



## Conclusions

- All soils are not treated on a level playing field currently for Olsen P.
- The need for different relationships for different soil groups in the recommendations for Olsen P by volume suggests the assumption that P availability is related to volume rather than weight may be wrong.
- Recommendations may be simplified and not be soil group dependent, and other factors such as ASC may also help to simplify recommendations.

# Use of NIR spectroscopy to determine major elements in wet and dry plant

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## Aim:

Evaluate the measurement of moisture and major elements using NIR in wet and dry plant material.

## Introduction

- Plant testing in agriculture is used as a means of monitoring nutrient deficiencies and imbalances to ensure maximum or sustainable crop/pasture production.
- Plant analysis are invariably carried out using wet chemical digestion techniques, followed by analysis of each specific target element in the digest solution using the appropriate instrumental method of analysis.
- It would be ideal for the New Zealand agricultural industry if a rapid non destructive technique such as NIR could accurately predict elemental concentrations in plant material.
- Literature suggests that NIR can indirectly measure the major elements because of their association with organic molecules such as chlorophyll.
- Literature suggests calibrations could accurately predict the major elements N, P, K, Ca and Mg if individual species calibrations were developed.
- Can NIR measure these elements if many species are included in the calibration?

## Method

### *Sample preparation and presentation*

- Measurements of major elements in plants were evaluated using a KES diode array NIR spectrometer.
- Plant samples were scanned over a 15-month period on one instrument. In total 276 samples comprising 27 species were scanned in a wet state and later when dried.
- A sample preparation procedure for field-moist plant samples was developed using carbon dioxide ($CO_2$) freezing. The procedure takes 2 minutes prior to NIR determination. The finely chopped sample is poured into a 145 mm diameter Petri dish and scanned.
- Samples were then oven-dried overnight at 65 °C then further ground to pass a 2-mm mesh sieve. The ground samples were also poured into a 145 mm diameter Petri dish and scanned.

*Carbon dioxide freezing method – frozen sample being shattered in a food processor.*

*Resulting 'shattered' (effectively finely chopped) wet plant sample in a Petri dish.*

*Processed sample presented to the KES NIR instrument.*

Compound preparation patent: patent number WO 2004/008109

### *Wet chemistry*

- Plant N was determined using a semi micro Kjeldahl method.
- The analysis of P, S, Mg, Ca, K, were determined using a nitric/perchloric ($HNO_3/HClO_4$) acid digestion procedure and then determined using ICP-OES.

### *Calibration development*

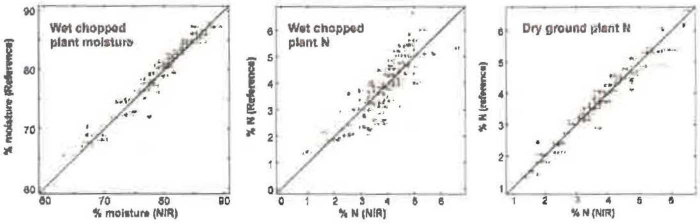
- After initial processing, samples were scanned using a KES NIR.
- Sample spectra were used to build calibrations for moisture, N, P, K, S, Mg and Ca using PLS.
- After initial processing, samples were scanned using a KES NIR diode array spectrometer.

## Results

### *Performance of the calibrations*

| Parameter | State | Range | Wet chemistry repeatability | RMSEP | NIR repeatability |
|---|---|---|---|---|---|
| Moisture (%) | wet | 60-88 | 0.26 | 1.3 | 0.6 |
| N (%) | wet | 1.3-6.8 | 0.13 | 0.51 | 0.13 |
| | dry | 1.4-6.7 | 0.13 | 0.25 | 0.09 |
| Ca (%) | dry | 0.1 - 3.2 | | 0.3 | 0.07 |

*Graphs of the validation set*



## Conclusion :

- Calibrations developed for Mg, S, K and P on dry and wet plant were not satisfactory.
- Calibration developed for moisture and N on dry and wet plant was accurately predicted using NIR.
- Calibrations developed for Ca on dry plant showed promise.

agresearch Farming, Food and Health. First

## 10.4 Patents

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
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(81) **Designated States** *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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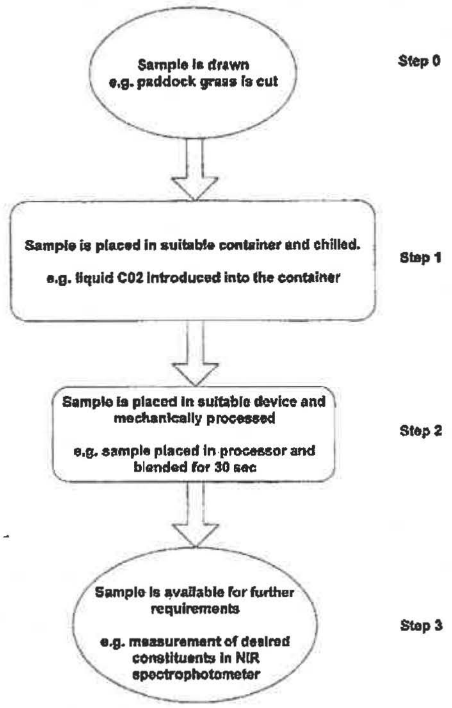
*[Continued on next page]*

(54) **Title:** SAMPLE PREPARATION METHOD INCLUDING COOLING AND CUTTING



(57) **Abstract:** The present invention relates to the provision of a compound preparation method and apparatus which can be used to prepare a compound or sample for a further analytical or reactive process. Preferably the present invention may be adapted to cool the compound in question to increase its rigidity and to subsequently allow for the mechanical processing of the compound to render it into a plurality of particles or components of substantially the same size.

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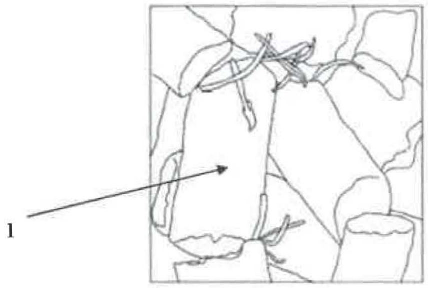

Figure 1

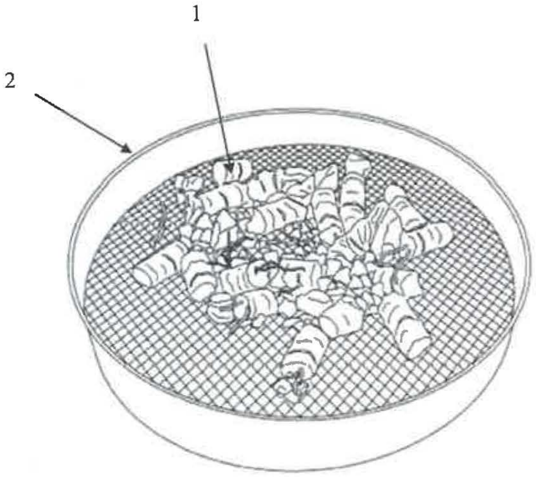

Figure 2.

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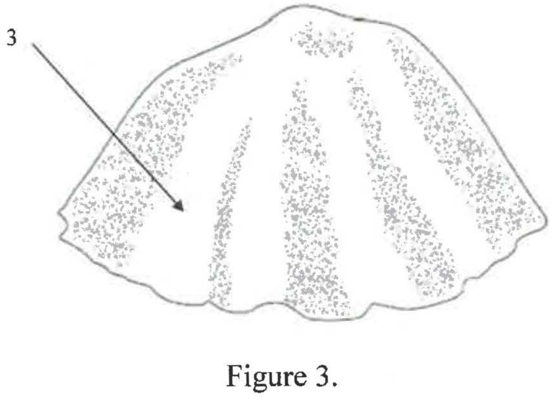
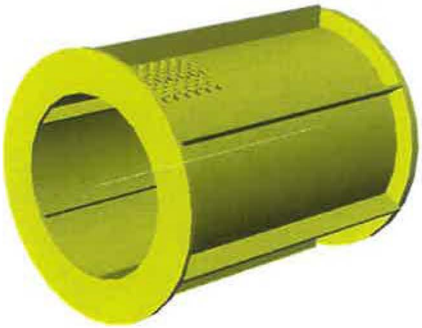
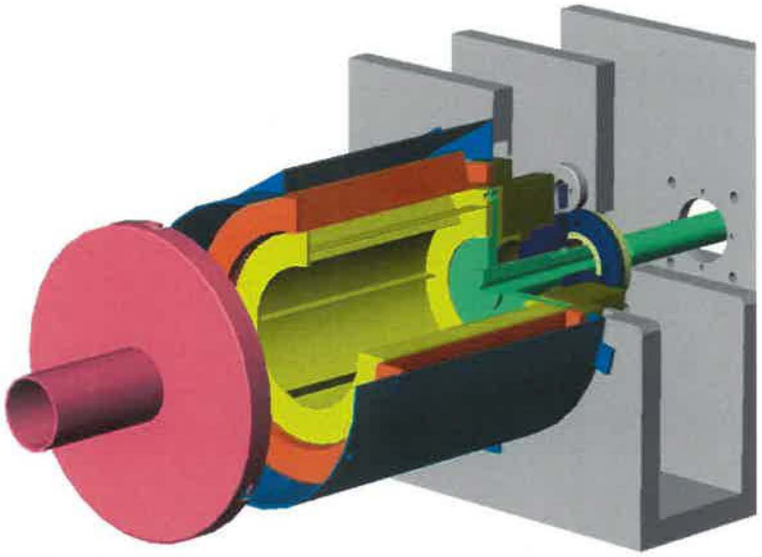


Figure 3.

2 mm outer sieve



4 mm inner sieve



Sectional view of the counter rotating soil dryer

Diagram shows prototype of drying equipment developed.

**WO 2004/008109 A1**

SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

# SAMPLE PREPARATION METHOD INCLUDING COOLING AND CUTTING

## TECHNICAL FIELD

This invention relates to a method of preparing a compound. Preferably the compound involved may be prepared for subsequent analysis of its components. However, in other embodiments, such compounds may be prepared with a view to providing a reactant for other processes. The present invention may preferably allow a compound to be rendered into a plurality of substantially homogenous sized particles.

## BACKGROUND ART

Some types of chemical analysis equipment require a sample for analysis to be supplied as a number of substantially homogenous particles. Furthermore, some types of chemical reactions can also require one of the reactant compounds involved again to be supplied as a plurality of particles of substantially the same size.

An existing technique used to prepare such samples or compounds employs a grinding procedure. If the compound involved is wet or composed of organic tissue, it will need to be thoroughly dried prior to grinding. Drying the sample prior to breaking it up ensures that it can be ground effectively from a large component element. The drying process involved can take some time as the sample is made up of relatively large component portions.

The need to grind thoroughly and also dry such compounds makes the preparation method employed relatively slow. Having to both dry and also grind a compound is both slow and relatively laborious work.

Furthermore, as the compound preparation time increases, so do the chances of the compound being exposed to some form of contaminant, or alternatively degrading with age.

This type of preparation work normally must also be completed within a laboratory environment. This again puts some limitations on the utility of such preparation methods, which cannot be employed out in the field where (for example) a sample has been freshly collected.

One application where an improved method of compound preparation would provide advantages is in the use of near infra-red (NIR) spectrophotometers. These devices can detect the presence and also the concentration of a wide range of analytes or compounds within a properly prepared sample. In addition, the analytes, which can be targeted by NIR spectrophotometers, encompass a wide range of compounds present in organic tissues, and as such, a preparation method which could quickly prepare an organic sample for analysis would be of advantage.

An improved method of preparing a compound which addressed any or all of the above issues would be of advantage. A method which could render a compound into a plurality of substantially homogenous size particles quickly without the need for expensive or complicated equipment, or a laboratory environment, would be of advantage.

All references, including any patents or patent applications cited in this specification are hereby incorporated by reference. No admission is made that any reference constitutes prior art. The discussion of the references states what their authors assert, and the applicants reserve the right to challenge the accuracy and pertinency of the cited documents. It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents form part of the common general knowledge in the art, in New Zealand or in any other country.

It is acknowledged that the term 'comprise' may, under varying jurisdictions, be attributed with either an exclusive or an inclusive meaning. For the purpose of this specification, and unless otherwise noted, the term 'comprise' shall have an inclusive meaning - i.e. that it will be taken to mean an inclusion of not only the listed components it directly references, but also other non-specified components or elements. This rationale will also be used when the term 'comprised' or 'comprising' is used in relation to one or more steps in a method or process.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

## DISCLOSURE OF INVENTION

According to one aspect of the present invention there is provided a compound preparation method characterised by the steps of:

(i) cooling the compound to increase its rigidity, and

(ii) mechanically processing the compound to render the compound into a plurality of particles or components of substantially the same size.

According to a further aspect of the present invention there is provided a compound preparation method characterised by the steps of:

(i) cooling the compound to increase its rigidity, and

(ii) mechanically processing the compound to render same into a plurality of particles or components of substantially the same size, and

(iii) subjecting the rendered compound to an analysis and/or reaction process.

According to a further aspect of the present invention there is provided a method of preparing a compound substantially as described above, wherein a compound is prepared to provide a sample for an analysis procedure.

According to yet another aspect of the present invention there is provided a method of preparing a compound substantially as described above, wherein the compound is cooled with liquid carbon dioxide.

According to a further aspect of the present invention there is provided a method of preparing a compound substantially as described above, wherein the compound is mechanically processed by at least one rotating blade.

According to yet another aspect of the present invention there is provided a compound preparation method substantially as described above, wherein the rendered or processed compound is analysed using a near infra-red spectrophotometer.

According to yet another aspect of the present invention there is provided a compound preparation method substantially as described above wherein the compound is composed of or formed from plant tissue.

According to a further aspect of the present invention there is provided a compound preparation apparatus which includes a cooling means adapted to cool the compound to increase its rigidity, and a mechanical processing means adapted to mechanically process a compound to render the compound into a plurality of components of substantially the same size.

The present invention relates to an improved method of preparing a compound. Any number and range of different types of compounds may be prepared using the present invention depending on the particular application which it is employed within. However, it is envisioned that the preparation method discussed below could primarily be used to prepare a small volume or weight of compounds or samples.

Those skilled in the art should appreciate that after preparation the compound involved may be subjected to various further processing, analysis or reactions depending on the application which the present invention is used within.

Reference throughout this specification will also be made to the present invention being used to provide a sample preparation method where the sample involved is to be analysed to investigate its constituent components. The present invention may provide a preparation method which can allow a sample compound to be rendered into a plurality of distinct particles that are substantially the same size. However, those skilled in the art should appreciate that other applications are also envisioned for the present invention and reference to the above only throughout this specification should in no way be seen as limiting. For example, in one alternative embodiment, the present invention may be used to prepare a compound to be reacted with other materials.

In a further preferred embodiment the compound to be prepared may be organic in nature, such as plant or animal tissue. Organic materials normally contain a high moisture content, and as such sample preparation time is relatively long using prior art preparation methods. However, through use of the present invention the time required to prepare such samples can be substantially reduced.

Reference throughout this specification will also be made to a sample prepared in accordance with the present invention being plant tissue. However, those skilled in the art should appreciate that other types of compounds or organic materials may also be prepared using the present invention, and reference to the above only throughout this specification should in no way be seen as limiting.

In a preferred embodiment the present invention may be used to prepare a sample for analysis by a near infra-red spectrophotometer. Near infra-red (NIR) spectrophotometers can detect the presence and also concentration of a wide variety of analytes, including those commonly found and of interest within organic materials such as plant tissue.

Preferably the first step employed in the method of the present invention is to cool the sample or compound to be prepared, thereby increasing its physical rigidity. The temperature of the compound may be lowered significantly, which in some instances will freeze the compound solid.

In a further preferred embodiment a sample may be exposed to a cooling agent to achieve the cooling effect required. Such a cooling agent may be a further compound which can be intimately exposed to a sample to cool same. Preferably a cooling means may be provided to facilitate or execute this operation.

For example, in a preferred embodiment a cooling means, agent or material may be provided through the use of liquefied carbon dioxide. A sample may be dipped or immersed in liquefied carbon dioxide to rapidly reduce its temperature and therefore substantially increase its physical rigidity. The time required for the cooling to be completed is relatively short with liquefied carbon dioxide, therefore providing a relatively short sample preparation time.

However, in alternative embodiments other means for cooling a sample may be employed. For example, in one alternative embodiment a sample may be immersed or dipped into liquid nitrogen, again to provide the cooling effect required. In yet another alternative embodiment a sample may be cooled using freeze drying equipment to again quickly reduce the temperature and increase the rigidity of the compound or sample.

Reference throughout this specification will however be made to a sample initially being cooled through immersion in liquefied carbon dioxide. However, those skilled in the art should appreciate that other types of cooling agents or equipment may also be employed and reference to the above only throughout this specification should in no way be seen as limiting.

Preferably after a sample has been cooled and its physical rigidity increased, it may then be subjected to a mechanical processing step. This mechanical processing can be used to render the sample into a plurality of particles or components which have substantially the same size. This in effect will homogenise the sample rendering it into a collection of particles or component pieces with a substantially uniform nature. The actual end product or final form of the rendered sample will be determined by the degree of mechanical processing employed in addition to the moisture content of the sample. Preferably a mechanical processing means may be used to facilitate or execute the operation required.

In a further preferred embodiment a mechanical processing means may include a rotating blade. The cooled sample or compound may be placed within a container which also houses a blade adapted to be driven in a circular motion. When activated, the blade will make a large number of cuts through the material of the sample which has been temporarily stiffened through the cooling step discussed above. The rotating blade employed can then shatter the relatively rigid sample to render same into a plurality of particles or portions of substantially the same size. Varying sizes of samples or compounds may also be processed depending on the capacity of the equipment used.

In a preferred embodiment, the mechanical processing means may be provided with a housing within which the compound to be processed is retained during use.

In a further preferred embodiment, the processing means housing may be substantially conical in shape with the active components used to cut, grind, pulverise or otherwise mechanically process the compound in question being located substantially at the bottom of this conical shaped housing. The use of this particular shape or type of housing ensures that any parts of the compound being process which are thrown upwards during the processing operation will be encouraged to fall directly back down into the active components of the processing means.

Reference throughout this specification will also be made to a sample or compound being mechanically processed through use of a rotating blade substantially as described above. However, those skilled in the art should appreciate that other types of mechanical processing systems may also be employed and reference to the above only throughout this specification should in no way be seen as limiting.

For example, in one alternative embodiment a mechanical processing means may be provided through a system or apparatus adapted to grind or pulverise a compound. In such an embodiment one or more grinding plates or weights may move over a surface with the compound to be processed trapped between same.

In a preferred embodiment the housing of the mechanical processing means may also be reinforced to withstand forces applied by relatively high pressure air, fluids or gases employed in conjunction with the present invention. For example, in one preferred embodiment the mechanical processing means housing may be reinforced to withstand pressures of up to 1.5 atmospheres to allow high pressure or high velocity fluids or gases to be introduced into the interior of the processing means if required.

In a preferred embodiment, the mechanical processing means may include one, two or more sets of pairs of opposed blades orientated substantially horizontally with respect to the housing of the processing means. One, two or more sets of opposed blade pairs may also be located on a central drive axis or axle adapted to rotate these blades when the processing means is used.

In a further preferred embodiment, the processing means may include two pairs of opposed blades, with only one pair disposed directly above the other. This combination of four distinct blades may be drive by a single common drive shaft to rotate in a substantially horizontal plane within the interior of the processing means housing.

Reference throughout this specification will also be made to the processing means including two paired sets of opposed blades substantially as described above. However, those skilled in the art should appreciate that other configurations of the processing means are envisioned and reference to the above only throughout this specification should in no way be seen as limiting.

In one further preferred embodiment of the present invention the processing means may also include a grinding mechanism in addition to one, two or more rotating blades. In such an embodiment a grinding mechanism may be located substantially within the base of the processing means housing so that once a compound has been rendered into a number of relatively small components, these components will in turn fall into the grinding means to be rendered into yet smaller components or particles. For example, in one embodiment a grinding means may be formed from a flat base to the housing in addition to a rotating semicircular weight which is disposed below a mesh grating or screen. Only particles or material of a size smaller than the apertures in the grating will be capable of falling into the interior of the grinding means and thereby be pulverised or ground further.

In a further preferred embodiment, the present invention may also include a flushing means. A flushing means may be adapted to flush out gas present within the mechanical processing means after a sample has been effectively homogenised and processed. The case of a preferred embodiment where a source of liquefied carbon dioxide is employed as a cooling means, the flushing means may be used to remove excess carbon dioxide from within the processing means and thereby ready the processed sample or compound for presentation to a further process or reaction.

In a further preferred embodiment, a flushing means may consist of or include a fan and/or a heating element. A fan may be employed to force pressurised atmospheric air into the interior of the processing means thereby flush excess carbon dioxide out from this region. Furthermore, the flushing means may also incorporate a heater element which can heat air driven into the interior of the processing means. Heated air will again heat the sample or compound further and liberate additional carbon dioxide from the interior of the processing means.

In a further preferred embodiment, the flushing means may also be used in some instances to further dry the compound or sample present within the processing means after homogenisation. The application of heated air into this region can be used to further dry an originally 'wet' sample if required depending on the next analytical process involved. In such instances, a stream of heated air may be supplied from the flushing means over a period of several minutes to dry the material of the processing means if required.

The present invention may provide many potential advantages over the prior art.

The combination of a cooling phase and mechanical processing phase allows a sample to be rendered into a plurality of substantially homogenous small particles which contain essentially the same moisture content as the sample at the start of the processing method. The moisture content already present within the sample allows analytes of interest to in effect remain "in solution", ready for presentation to the NIR spectrophotometer or other similar instrument.

Eliminating the need for drying further simplifies and speeds up the sample or compound preparation method provided. After mechanical rendering has been completed, a sample may then be directly presented to a spectrophotometer.

The present invention may also be used to quickly, easily and inexpensively prepare numerous different types of compounds for subsequent analysis or further reactions with other compounds. The present invention can be used to break up a compound into a large number of small, even or homogenous particles relatively quickly for use in a large number of applications.

Furthermore, the equipment or apparatus employed in conjunction with the present invention is readily portable and can be used in the field at sample or compound collection sites, to immediately prepare a sample for further analysis or reaction. This reduces the chances of the sample becoming contaminated through long periods of storage or handling and also reduces the chances of the sample degrading over time.

The use of liquefied carbon dioxide in preferred embodiments also allows a sample or compound to be cooled rapidly and effectively. Liquefied carbon dioxide is a relatively inexpensive cooling material and is safer for operators to handle than liquid nitrogen at lower temperatures. Furthermore, the use of carbon dioxide is preferable where a sample to be prepared is to be analysed for its nitrogen content. In addition, carbon dioxide being higher temperature than liquid nitrogen will extend the lifespan of the equipment used in conjunction with the present invention. As the carbon dioxide employed is of a higher temperature, it degrades the equipment used slower than liquid nitrogen.

The provision in some embodiments of a flushing means can also allow excess carbon dioxide or other types of cooling agents to be flushed from the interior of the processing means employed. Furthermore, the provision of a source of heat within such a flushing means also allows the homogenised sample or compound to be dried easily and quickly when preferably in a particulate form.

## BRIEF DESCRIPTION OF DRAWINGS

Further aspects of the present invention will become apparent from the following description which is given by way of example only and with reference to the accompanying drawings in which:

| | |
|---|---|
| Figure 1 | illustrates a block schematic diagram of the processes executed by a method of preparation in accordance with a preferred embodiment of the present invention; |
| Figure 2 | illustrates a block schematic diagram of apparatus and components employed to provide a compound processing apparatus in accordance with an alternative embodiment of the present invention. |

## BEST MODES FOR CARRYING OUT THE INVENTION

Figure 1 illustrates a block schematic diagram of the steps executed in a method of preparation provided in accordance with a preferred embodiment.

In the instance discussed, the present invention is adapted to prepare a plant tissue sample for subsequent analysis by a near infra-red spectrophotometer.

The sample to be prepared is initially drawn in Step 0. For example, in a preferred instance a grass sample is cut from a paddock to provide the sample required.

In the schematic diagram shown, Step 1 is implemented to cool the sample provided and therefore increase its rigidity. Preferably this step is executed through immersing the sample in a container of liquefied carbon dioxide. This will snap-freeze the vegetative sample, substantially increasing the rigidity of the vegetative material, while also preserving the moisture content present within the vegetation.

After the sample has been retrieved from the carbon dioxide it is then presented to a mechanical processing means at Step 2 of the methodology executed. The processing means with an associated set of rotating blades can be used to cut up and mechanically render the snap frozen vegetative sample into a plurality of distinct and substantially homogenised particles. A large number of relatively small particles of substantially the same size may be provided through this action. The increased rigidity of the frozen vegetation allows the rotating blades to shatter and cut the vegetation into a collection of small particles.

Once the cooling and subsequent mechanical processing Steps 1 and 2 are completed, the processed sample can be presented to a NIR spectrophotometer at Step 3. The sample can be directly presented to the spectrophotometer after mechanical processing Step 2. Through preserving the moisture content of the sample during the processing method executed, analytes of interest remain free for a spectrophotometer to detect same without a solvent being applied or used.

Figure 2 shows a compound preparation apparatus (1) as configured in accordance with an alternative embodiment of the present invention to that discussed with respect to figure 1. The apparatus (1) includes a cooling means (2), composed in the embodiment shown from a bottle of liquefied carbon dioxide (2a) linked to a supply line and solenoid valve (2b). The operation of the solenoid valve is controlled in turn by a control box (2c) which includes a number of user operable switches.

The cooling means (2) is adapted to supply liquefied carbon dioxide on demand into the interior of a mechanical processing means (3), shown in this embodiment as being provided with a pair of rotating blades.

The compound or sample to be processed is first placed within the interior of the processing means. Initially a stream of liquefied carbon dioxide is supplied from the cooling means to immerse the sample and subsequently increase its rigidity. After the sample has been immersed and frozen, the blades of the processing means are rotated to shatter and chop the sample into a large number of relatively small homogenous particles.

At this stage, the last component shown, being a flushing means (4) is activated. The flushing means includes a fan based component and an associated heater (not shown) both of which are adapted to supply heated air into the interior of the processing means (3). This heated air will drive excess carbon dioxide out of the sample and potentially also dry the now homogenised particular sample compound.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof as defined in the appended claims.

**CLAIMS:**

1. A compound preparation method characterised by the steps of:

   (i) cooling the compound to increase its rigidity, and

   (ii) mechanically processing the compound to render the compound into a plurality of particles or components of substantially the same size.

2. A compound preparation method as claimed in claim 1, further characterised by the additional subsequent step of

   (iii) subjecting the rendered compound to an analysis and/or reaction process.

3. A compound preparation method as claimed in claim 2, wherein the compound is prepared prior to an analysis process used to investigate the compounds constituent components.

4. A compound preparation method as claimed in claim 3 wherein the compound is analysed using a near infra-red spectrophotometer.

5. A compound preparation method as claimed in any previous claim wherein the compound is cooled using a cooling agent.

6. A compound preparation method as claimed in claim 5 wherein the compound is immersed in the cooling agent to cool the compound and increase the compounds rigidity.

7. A compound preparation method as claimed in any previous claim wherein the compound is cooled using liquid carbon dioxide.

8. A compound preparation method as claimed in any previous claim wherein mechanical processing of the compound homogenises the compound.

9. A compound preparation method as claimed in any one of claims 1 to 7 wherein the mechanical processing of the compound renders the compound into a plurality of distinct particles of substantially the same size.

10. A compound preparation method as claimed in any previous claim wherein the compound is mechanically processed using at least one rotating blade.

11. A compound preparation method as claimed in any previous claim wherein the compound is an organic compound.

12. A compound preparation method as claimed in claim 11 where the compound is formed from or includes plant tissue.

13. A compound preparation apparatus which includes a cooling means adapted to cool the compound to increase the compounds rigidity, and a mechanical processing means adapted to mechanically process the compound to render the compound into a plurality of components of substantially the same size.

14. A compound preparation apparatus as claimed in claim 13 wherein the cooling means is adapted to supply a cooling agent to cool the compound and increase the compound's rigidity.

15. A compound preparation apparatus as claimed in claim 14 wherein the cooling means includes a source of liquefied carbon dioxide.

16. A compound preparation apparatus as claimed in any one of claims 13 to 15 wherein the mechanical processing means includes at least one blade adapted to rotate to mechanically process a compound.

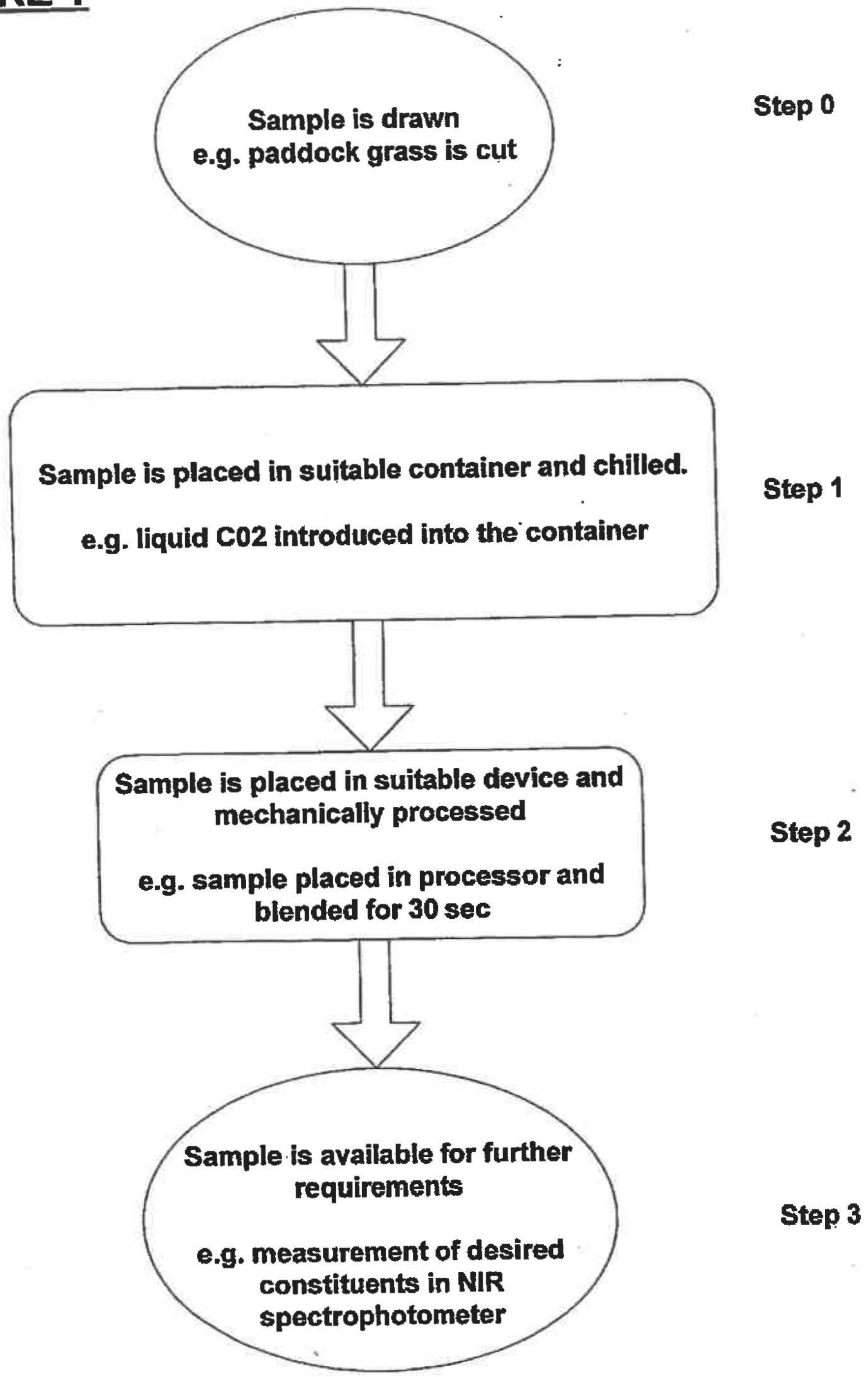
17. A compound preparation apparatus as claimed in any one of claims 13 to 16 which includes a flushing means adapted to flush gas from within the mechanical processing means.

18. A compound preparation apparatus as claimed in claim 17 wherein the flushing means includes at least one fan and/or heating element combination.

19. A method of preparing a compound substantially as herein described with reference to and as illustrated by the accompanying drawings and/or examples.

20. A compound preparation apparatus substantially as herein described with reference to and as illustrated by the accompanying drawings and/or examples.

**FIGURE 1**


Sample is drawn
e.g. paddock grass is cut
Step 0
Sample is placed in suitable container and chilled.
e.g. liquid C02 introduced into the container
Step 1
Sample is placed in suitable device and mechanically processed
e.g. sample placed in processor and blended for 30 sec
Step 2
Sample is available for further requirements
e.g. measurement of desired constituents in NIR spectrophotometer
Step 3

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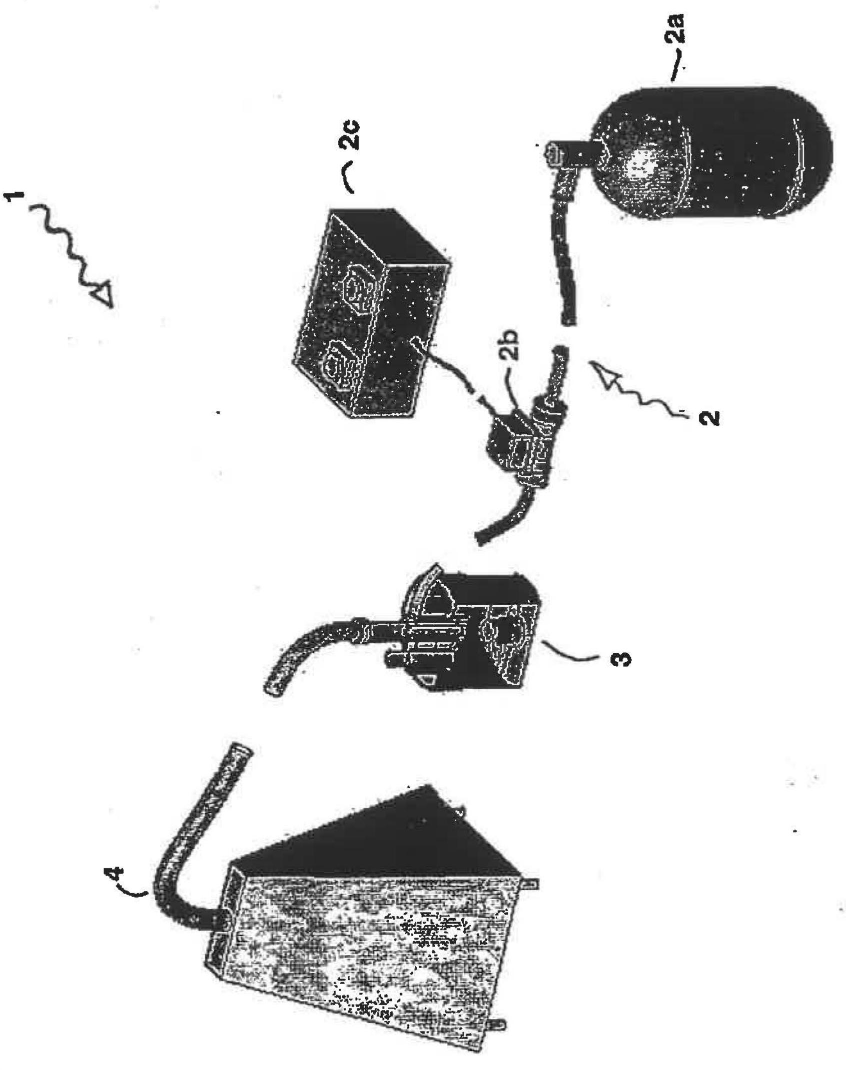

FIGURE 2

2/2

**PATENTS FORM NO. 4**
Appln Fee: $50.00
James & Wells ref: 31337

## PATENTS ACT 1953
## PROVISIONAL SPECIFICATION

## A METHOD FOR THE PREPARATION OF SOIL SAMPLES

WE AGRESEARCH LIMITED, a New Zealand Company of East Street, Ruakura Campus, Hamilton, New Zealand.
do hereby declare this invention to be described in the following statement:

## A METHOD FOR THE PREPARATION OF SOIL SAMPLES

### TECHNICAL FIELD

This invention is related to a preparation and extraction method for use in analysing elements within the soil.

### BACKGROUND ART

The current soil testing practice, for determining key nutrient levels in the soil for making fertiliser recommendations, are carried out in Laboratories using dried and ground soils.

Soil cores collected are in the field then couriered to labs where they are dried overnight (for at least 20 hours) at temperatures of 30 –35 degrees Celsius. The following day the samples are ground and passed through a 2mm sieve, at which point the samples are then ready for chemical or physical analysis.

The drawback of the above practice is that it is least 2 days before chemical analysis can commence. In addition another 2-3 days are required for chemical analysis and reporting. This equates to an average of 5 – 7 days before a farmer or advisor receives the laboratory result from the time of sampling.

There are currently no testing methods available which allow for a soil sample to obtained and then tested on site so that a farmer or advisor may receive the results within a short space of time. Any testing method that did achieve this would therefore allow for appropriate recommendations, with regard to application of fertiliser, to be made on the same day the soil sample was obtained.

The following soil nutrients are currently tested routinely by Laboratories: Olsen P (phosphate), sulphate, pH and the four cations (Potassium (K), Sodium (Na), Calcium(Ca) and Magnesium (Mg)). The most widely used and valuable of these tests are Olsen P, K and pH in terms of fertilizer recommendations.

In the Laboratory, potassium (K) is normally extracted from soil using 1.0M Ammonium Acetate (Helmke & Sparks 1996). The K in extracts is then measured using either flame spectrophotometer, Atomic absorption spectrometer or Inductively Coupled AES spectrometry.

Phosphorus (P) in the form of phosphate (Olsen P) is measured using a modified method of Olsen (Olsen *et al* 1954). The soil is extracted for 30 minutes using 0.5M $NaHCO_3$ using an end over end shaker. The phosphorus in the extractant is then determined by complexing the phosphate with Molybdate, otherwise known as the Murphy and Riley method (Murphy & Riley 1962; Watanabe & Olsen 1965). The concentration of the complex is determined with UV/Vis spectrometry at a wavelength of 880 nm.

The equipment currently required for testing both phosphorus and potassium is expensive and can only be operated in a laboratory environment and are carried out on dired soil samples. This would therefore not allow for field testing or prompt laboratory testing of samples via this method.

Soil pH is usually measured using a pH meter with a soil to water ratio being 1:2. Currently, soil samples are left overnight in the water before the samples can be read. Therefore, direct measurement of pH on site is currently not possible.

Analysis of labile elements extracted from soil samples can not normally be performed directly by NIR or UV/Vis spectroscopy as these spectrophotometers can not detect labile elements when in their native form.

However, as NIRS can provide results of analyses within minutes and are more reliable and faster to calibrate than standard research spectrophotometers it would be beneficial if a method of soil preparation could be developed so that NIRS could analyse labile elements. It may also be of use to develop soil preparation methods for use with UV/Vis spectrophotometers due to the fact there are currently portable versions available which could be used in the field.

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It is acknowledged that the term 'comprise' may, under varying jurisdictions, be attributed with either an exclusive or an inclusive meaning. For the purpose of this specification, and unless otherwise noted, the term 'comprise' shall have an inclusive meaning - i.e. that it will be taken to mean an inclusion of not only the listed components it directly references, but also other non-specified components or elements. This rationale will also be used when the term 'comprised' or 'comprising' is used in relation to one or more steps in a method or process.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

## SUMMARY OF INVENTION

The present invention relates to a rapid sample preparation method of field moist or dried soils for the measurement of Phosphate, Potassium and pH using Near Infrared (NIR) and/or UV/Vis Spectroscopy

## DISCLOSURE OF INVENTION

According to one aspect of the present invention there is provided a method for the preparation of a soil sample for analysis, said analysis investigating the elements contained within said sample, the method of preparation including the steps of:

a) solubilising compounds within the sample by adding an aqueous solution to the sample; and

b) adding a complexing agent to the sample.

According to another aspect of the present invention there is provided a method for the preparation of a soil sample for analysis, said analysis investigating the elements contained within said sample, the method of preparation including the steps of:

a) solubilising compounds from the sample by adding an aqueous solution to the sample;

b) separating the aqueous phase of the mixture obtained in step a above; and

c) adding a complexing agent to the aqueous phase.

According to another aspect of the present invention there is provided a method for the preparation of a soil sample for analysis, said analysis investigating the elements, excluding phosphorus, contained within said sample, the method of preparation including the steps of:

a) solubilising compounds from the sample by adding an aqueous solution to the sample;

b) separating the aqueous phase of the mixture obtained in step a above; and

c) adding a complexing agent to the aqueous phase.

According to another aspect of the present invention there is provided a method for the preparation of a soil sample for analysis, said analysis investigating the elements contained within said sample, the method of preparation including the steps of:

a) drying the soil sample;

b) solubilising compounds from the sample by adding an aqueous solution to the sample;

c) separating the aqueous phase of the mixture obtained in step b above; and

d) adding a complexing agent to the aqueous phase.

According to a further aspect of the present invention there is provided a method for the preparation of a soil sample substantially as described above wherein the analysis required is completed using UV/Vis spectroscopy.

According to a further aspect of the present invention there is provided a method for the preparation of a soil sample substantially as described above wherein the analysis required is completed using NIR spectroscopy.

According to a further aspect of the present invention there is provided a method of preparation of a soil sample substantially as described above wherein the sample is analysed for hydrogen content to determine pH.

According to a further aspect of the present invention there is provided a soil extract prepared to allow for elements within a soil sample to be analysed wherein the extract includes a complexing agent adapted to complex elements in the soil.

The term "complexing agent" as used herein refers to a compound which is capable of complexing or chelating an element such that the element is reversibly bound to the compound.

The term "UV/Vis" as used herein refers to the ultra violet to visible light range.

The term "sample" as use herein refers to at least one, but preferably several cores taken from the area or region of soil to be tested.

Generally, the analysis carried out will determine the amount or concentration of an element within a sample by measuring the element in its ionic form.

Generally the analysis will determine the concentration of the elements extracted from the soil sample. However, other aspects of the elements present within the soil could also equally be measured.

In one preferred embodiment the concentration of hydrogen ions is determined so that soil pH may be calculated.

Generally the soil samples are prepared for the analysis of labile elements within the soil. However, this should not be seen as limiting the scope of the present invention.

Labile elements to be analysed may be selected from the following: Phosphorus, Nitrogen, Potassium, Sodium, Calcium, Magnesium, Sulphur, and Hydrogen.

In preferred embodiments the elements that are analysed may be Phosphorus, Potassium and/or Hydrogen.

Generally, when Phosphorus is measured it may be measured in the form of Phosphate ions.

The extract may be prepared using a variety of aqueous solutions without departing from the scope of the present invention.

Generally, the aqueous solution may be selected from the group comprising; Sodium bicarbonate, Sodium chloride, Caesium chloride or water.

In one preferred embodiment the aqueous solution may be Sodium bicarbonate.

In another preferred embodiment the aqueous solution may be water.

Generally the aqueous phase may be separated from the solid soil matter prior to the complexing agent being added to the remaining solution. However, in some embodiments the complexing agent may be added directly to the aqueous solution and soil mixture and be measured with the solid soil matter remaining in the sample which is analysed.

The aqueous phase may be separated from the solid matter of the sample by a variety of different methods without departing from the scope of the present invention.

In one preferred embodiment the aqueous phase may be separated by filtration.

In another embodiment the aqueous phase may be separated by centrifugation.

A variety of complexing agents may be used with the soil extracts without departing from the scope of the present invention.

Generally the complexing agent is a binding or chelating compound which specifically binds to the elements being analysed.

In some embodiments the complexing agent may form a precipitate when bound in to the element(s) the soil extract.

In other embodiments the complexing agent may be capable of changing colour when bound to the element(s) in the soil extract.

In preferred embodiments the complexing agent may be selected from: Sodium tetraphenylborate (NaTPB), Ammonium Molybdate, Ascorbic acid, EDTA, Resazurin or any other chelating agents for example; NTA, DTPA, HEDTA, PDTA and EDDHA.

Generally the extract is prepared using field moist soil samples. However, this should not be seen as limiting the present invention as dried soil samples may also be prepared for analysis using the method of the present invention.

Generally, the complexed extracts are analysed via NIR however, this should not be seen as limiting the present invention.

Thus, preferred embodiments of the present invention may provide one or more of the following advantages over the prior art:

a) providing a method to allow for on site testing;

b) reducing the time required in soil sample preparation before a sample may be analysed;

c) providing a method that can be used to analyse field moist samples; and

d) using a complexing agent in the sample preparation so that NIR may be used to measure labile elements which were previously considered as undetectable by NIR.

## BRIEF DESCRIPTION OF DRAWINGS

Further aspects of the present invention will become apparent from the following description which is given by way of example only and with reference to the accompanying drawings in which:

| | |
|---|---|
| Figure 1 | A flow chart outlining the general procedure for rapid extraction and measurement of Olsen P and Potassium; |
| Figure 2 | A flow chart outlining the general procedure for rapid extraction and measurement of pH; and |
| Figure 3 | Graph showing the Relationship between NIR predicted and Wet chemistry for Olsen P |

## BEST MODES FOR CARRYING OUT THE INVENTION

## EXPERIMENTAL

Non-limiting examples illustrating the invention will now be provided. It will be appreciated that the below description is provided by way of example only and variations in materials and technique used which are known to those skilled in the art are contemplated.

*Soil sampling.*

Soil samples are obtained by using a standard 20 or 25mm diameter corer of either 7.5 or 15cm in length depending on whether the area where the sample is taken from is to be used for agricultural or horticultural purposes respectively. Each sample will normally contain 15-20 cores.

*Sample preparation.*

Each sample is placed onto a tray and is dried in a vented oven at 30-35 °C for 24 – 72 hours. When field moist samples are tested the drying process is omitted.

The samples are then individually passed through a 2mm sieve and the ground soil sample is collected.

*Extraction method*

Five grams of soil as prepared above is added to 100ml of 0.5M $NaHCO3$ (pH 8.5) and stirred on using a magnetic stirrer for 10minutes. The extract is filtered from the solid soil matter by a Whatman 42 filter paper.

*Decolourisation of the extract*

Decolourisation of the extracts is currently required when $NaHCO3$ is used as the extractant. However, if other extractant solutions, such as NaCl are used then decolourisation of the extract is not required.

The extract is decolourised either by the addition of a small amount of charcoal (approximately 1-2g) which is then separated from the extract by filtration. Alternatively the extract could be passed through a charcoal filter.

*Complexation*

**Phosphate**

The complexation of phosphate is via Ammonium Molybdate as outlined in the Murphy Riley Method (Murphy & Riley 1962; Watanabe & Olsen 1965).

A 1400µl aliquot of the filtrate is then mixed with 800µl of the Murphy Riley Reagent and 150µl of Sulphuric acid (5N) and made up to a final volume of 10mls with distilled water. The final mixture is left to mix and allow for the colour to develop for 20 minutes.

**Potassium**

The complexation of Potassium is via Sodium Tetraphenylborate (NaTPB). A solution containing 50mls of water, 3.25g NaTPB and 2 mls of NaOH (1M) is prepared. The quantity of 1.0 ml of the above solution is added to the soil extract.

*Measurement of samples via NIR Spectrophotometer*

The complexed sample is then placed into a 100ml petri-dish and placed in the NIR spectrophotometer. The NIR simultaneously scans the sample from 400-1700nm. The results from the NIR data are calculated by Galactic Grams/32 PLS Software.

*Discussion*

The ability to complex samples prior to NIR measurements has enabled accurate determinations of the nutrients P and K, and pH. An example is given for Olsen P (Figure 3) in illustrating the prediction accuracy of the method. Calibration coefficient where $R^2 = 0.97$ has been obtained for the K method (data not shown).

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof.

AGRESEARCH LIMITED

by its Attorneys

**JAMES & WELLS**

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**PATENTS FORM NO. 4**
Appln Fee: $50.00
James & Wells ref: 42480/29

## PATENTS ACT 1953
## PROVISIONAL SPECIFICATION

## RAPID SOIL DRYING

We, AGRESEARCH LIMITED, a New Zealand Company of East Street, Ruakura Campus, Hamilton, New Zealand do hereby declare this invention to be described in the following statement:

James & Wells Ref: 42480/29

## RAPID SOIL DRYING

### TECHNICAL FIELD

This invention is related to rapid soil drying. The present invention discloses a method and device that can be used prior to the measurement of chemical and physical properties within soil.

### BACKGROUND ART

Soil testing is a common occurrence for a variety of industries including farming. In farming, it is desirable to know the levels of various soil constituents such as potassium, magnesium, sodium, calcium, phosphorus and sulphur so that, for example fertiliser is applied at correct concentration and frequency. Other testing applications include soil testing of constructions sites, industrial sites such as chemical processing facilities and mining sites, for example to determine if contamination has occurred from chemicals or heavy metals.

Current testing practice for determining key nutrient levels in soil is carried out in laboratories where samples are prepared for analysis. It is a standard to firstly prepare the soil sample via drying or moisture removal. By removing moisture from the soil sample, the sample becomes more stable and key constituents are less likely to alter over time. Changes that may occur include mineralisation of some nutrients and soil pH changes. Traditionally, samples are dried to a point where there is minimal residual moisture – i.e. if the sample was re-dried, there would be no detectable loss in weight.

At present, soil cores are collected in the field and then transported to laboratories where they are kept intact and dried overnight (for at least 20 hours) at temperatures of 30 –35 °C. The following day the samples are ground and passed through a 2mm sieve, at which point the samples are then ready for chemical or physical analysis.

Alternative methods of drying such as freeze drying and microwave drying are not generally used in standard laboratory testing. Both of these alternative methods are comparatively expensive and require specialised equipment.

The soil cores are intact plugs of soil approximately 2.5 x 7.5 cm (agricultural) and 2.5 x 15 cm (horticultural) which are used to determine the nutrient status. The recommendation is that 15 – 20 cores are taken of the area where the nutrient status of the soil is desired.

A key drawback of the above standard soil preparation practice is that at least one day is lost before chemical analysis can commence.

A further disadvantage of present practice is that samples must be transported to a remote site i.e. the laboratory. Besides the extra cost of transport, this additional step introduces possible contamination of the samples e.g. through mishandling of the samples or exposure to heat or moisture during transportation.

It is therefore highly advantageous if soils can be dried rapidly, without compromising chemical and physical test results so that test results can be obtained more quickly.

It is an object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

All references, including any patents or patent applications cited in this specification are hereby incorporated by reference. No admission is made that any reference constitutes prior art. The discussion of the references states what their authors assert, and the applicants reserve the right to challenge the accuracy and pertinency of the cited documents. It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents form part of the common general knowledge in the art, in New Zealand or in any other country.

It is acknowledged that the term 'comprise' may, under varying jurisdictions, be attributed with either an exclusive or an inclusive meaning. For the purpose of this specification, and unless otherwise noted, the term 'comprise' shall have an inclusive meaning - i.e. that it will be taken to mean an inclusion of not only the listed components it directly references, but also other non-specified components or elements. This rationale will also be used when the term 'comprised' or 'comprising' is used in relation to one or more steps in a method or process.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

## DISCLOSURE OF INVENTION

According to one aspect of the present invention there is provided a method for drying soil including the steps of:

(a) increasing the surface area of the soil;

(b) forcing a substantially inert gas through the soil;

(c) subjecting the soil to an elevated temperature.

The present invention relates to a method of drying soil in a manner that removes moisture from the soil, whilst also substantially not altering chemical and/or physical characteristics of the soil, other than removal of moisture (water).

In one embodiment, steps (a) to (c) as described above may be performed sequentially. In alternate embodiments, steps (a) and (b), (b) and (c), (a) and (c), or (a), (b) and (c) may be performed at substantially the same time.

In preferred embodiments, the speed of drying may be substantially more rapid when compared to prior art methods (i.e. less than 24 hours). It has been found by the inventor that the speed of drying may be reduced to less than substantially one hour. More preferably, the speed for drying may be less than substantially 20 minutes. Those skilled in the art should appreciate that the rate of drying may be dependent on the soil type. It is the inventor's experience that clay soils tend to take the longest to dry whereas sandy soils are by comparison, quicker to dry.

The present invention can be used in relation to soils taken from a wide variety of sites. In preferred embodiments, the soil may be a sample taken from arable land. In other embodiments, soil may be taken from construction sites, forestry sites, or industrial manufacturing facilities. This list should not however be seen as limiting.

It should be appreciated by those skilled in the art that the drying method may be performed at the test site (in-situ) or in a laboratory or other testing facility.

It is envisaged that the present invention is robust enough that it may be used for all varieties of soil types. The fact that the present invention removes moisture rapidly from the sample without substantially altering the chemical and/or physical characteristics of the soil is a critical factor in laboratory analysis where the sample, when measured, must still be representative of the area from which the sample was taken. Characteristics of particular note that the soil sample should remain representative of, with respect to the site where the sample was taken, may include the level of phosphorus (or Olsen P), sulphur, heavy metals, potassium, magnesium, sodium and calcium and other elements or compounds that are routinely required to be analysed. Further characteristics in relation which the sample should remain representative of the original site, include the degree of elasticity of the soil sample or friability / texture properties of the soil generally.

Preferably, the increase in surface area may be achieved by breaking the soil down into smaller particles by mechanical motion, for example by hand, or in a machine, by pressing the soil through a sieve. Most preferably the mean particle size may be substantially less than 10mm, although it should be appreciated that the soil need not be of a uniform particle size. It is the inventor's experience that a reduced particle size increases the speed with which moisture is removed from the soil particles.

In preferred embodiments, the inert gas may be air. Most preferably, the gas may be moisture free. It alternative embodiments, the method may include gas conditioners such as a dehumidifier step and/or use of a desiccating gel to remove moisture from the gas prior or during use in the present invention. Those skilled in the art should appreciate that the use of dry air mimics the effect of wind drying.

Preferably, gas may be forced across the soil particles. In general, the air is fan forced. Most preferably the gas velocity may be less than 4 m/s. Most preferably, the velocity may be approximately 2 m/s.

Preferably, the temperature to which the soil may be elevated is high enough to allow sample drying without impacting on the chemical and/or physical properties of the soil, apart from moisture reduction. In the inventor's experience this temperature may be critical and preferably, the temperature range varies from approximately 20°C to 50°C, although lower temperatures are also envisaged. It is likely that temperatures above approximately 50°C result in not only moisture loss, but also deterioration of the chemical and/or physical structure of the soil. In preferred embodiments, the temperature to which the soil may be elevated varies from approximately 30°C to 40°C. Most preferably the temperature may be substantially 35°C.

In a further embodiment, the drying equipment may be preheated before step (c).

In an alternative embodiment, the method may also include a further step (d) of:

(d) keeping the soil in motion.

Preferably, the particles remain in motion for substantially all of the drying time. In an alternative embodiment, particles may only be kept in motion for a discrete portion of time and/or discrete portions of time.

Methods envisaged by the inventor for keeping the soil in motion may include tossing, vibration, oscillation or shaking the soil in a dish or in a container or containers such as a container or series of containers, either in series or nested within each other

According to a further aspect of the present invention there is provided an assembly for drying of soil which includes:

(a) an inert gas supply device which is capable of forcing inert gas through the soil;

(b) a heating element which is capable of subjecting the soil to an elevated temperature.

Preferably the assembly described above further includes a soil crusher device which is capable of increasing the surface area of the soil.

Preferably the assembly described above further includes a device capable of keeping the soil in motion.

According to a further aspect of the present invention there is present the use of a method and/or device substantially has described above for the removal of moisture from a soil sample.

From the above description, those skilled in the art should appreciate that the invention offers a fast alternative to present soil drying methods that allows for faster testing of soil samples. The method includes the steps of increasing particle surface area, forced air circulation and elevated temperature. A device is also described which incorporates the above steps. As the process is quick and the device simple, measurements can be made in situ to avoid complications of transporting the sample to a laboratory.

## BRIEF DESCRIPTION OF DRAWINGS

Further aspects of the present invention will become apparent from the following description which is given by way of example only and with reference to the accompanying drawings in which:

| | |
|---|---|
| Figure 1 | is a drawing of a soil core sample; |
| Figure 2 | is a drawing of soil core samples on a sieve; and, |
| Figure 3 | is a drawing of a sub-sample from the core samples. |

## BEST MODES FOR CARRYING OUT THE INVENTION

Non-limiting examples illustrating the invention will now be provided. It will be appreciated that the below description is provided by way of example only and variations in materials and technique used which are known to those skilled in the art are contemplated.

In order to determine if there may be a difference in key nutrient results, tests were completed where soils were dried at differing rates. Soil core samples are currently dried at 30-35°C overnight (20 – 24 hours) and control samples using this method of drying were used for comparison.

Soils encompassing many soil groups were collected for analysis. These soils were sieved and mixed thoroughly.

### Example 1:

Referring to Figure 1, core samples 1 of granular soil (clay loam) were received (soil samples 1A and 1B as shown in the table below) and placed into a 2 mm sieve 2 as shown in Figure 2. The soil core samples were broken down and forced through the sieve to reduce the particle surface area. A sub-sample 3 (labelled 1B) was then taken as shown in Figure 3 which was then placed into a soil dryer of the present invention (not shown) and dried at 35°C, with air flow and particle motion for 20 minutes. A further sub-sample (1A) was taken and placed into a traditional dryer and dried overnight at 35° as per standard technique. Further samples 1C and 1D were also taken and dried at 48°C, with air flow and particle motion for 20 minutes and 15 minutes respectively.

Before drying, the moisture content of each sample was measured as having a moisture content of 32.1% wt.

After the times defined above, the samples were measured for phosphorus levels (Olsen P). Phosphorus tests were chosen as phosphorus this is a very important agronomical test for pastoral farming as phosphate fertiliser incurs the majority of the cost of fertilisation, particularly in New Zealand farming.

The moisture content after drying in the case of sample 1A, the traditional method, was 0.0%wt. For samples 1B, 1C and 1D, the residual moisture contents were 2.2%wt, 0.2%wt and 0.0%wt respectively.

Olsen phosphorus (P) levels after drying were measured in duplicate and shown in **Table 1** below.

**Table 1**: Olsen P Levels Example 1

| Soil Sample | Olsen P – Test 1 | Olsen P – Test 2 |
|---|---|---|
| 1A | 45 | 45 |
| 1B | 45 | 46 |
| 1C | 51 | 54 |
| 1D | 47 | 50 |

**Example 2:**

The same soil type as Example 1 was tested using different samples and the same method as described in Example 1 with soil samples 1 labelled 2A (traditional drying at 35°C overnight), 2B (35°C, with air flow and particle motion for 20 minutes) and 2C and 2D (48°C, with air flow and particle motion for 20 and 15 minutes respectively).

Before drying, the moisture content of each sample was measured as having a moisture content of 31.1% wt.

The moisture content after drying in the case of sample 2A, the traditional method, was 0.0%wt. For samples 2B, 2C and 2D, the residual moisture content was 3.7%wt, 0.0%wt and 0.2%wt respectively.

Olsen phosphorus (P) levels after drying were measured in duplicate and shown in **Table 2** below.

**Table 2**: Olsen P Levels Example 2

| Soil Sample | Olsen P – Test 1 | Olsen P – Test 2 |
|---|---|---|
| 2A | 20 | 22 |
| 2B | 20 | 21 |
| 2C | 23 | 22 |
| 2D | 23 | 24 |

**Example 3:**

The same soil type as Example 1 was tested using different samples and the same method as described in Example 1 with soil samples 1 labelled 3A (traditional drying at 35°C overnight), 3B (35°C, with air flow and particle motion for 20 minutes), and 3C and 3D (48°C, with air flow and particle motion for 20 and 15 minutes respectively).

Before drying, the moisture content of each sample was measured as having a moisture content of 31.1% wt.

The moisture content after drying in the case of sample 2A, the traditional method, was 0.0%wt. For samples 3B, 3C and 3D, the residual moisture content was 7.4%wt, 0.4%wt and 2.4%wt respectively.

Olsen phosphorus (P) levels after drying were measured in duplicate and shown in **Table 3** below.

**Table 3**: Olsen P Levels Example 3

| Soil Sample | Olsen P – Test 1 | Olsen P – Test 2 |
|---|---|---|
| 3A | 25 | 25 |
| 3B | 25 | 28 |
| 3C | 33 | 34 |
| 3D | 35 | 36 |

**Example 4:**

Different soil types were tested, gley soil (silt loam), using the same method as described in Example 1 with soil samples 1 labelled 4A (traditional drying at 35°C overnight), 4B (35°C, with air flow and particle motion for 20 minutes) , and 4C and 4D (48°C, with air flow and particle motion for 20 and 15 minutes respectively)..

Before drying, the moisture content of each sample was measured as having a moisture content of 39.5% wt.

The moisture content after drying in the case of sample 4A, the traditional method, was 0.0%wt. For samples 4B, 4C and 4D, the residual moisture content was 8.9%wt, 0.2%wt and 2.8%wt respectively.

Olsen phosphorus (P) levels after drying were measured in duplicate and shown in **Table 4** below.

**Table 4**: Olsen P Levels Example 4

| Soil Sample | Olsen P – Test 1 | Olsen P – Test 2 |
|---|---|---|
| 4A | 13 | 13 |
| 4B | 12 | 12 |
| 4C | 14 | 15 |
| 4D | 14 | 13 |

**Example 5:**

Different soil types were tested, allophanic soil (sandy loam) using the same method as described in Example 1 with soil samples labelled 5A (traditional drying at 35°C overnight), 5B (35°C, with air flow and particle motion for 20 minutes) and 5C and 5D (48°C, with air flow and particle motion for 20 and 15 minutes respectively).

Before drying, the moisture content of each sample was measured as having a moisture content of 30.9% wt.

The moisture content after drying in the case of sample 5A, the traditional method, was 0.0%wt. For samples 5B, 5C and 5D, the residual moisture content was 5.0%wt, 0.0%wt and 0.4%wt respectively.

Olsen phosphorus (P) levels after drying were measured in duplicate and shown in **Table 5** below.

**Table 5**: Olsen P Levels Example 5

| Soil Sample | Olsen P – Test 1 | Olsen P – Test 2 |
|---|---|---|
| 5A | 17 | 18 |
| 5B | 17 | 17 |
| 5C | 21 | 21 |
| 5D | 21 | 25 |

The above examples showed that the two methods of preparation compared well with a statistical analysis showing no significant difference in Olsen P levels using either traditional methods of preparation or rapid drying at 35°C. A variation of up to 16% was noted for rapid drying at 48°C.

The above examples show that the method and device of the present invention may allow soil to be dried faster than conventional methods with a similar degree of accuracy in measurement of chemical and physical characteristics, however taking less time for sample preparation than traditional methods.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof.

AGRESEARCH LIMITED
by their Attorneys
**JAMES & WELLS**

James & Wells Ref: 42480/29

1/2

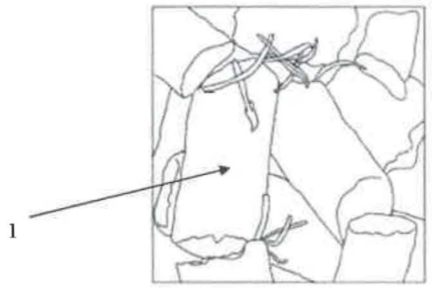


Figure 1

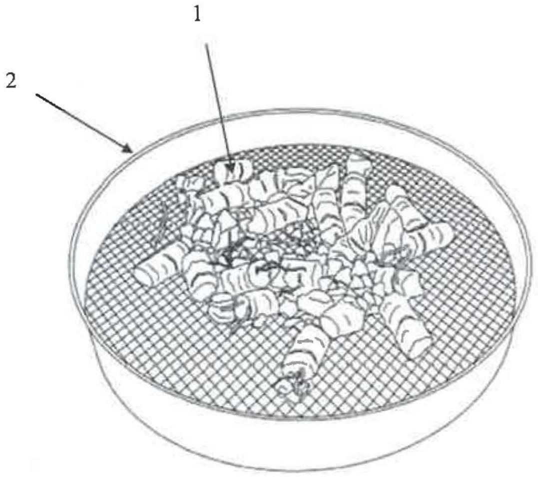


Figure 2.

2/2

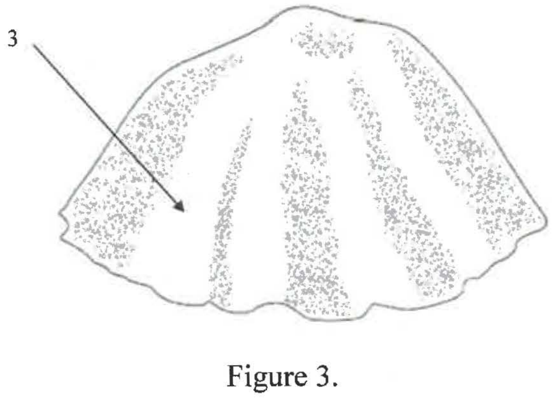
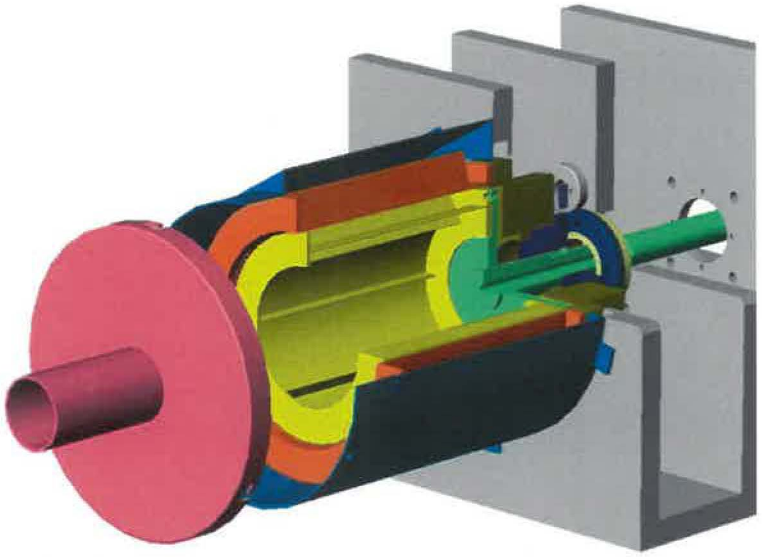


Figure 3.

2 mm outer sieve

4 mm inner sieve



Sectional view of the counter rotating soil dryer

Diagram shows prototype of drying equipment developed.

**PATENTS FORM NO. 4**
Appln Fee: $50.00
James & Wells ref: 42478/20

## PATENTS ACT 1953
## PROVISIONAL SPECIFICATION

# DETERMINATION OF SOIL SULPHUR

We AGRESEARCH LIMITED, a New Zealand company of East Street, Ruakura Campus, Hamilton, New Zealand do hereby declare this invention to be described in the following statement:

## DETERMINATION OF SOIL SULPHUR

### TECHNICAL FIELD

The present invention relates to a determination of the total sulphur content of soils and to a method of determining soil sulphur requirements for plant growth.

### BACKGROUND ART

Sulphur has often been considered a secondary nutrient in respect to the nutrient requirements of plants, however the importance of sulphur varies around the globe and is dependent on soil type, the plant species grown and the sulphur status of the soil.

One of reasons so little work has been done on sulphur relative to other plant nutrients has been the difficulty of measuring sulphur in soils accurately. The development of methods for sulphate-S via ion chromatography and total sulphur (TS) via ICP-AES (discussed below) has increased accuracy. Previous to these methods sulphate-S and sulphur were measured turbidimetrically, which is known to often produce inaccurate results for soils, particularly New Zealand soils.

The amount of total organic sulphur (OS) in soils is soil type-dependent and is related to both the level of organic matter and the amounts of sulphur input. As a general rule soils derived from volcanic ash (Allophanic and Granular soils) have higher organic matter content and organic sulphur levels, relative to soils derived from sedimentary rocks.

The TS in New Zealand pastoral topsoils ranges from approximately 0.01 – 0.25% of which 90-98% is present as organic sulphur (OS) (Perrott and Sarathchandra, 1987). Generally the remainder is present as inorganic forms of sulphur, usually sulphate-S. In most well drained pastoral soils sulphate-S constitutes 1-2 % of TS.

There are a set of two soil sulphur tests used in New Zealand labs today. One of the tests measures the immediately available sulphur ("sulphate-S"). In this test, four grams of soil is extracted with 20 mls of the extractant for 30 minutes using an end over end shaker (Watkinson and Kear, 1996b). The measurement of sulphate-S uses High Pressure Ion chromatography (HPIC) in the extract (Watkinson and Kear, 1994). On the same extractant the second test measures the total extractable sulphur (TES) using Inductively Coupled Plasma Spectrometry (ICPS). The easily mineralisable component of organic-sulphur is determined by difference between ICP measured TES and HPIC sulphate-S. The mineralisable OS is slowly available to pasture over the season and gives an indication of the longer-term sulphur supply of the soil to plants. The test uses 0.02 mol/L $KH_2PO_4$ as the extractant.

The easily mineralised OS is approximately 1-2% of the OS in soil. The easily mineralisable OS (also known as easily extractable organic-S ("EOS")) ranges from approximately 2–30 mg/kg in New Zealand pastoral soils. Soil sulphate-S in New Zealand pastoral soils have a similar concentration range to EOS if it is not influenced by external sources such as fertilisers.

The EOS test was developed to overcome some of the problems associated with the sulphate-S test. The sulphate-S test values are influenced particularly by fertiliser, dung and urine patches (Kear and Watkinson, 2003) and leaching. Leaching studies have showed that invariably sulphate-S concentrations in leachate remained relatively constant at 10 mg $L^{-1}$ over the leaching period from grazed pastures in Waikato with leaching losses of 40 – 70 kg $ha^{-1}$ $yr^{-1}$ sulphur as sulphate-S (Rajendram et al, 1998). Typically sheep/beef and dairy farms apply sulphur in the range of 30-100 kg $ha^{-1}$ $yr^{-1}$. Applied sulphur from fertiliser has no effect on EOS but increases sulphate-S by the amount added.

The amount of sulphur deposited via rainfall at a site is dependent on the distance of the site from the nearest coast. Atmospheric inputs of sulphur via rainfall has been measured at 12 kg ha$^{-1}$ yr$^{-1}$ (near the coast) and 1 kg ha$^{-1}$ yr$^{-1}$ at 99 km inland (Ledgard and Upsdell, 1991). Inputs of 5 and 7 kg ha$^{-1}$ yr$^{-1}$ were found in sites in the Waikato and Taranaki Dairy regions with the sites approximately 35 and 10 km from the coast respectively (Rajendram et.al., 1998 and unpublished data).

The application rates on pastoral soil from urine and dung patches are on average 35 and 100 kg/ha respectively. Urine from dairy cows increases the EOS by about 10 mg/kg but this disappears within a week, whereas sulphate-S increases by about 20 mg/kg and disappears within 2 weeks. Dung from cows increases EOS by about 5 mg/kg but persists for up to 2 years, however sulphate-S increases by about 150 mg/kg initially and introduces an appreciable error for over a year (Watkinson and Kear, 1996b and Kear and Watkinson, 2003). Seasonal changes or leaching events generally have no effect on EOS values but can affect sulphate-S values (Ghani et.al. 1990). The sulphate-S values are generally higher during the summer periods.

Presently in New Zealand the EOS test complements the sulphate-S test for fertiliser decision- making. It is especially relevant on soils with low anion storage capacity (ASC) e.g. pumice, peat and sedimentary derived soils.

Plants take up sulphur as the anion sulphate-S. Annual plant sulphate-S uptake is greater than that measured by sulphate-S in topsoil (0 - 7.5 cm) at any given time. Therefore, as an example, if pastures produces 12 - 15 tonne of dry matter per annum and the average concentration of sulphur in the herbage is 0.30 % (i.e., sulphur is not limiting), the uptake by pasture is 36 - 45 kg ha$^{-1}$ yr$^{-1}$ sulphur. In comparison the soil sulphate concentration of 10 mg/kg in the 0 – 20 cm (average A horizon depth), which gives an adequate sulphate-S to maintain maximum pasture production, supplies plants with only 18 kg ha$^{-1}$ yr$^{-1}$ sulphur. Therefore a large proportion of sulphur, which is taken up by pasture in a season is the result of mineralisation of organic matter.

If sulphur fertiliser in the form of superphoshate is applied at normal rates for pastoral farming, it will overcome any deficiency for approximately one year. Generally if soil sulphur levels are below optimum, maximum production can be achieved if maintenance levels of phosphorus are applied in the form of a superphosphate or it's equivalent. Single super phosphate (SSP) contains approximately 12.5 % sulphur. The amount of sulphur to overcome deficiency for ash, sedimentary and pumice soils is 25, 35 and 45 kg/ha respectively. Sulphur recommendations are designed to eliminate any sulphur deficiency since it is a very cheap fertiliser, for example relative to phosphate. Elemental sulphur is used on sites or soil types where leaching of the mobile sulphate-S can be a problem.

In dairy farms typical application rates are in the range of 500 – 800 kg super phosphate or its equivalent per annum. This is equivalent to 62 – 100 kg of sulphur per annum. On sheep/beef farms the application rates are in the range of 250 – 375 kg super phosphate per annum. This is equivalent to 30 – 47 kg of sulphur per annum.

All references, including any patents or patent applications cited in this specification are hereby incorporated by reference. No admission is made that any reference constitutes prior art. The discussion of the references states what their authors assert, and the applicants reserve the right to challenge the accuracy and pertinency of the cited documents. It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents form part of the common general knowledge in the art, in New Zealand or in any other country.

It is acknowledged that the term 'comprise' may, under varying jurisdictions, be attributed with either an exclusive or an inclusive meaning. For the purpose of this specification, and unless otherwise noted, the term 'comprise' shall have an inclusive meaning - i.e. that it will be taken to mean an inclusion of not only the listed components it directly references, but also other non-specified components or elements. This rationale will also be used when the term 'comprised' or 'comprising' is used in relation to one or more steps in a method or process.

It is an object of the present invention is to provide a single test determining sulphur requirements in soils.

It is a still further object of the present invention to address the foregoing problems or at least to provide the public with a useful choice.

Further aspects and advantages of the present invention will become apparent from the ensuing description which is given by way of example only.

## DISCLOSURE OF INVENTION

According to one aspect of the present invention there is provided a method of determining soil sulphur requirements at a site by:

1. Collecting one or more soil samples from the site,
2. Measuring the total sulphur content (TS) of the or each sample to arrive at a representative value for TS;
3. obtaining a figure for the relative yield of pasture growth; and
4. Using a relationship between TS and relative yield of pasture growth to determine the amount of sulphur to be applied to the site, wherein within the relationship:
    - (i) if the value of the TS content is less than 0.04% of total soil weight, sulphur must be applied;
    - (ii) if the value of the TS content is 0.04 to 0.06% of total soil weight, maintenance levels of sulphur needs to be applied to the site;
    - (iii) if the value of the TS level is 0.06 to 0.08% of total soil weight, sulphur need not be applied if the site is used for general farming applications, but can be for dairying applications;
    - (iv) if the value of the total sulphur level is greater than 0.08% of total soil weight, sulphur is not added.

The relative yield of pasture growth is preferably calculated from the same soil samples or from separate testing of the site. Optimally the relative yield is calculated as the relative amount of pasture grown over a year on the site compared with the amount of pasture on the site over a year with excess sulphur applied.

Optionally, the TS value of each sample is determined by measuring by acid digestion using a mixture of $HNO_3/HClO_4$ followed by determination on ICP using the 1819.05 with off line background correction (Perrott *et.al.*,1991). The measurement of TS is optionally carried out on each sample after being finely ground using a mortar and pestle.

Optionally, the TS for each sample is determined in duplicate and the mean result used as the TS value.

Optionally the EOS value for each sample is evaluated and compared to the TS for each sample.

According to a further aspect of the present invention there is provided a method of determining soil sulphur requirements at a site by:

1. Collecting one or more soil samples from the site,
2. Measuring the Easily extractable Organic Sulphur (EOS) of the or each sample to arrive at a representative value for EOS;
3. Obtaining a figure for the relative yield of pasture growth; and
4. Using a relationship between EOS, total sulphur (TS) and relative yield of pasture growth to determine the amount of sulphur to be applied to the site, wherein within the relationship:
    - (i) if the value of the EOS content is less than 14 mg/kg of total soil weight, sulphur must be applied;
    - (ii) if the value of the EOS content is 14 mg/kg to 20 mg/kg of total soil weight, maintenance levels of sulphur needs to be applied to the site;
    - (iii) if the value of the EOS level is 20 mg/kg to 25 mg/kg of total soil weight, sulphur need not be applied if the site is used for general farming applications, but can be for dairying applications;
    - (iv) if the value of the EOS is greater than 25 mg/kg of total soil weight, sulphur is not added.

According to a further aspect of the present invention there is provided a method of determining soil sulphur requirements at a site by use of sulphate-S tests of levels of sulphate-S in the above described method. However, as discussed above, the sulphate-S test provides the least reliable results.

Studies done by AgResearch on soil testing where data from a number of field trials were combined showed between year coefficients of variability for hill country and flat to rolling land were 37.4 % and 45.8 % respectively for sulphate-S. This suggests a flat site considered to have adequate sulphate-S (10 mg/kg) could the following year have a test result with a 95% confidence interval ranging from 1 – 19. A sulphate-S value of < 10 would indicate deficiency.

The work indicated that sulphate-S was the most variable soil test when compared to other major soil tests. The slightly larger variability found in flat to rolling land when compared to hill country can be attributed to different sampling regimes used.

From a practical point of view when farm advisors/consultants or fertiliser representatives collect samples from farms they try and fit in with the farmers rotation. Invariably the soil samples from the paddock they have collected may have been recently grazed. The standing recommendation for the currently available tests is that soil or plant samples are to be collected just prior to grazing and collected from non-excreta affected areas. However, this pragmatically never happens. If a paddock is regularly sampled every year and if animals were in the paddock 1 week earlier, practically a collector is not going to come back in 2-3 weeks time to collect the sample. It is very difficult if not impossible to distinguish a urine-affected area on recently grazed paddocks i.e. < 3 weeks. Therefore many of these samples will not give a good indication of the sulphur status if sulphate-S (particularly) or EOS (lesser extent) is determined.

Williams et al (1988) calculated that on dairy farms with a stocking rate of 3 cows per hectare, excreta would cover approximately 23% of pasture in 1 year and the area affected by excreta may be at least twice that covered. Advisory recommendations are that a soil sample comprising approximately 15-20 cores be taken from a site or paddock therefore it is expected that 4 of these cores will be affected and give a higher sulphur status than it actually is.

When it was first developed the EOS tested was widely adopted and was used to complement sulphate-S, but now the applicant estimates that EOS is determined on approximately only 10 % of all soil samples submitted for S testing. There are also problems associated with measuring EOS by difference on a routine basis, both instruments need to be working optimally otherwise accuracy is compromised. Because EOS is measured by difference increased laboratory variance for EOS will be expected in theory because it is affected from both the measures it is calculated from. The cost of analysing the two tests is approximately $10 each in New Zealand, with the cost of sulphate-S included in the basic soil test and EOS offered as an extra test. This has therefore led to reduced usage of the EOS test with the majority opting for the measurement of sulphate-S only. Of the two tests EOS is a much better indicator of the sulphur status of New Zealand soils but in order to determine EOS measurements on two different instruments are made with the difference calculated as EOS.

The organic-S component on average for these soils is 97 % of the TS of which EOS consists of on average 3 %. The sulphate-S component consists on average by 3 % of the TS. The Total Sulphur pool, because of its magnitude, is not influenced to the extent that EOS and particularly sulphate-S. Therefore the TS pool is a better measure of the supply of S to NZ pastures than either the EOS or sulphate-S tests. Pot trial studies by Goh and Pamidi showed that soil S taken up by plants after the 8th week period originated directly from the mineralization of soil organic S from S pools other than those present in extractable forms.

The determination of TS via traditional methods is time consuming and expensive as it normally employs a digestion procedure. Advances in new measurement technology such as Total Sulphur Analysers, Near IR and Mid IR enable the measurement of TS to be fast and cheap and therefore be used to accurately predict the sulphur status of New Zealand pastoral soils.

## BRIEF DESCRIPTION OF DRAWINGS

Further aspects of the present invention will become apparent from the following description which is given by way of example only and with reference to the accompanying drawings in which:

Figure 1 is a graph showing the relationship between EOS and RY for the method of the present invention;

Figure 2 is a graph showing the relationship between TS and RY for the method of the present invention, and

Figure 3 is a graph showing the relationship between EOS and TS for the method of the present invention.

## BEST MODES FOR CARRYING OUT THE INVENTION

For this study the same 43 air-dried soils used by Watkinson and workers of AgResearch to develop the two soil sulphur tests in use by New Zealand laboratories were used. The soils were from field trials conducted throughout the country to determine pasture yield responses to S fertiliser application. Sulphur Fertiliser had not been applied to the trial sites for at least one year prior to the commencement of the trial.

The topsoil was taken to a depth of 7.5 cm from control (untreated) plots using standard agricultural soil corers. These cores were taken prior to the commencement of the trial. Sulphur in the form of gypsum was applied in excess of that needed to prevent pasture growth deficiency for one year.

Kear and Watkinson (1991) showed that long-term storage of air-dried soil samples had little affect on sulphate-S and EOS concentrations. EOS was determined by difference between ICP measured TES and HPIC sulphate-S.

TS was measured by acid digestion using a mixture of $HNO_3/HClO_4$ followed by determination on ICP using the 1819.05 with off line background correction (Perrott et al, 1991). The measurement of TS was carried out on the sample after being finely ground using a mortar and pestle.

Both EOS and TS were determined in duplicate and the mean result for each soil was used in the comparison. The Anion storage capacity (ASC) was also measured for each soil.

The relative yield was calculated as the relative amount of pasture grown over that year on the control plots compared with that on plots applied with sulphur. The relative yield (RY) was calculated by the following equation:

$$RY = (100 / (\% \text{ Response} + 100)) \times 100 = 100 \times \text{untreated} / \text{treated}$$

RY was then regressed on TS, EOS and sulphate-S (separately).

**Results**

A summary of results which includes relative yield (RY), mean concentration and concentration range of TS, EOS and sulphate-S for the 43 soils are shown in Table 1. The proportion of EOS and sulphate-S in relation to TS is also given in Table 1.

The range of TS values found were similar in range to those found by Perrott and Sarathchandra (1987) when they studied nutrient and organic matter levels in New Zealand soils under established pasture.

The mean sulphate-S and EOS concentration is very similar for these soils but there is a greater spread or range for sulphate-S (2 –77 mg/kg) in comparison to EOS (5 –32 mg/kg). This indicates that possibly even in a field trial scenario where the trial site was fenced off prior to commencement of the trial that sulphate-S has been influenced to a large extent by previous urine and dung affected areas within the site or possibly from previous fertiliser applications. This is possibly true for 4 or 5 sites out of the 43 used in this trial.

The mean percentage of sulphate-S and EOS concentration in relation to TS is similar at 3%.

The relative standard deviation of the samples analysed in duplicate (precision) of the wet chemistry for EOS is 1.1 mg/kg, S-sulphate is 1.6 mg/kg and for TS is 0.006%.

Table 1.

| | R.Y | TS | EOS | sulphate-S | EOS of TS | sulphate-S of TS |
|---|---|---|---|---|---|---|
| | (%) | (%) | mg/kg | mg/kg | (%) | (%) |
| Mean | 83 | 0.06 | 18 | 17 | 3 | 3 |
| Range | 12 - 102 | 0.01 – 0.11 | 5 - 32 | 2 - 77 | 2 – 5.5 | 1 – 7.5 |

EOS accounted for 58 % of the variation when compared with RY for 43 field trials (Figure 1) and sulphate-S accounted for 59 % of the variation.

TS accounted for 71 % of the variation when compared with Relative yield for 43 field trials (Figure 2). Using ASC did not improve the predictive value of the model.

Figure 3 illustrates the relationship between EOS and TS for the 43 field trial soils ($R^2$=0.74). Watkinson and Perrott (1990) also found in their study that there was a good relationship between EOS and TS for the Taupo Series soils (Pumice soils).

It was found that the relationships between TS and S-sulphate was $R^2$=0.49 with indications that 4 or 5 sites were markedly influenced by dung, urine or past fertiliser applications.

Table 2 provides the relative ranges of TS, the likelihood of response to sulphur fertiliser application, the expected RY range, and fertiliser recommendations.

Table 2.

| TS (%) | Likelihood of Response | R.Y (%) | Recommendation |
|---|---|---|---|
| <0.04 | High | <75 | Definitely needs sulphur |
| 0.04 – 0.06 | Medium | 75 - 90 | Maintenance levels needed.<br>Apply S if non-S fertiliser i.e. rock phosphate<br>If sheep or beef farm this range could be adequate |
| 0.06 – 0.08 | Low | 90 - 95 | If dairying should be in this range or apply S |
| >0.08 | Nil | >95 | S fertiliser not needed |

For mineral soils if TS is < 0.04% the R.Y will be poor (<75%) and very good responses to sulphur fertiliser will be achieved. Soils with TS levels < 0.04% will critically limit pasture growth.

Soil TS in range 0.04 - 0.06% should achieve moderate response to sulphur fertiliser application. For sheep or beef farming TS in this range may need no sulphur fertilizer or its application may be economically feasible as sulphur is a cheap form of fertiliser relative to phosphate fertiliser.

Levels between 0.06 – 0.08% should need no application of sulphur fertilizer; although small responses to sulphur application may be achieved from majority of sites in this range. It will be essential that in a dairying situation that the TS status be in this range or sulphur should be added to make sure the RY is 95% or better because of dairying economics.

Trials done throughout New Zealand showed that a single relationship between pasture growth and soil test could be applied to all soil groups. The EOS and sulphate-S levels, which will sustain near maximum pasture production, are found to be 15-20 and 10-12 mg/kg respectively. The TS levels required to sustain near maximum pasture production is >0.06%. The single relationship also holds true for the TS test for all mineral soil groups. This single relationship for sulphur is possible for all soil groups because the soil is weighed before extraction for quick test determination (QT). This is in comparison with other quick tests (Olsen P and K etc) where they are determined on a volume basis for laboratory ease. Consequently no single relationship for Olsen P and K was found using field trial data for the major soil groups and as a consequence segregated into 4 major classes for fertiliser recommendation purposes.

Aspects of the present invention have been described by way of example only and it should be appreciated that modifications and additions may be made thereto without departing from the scope thereof.

AGRESEARCH LIMITED
by their authorised agents
JAMES & WELLS
per:

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Figure 1

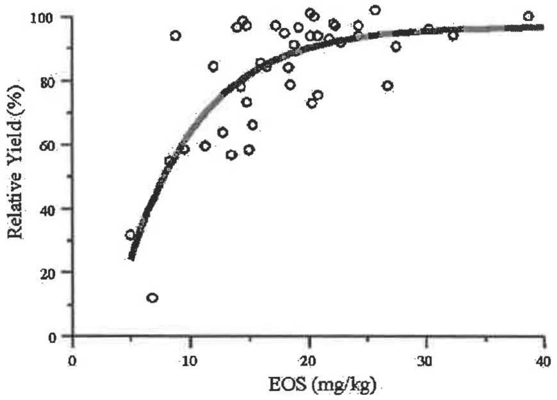

Figure 2:

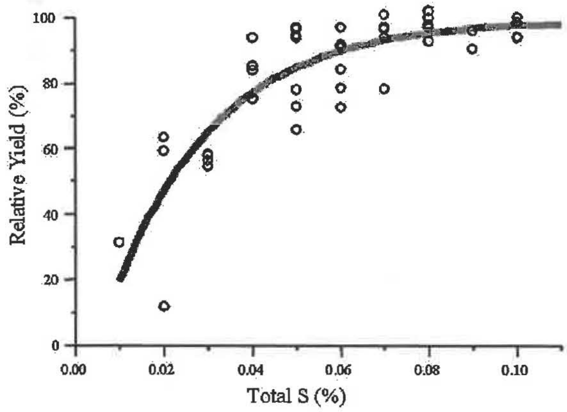

Figure 3: