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Prediction of Extractive Content of *Eucalyptus globoidea* Heartwood Using Near Infrared Spectroscopy

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Prediction of Extractive Content of *Eucalyptus globoidea* Heartwood Using Near Infrared Spectroscopy

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Abstract

Natural durability of wood is highly sought for a number of wood products due to the emerging concern over and tightening regulations on the use of toxic preservatives. In New Zealand, various wood properties of several naturally durable Eucalyptus species have been investigated in order to provide potential alternatives to CCA (Copper Chromium Arsenic) treated timber of radiata pine, the widely planted commodity species. Extractive content (EC) in wood plays an important role in determining the natural durability. In this study, near infrared (NIR) spectroscopy was used to predict the extractive content of *E. globoidea* heartwood. The EC of the wood powder samples ranged between 0.54 and 13.51%. A number of Partial Least Squares (PLS) regression models were developed to predict EC from the NIR spectra of the samples. Several spectra pre-processing techniques were applied. The significance Multivariate Correction (sMC) variable selection was also applied to improve the model accuracy. Of all models, 1st derivative NIR spectra with sMC variable selection gave the best results (R2v = 0.97; RMSEv = 0.52%). Spectral bands around 4,700 cm-1 (2112 nm), a spectral region assigned to the bond vibration of chemical components characteristic of lignin and extractives, explained much of the variance of the EC. Calibration of NIR for the EC of *E. globoidea* heartwood was successful. The model can potentially be used in the future to accurately and rapidly predict the EC for a breeding programme which aims to improve the natural durability of this species.

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Introduction

Natural durability is an important characteristic for some wood products. It determines the longevity in or above the ground without treatment. The application of preservatives to timber has been a common practice worldwide and effectively reduces the rate of decay by saproxylic (i.e. wood-decaying) fungi. As mentioned by Schultz, Nicholas, and Preston (2007), laws and governmental regulations on preservatives have become more stringent over the last two decades. For example, by the end of 1990s the application of CCA (Cooper Chromium Arsenic) to wood material was banned for many end uses in Europe and Japan (Preston, 2000). Alternative treatments such as acetylation and thermal modification of wood can be applied but these are relatively costly and do not necessarily result in the same level of durability. Alternatively, decay can be greatly ameliorated by using tree species that are naturally durable. Today, high natural durability of wood is sought for many applications of wood materials due to the prohibition of some preservatives and also the high cost of alternative treatments. Furthermore, natural durability is partly under genetic control so it is possible to breed for natural durability (Paques & Charpentier, 2015). For these reasons, the natural durability of various wood species has been investigated in the last few decades.

In New Zealand, a number of studies have been published on the natural durability and other wood properties of various Eucalypts such as *E. bosistoana, E. argophloia, E. quadrangulata*, and *E. globoidea* (Li & Altaner, 2017; Monika & Altaner, 2017 ; Salekin, Morgenroth, & Mason, 2017) These species are known to be naturally durable and regarded as an alternative to the widely-used *Pinus radiata* which requires preservatives in many end used such as structural applications and posts and poles. However, natural durability is highly variable between species, within species and within trees. One of the most important factors in determining natural durability is extractive content (Aloui, Avadi, Charrier, & Charrier, 2004; Hills, 1987). Extractives are biologically synthesised secondary metabolites produced within the wood and deposited in heartwood. Extractives can act as natural repellent and render the timber resistant against saproxylic organisms. Extractives have been shown to inhibit growth of saproxylic organisms.

Natural durability of wood is typically determined either by a long-term field test (i.e. graveyard experiment) or by a laboratory *in vitro* (i.e. in culture) test to determine the rate of mass loss by fungi. However, these methods are both labour and time intensive so

not ideal for screening a large number of samples (Edlund, Evans, & Henriksen, 2006). Alternative to these methods is to use near infrared (NIR) spectroscopy to predict the mass loss by fungi or the extractive contents. This method has become increasingly popular over the last few decades due to its quick measurement and nondestructiveness. NIR has been mainly used in the food and agriculture industry for predicting chemical properties and physical characteristics (Brimmer, DeThomas, & Hall, 2001; Osborne, Fearn, & Hindle, 1993; Shenk, Workmann, & Westerhaus, 1992). Today, NIR spectroscopy is also used to predict a variety of chemical and physical properties of wood (Hoffmayer & Pederson, 1995; Schimleck, Evans, Ilic, & Matheson, 2002; Schimleck, Michell, Raymond, & Muneri, 1999; Thumm & Meder, 2001). Researchers successfully Calibrated NIR spectra for predicting extractive content of various species (Baillères, Davrieux, & Ham-Pichavant, 2002; da Silva et al., 2013; He & Hu, 2013; Üner, Karaman, Tanrıverdi, & Özdemir, 2011).

The NIR region of the electromagnetic spectrum spans from approximately 12,820 cm^{-1} (780 nm) to 4,000 cm^{-1} (2,500 nm) and is characterised by overtones of molecular bonds associated with hydrogen (Flæte & Haartveit, 2004). NIR spectra require a multivariate data analysis to give useful information about the parameter of interest. Moreover, a variety of factors such as background noise and effective path length present more challenges. Therefore, a number of studies used several pre-processing techniques as well as variable selection methods on the NIR in order to obtain useful information (Bush, McCarthy, & Meder, 2011; He & Hu, 2013; Li & Altaner, 2017).

This dissertation aims to calibrate NIR spectra for the prediction of extractive content of *Eucalyptus globoidea* heartwood and investigate the prediction capability of the model. *E. globoidea* heartwood was reported to have Class 2 natural durability by the AS 5604 (Standards Australia, 2005). This dissertation was motivated by New Zealand Dryland Forests Initiative) whose overall objective is to produce naturally durable timber from eucalypts for posts and poles (Ballekom & Millen, 2017). NZDFI has selected several naturally durable *Eucalyptus* species, including *E. globoidea*, as an alternative to CCA treated timber and has been investigating the growth and wood properties of each species.

Literature Review

Cause of decay

Fungi

Fungi are main saproxylic (i.e. wood-decaying) organisms which utilise non-enzymatic and enzymatic compounds to break down the structural components of wood. There are three broad categories of saproxylic fungi: brown rot fungi; white rot fungi; and soft rot fungi (Schmidt, 2006). Brown rot fungi primarily decompose carbohydrates such as cellulose and hemicellulose. The majority of brown rot fungi do not have an ability to break down lignin, thus making the affected wood browner in appearance. Brown rot fungi predominantly attack conifers and occur on standing trees, dead trees, and processed timber (Ryvarden & Gilbertson, 1993). Brown rot fungi can affect both sapwood and heartwood.

White rot fungi are different to brown rot fungi in that white rot fungi can break down carbohydrates and lignin uniformly and simultaneously (Messner et al., 2003). Furthermore, white rot fungi attack hardwood more frequently compared to brown rot fungi. Because of the simultaneous decomposition of cellulose and lignin, the rate of carbohydrate decomposition is comparatively small to that of brown rot fungi and thus the structural integrity of the wood remains for longer (Schmidt, 2006).

Soft rot is caused by fungi in the division of Ascomycota and Deutromycota (Eaton & Hale, 1993). Similar to brown rot fungi, soft rot fungi primarily decompose cellulose and hemicellulose. However, soft rot fungi are different from brown rot fungi and white rot fungi in that they grow hyphae mainly in the woody cell wall, and many soft rot fungi can tolerate water saturation. Soft rot fungi can cause a significant carbohydrate degradation, resulting in the loss of dimensional stability and a 50% decrease in impact bending at only 5% loss in mass (Schmidt, 2006).

Bacteria

In comparison to the well-established knowledge of the mechanism of wood degradation by fungi, wood degradation by bacteria has been poorly understood (Clausen, 1996; Johnston, Boddy, & Weightman, 2016). This is attributable to the fact that the large proportion of saproxylic bacteria cannot be studied *in vitro* (i.e. in culture), and that it is difficult to isolate the effects of bacteria on wood from saproxylic fungi. Researchers have

identified multiple modes of interactions between bacteria and fungi, including antagonism, commensalism and several modes of symbiosis(Johnston et al., 2016). Bacteria are capable of decomposing carbohydrates in the wood. The rate of decomposition, however, is relatively small compared to saproxylic fungi because of the size, and the limited movement (Johnston et al., 2016). It has also been found that some bacteria can decompose some other wood substances such as pectin (Schink, Ward, & Zeikus, 1981) or even lignin (Brown & Chang, 2014) albeit very slowly. Bacteria seems to play a major role in the decomposition of wet or waterlogged wood where the low-oxygen environment is unsuitable for fungal growth. In such environments, the decomposition is significantly slow (Clausen, 1996). However, Blanchette and Shaw (1978) reported that fungal decay of wood was increased in the presence of nitrogen-fixing bacteria and yeast. Importantly, Brunner and Kimmins (2003) reported that bacterial activity in the heartwood was slower compared to sapwood, presumably due to the presence of inhibitory extractives and the reduced accessibility.

Insects

A number of wood-boring insects attack dying wood, dead wood, and logs. The majority of these insects belong to the order Coleoptera. Larvae of wood-boring insects enter the wood and start feeding on sapwood as they tunnel through the wood. The tunnels created by these insects can facilitate the invasion of wood by other wood-degrading organisms such as fungi and bacteria, thereby accelerating the decay process (Ulyshen, 2016). Also, some beetles have a symbiotic relationship with certain fungi that breaks down cellulosic materials for the beetle (Peters, Creffield, & Eldridge, 2002). Unlike saproxylic bacteria and fungi, wood-boring insects do not rely on the presence of water, so even dried timber can be attacked by them.

Termites are detrivorous insects that mainly decompose cellulose. Thermites can be categorised into three groups based on their feeding mechanisms: Non-termitid termites (i.e. lower termites); termitid termites (i.e. 'higher' termites); and the termites of the subfamily *Macrotermitinae (Maynard, Crowther, King, Warren, & Bradford, 2015).* Non-termitid termites (i.e. lower termites) utilise symbiotic protozoa in their guts to break down cellulose. On the other hand, termitid termites produce their own enzymes to break down cellulose. Termites of the subfamily *Macrotermitinae* are the only group of termites that decompose cellulosic materials by utilising symbiotic basidiomycetes within their

nests. The subfamily is restricted to the tropical Africa and Asia. Termites are known to be one of the biggest consumer of cellulosic materials, especially when the wood is in contact with soil (Maynard et al., 2015). The most common termites in temperate regions are lower termites (Ulyshen, 2016). The impact of termites on heartwood was found to be significantly lower owing to the presence of extractives, reduced permeability and nutrient availability.

Natural Durability

Sapwood vs Heartwood

Sapwood is the physiologically active part of stems and branches, and is composed of living cells such as ray parenchyma and axial parenchyma. Sapwood conducts water and nutrients and stores reserve materials such as starch and lipids (Gartner, 1995). Heartwood, on the other hand, is a physiologically dead part of stems and is void of living parenchyma cells (Taylor, Gartner, & Morrell, 2002). Heartwood is formed around the pith and can often be distinguished from sapwood by its distinctive colour. For example, heartwood of Rimu (*Dacrydium cupressinum*) has a unique dark reddish colour while the sapwood is brown. As heartwood formation commences, the water conduction capability is first lost through tylosis and pit aspiration. It is followed by the death of parenchyma cells and synthesis of extractives (Hills, 1987). During heartwood formation, the reserve materials from the dying cells are mobilised into soluble glucose and removed either into the transition zone in between sapwood and heartwood, or to the cambium to aid tree growth. The relocated carbohydrates in the transition zone can be used in combination with photosynthates for the synthesis of extractives (Taylor et al., 2002).

The presence of toxic extractive compounds is associated with the increased resistance to decay by saproxylic organisms (Bamber & Fukazawa, 1985; Hills, 1987). However, it should be noted that the heartwood extractives in some species are of low toxicity (Schultz et al., 1995) and that some extractives are only resistant to some specific organisms (Taylor et al., 2002).The location of inhibitory extractives also seems to play an important role in determining the resistance to decay. Extractives impregnated in the cell wall were found to be more effective against saproxylic microorganisms than extractives stored in the cell lumen (Kleist & Schmmit, 1999; Taylor et al., 2002).

Traditional methods of measuring natural durability

There are many ways in which natural durability of a particular species is determined. First, field tests are carried out to investigate how long timber can last in and/or above ground conditions. According to the European Standard EN252 which describes the standard methods of determining in-ground natural durability, the test should run for at least five years to determine the durability of natural timber as well as timber impregnated with preservatives (CEN, 1989). However, Edlund et al. (2006) argue that five years is too short to determine the durability of highly durable timber or timber treated with effective preservatives and that other approaches need to be taken in combination with the test. It can also be argued that five years is too long to gain an approval for a new preservative. Also the timeframe would not be suitable for a breeding programme which aims to breed for high natural durability.

Laboratory *in vitro* tests can shorten this process by applying saproxylic fungi to wood specimen in a culture and determine the mass loss (CEN, 1994, 1996). Depending on its mass loss, each sample is given a durability class ranging from 1to 5 (very durable to not durable). The whole process takes approximately 5-6 months, a significantly shorter period compared to field tests (Meyer et al., 2014). However, the test requires destructive samplings and is also quite labour intensive.

Use of Near Infrared Spectroscopy to predict natural durability

Near infrared (NIR) spectra is a spectral region of the electromagnetic spectrum between 12,820 cm^{-1} (780 nm) and 4,000 cm^{-1} (2,500 nm). The NIR spectra is characterised by various molecular overtones and combination vibrations of molecular bonds of various substances present in wood such as cellulose, hemicellulose, lignin and extractives (Schwanninger, Rodrigues, & Fackler, 2011). NIR spectroscopy utilises the spectral information to gain useful data from the spectra. NIR light has better penetration into the sample than mid and far infrared, meaning that less sample preparation is required (Abdi, 2003). Powder samples were also found to be a better material for NIR spectroscopy in comparison with solid samples due to better penetration of NIR light(Workmann & Weyer, 2012). Today, the application of NIR spectroscopy is widespread and it is used in fields such as agriculture, the pharmaceutical industry, food processing, and remote sensing (Aloui et al., 2004; Gao, 1996; Osborne et al., 1993; Shenk et al., 1992).

NIR spectroscopy has also been used in the field of wood chemistry and physics as various components and properties of wood can be correlated with NIR spectra. Applications of

NIR spectroscopy on wood materials include 1) quality assessment of heated and chemically treated timber (Esteves & Pereira, 2008; Feldhoff, Huth-Fehre, & Cammann, 1998); 2) assessment of crystalline structure of cellulose (Schenzel & Fischer, 2001); 3) assessment of sapwood depth (Pfautsch, Macfarlane, Ebdon, & Roger, 2012); 4) prediction of dry matter and basic density (Schimleck et al., 1999); and 5) the aforementioned quantitative analysis and prediction of wood components such as lignin, hemicellulose and extractives (Baillères et al., 2002; Schwanninger et al., 2011).

It has been shown that NIR spectra are correlated with mass loss by the laboratory fungi., Gierlinger et al. (2003) used NIR to predict natural durability of larch heartwood and found that the calibration model for prediction of relative resistance to decay (*x* value) was quite successful with high coefficients of correlation (r = 0.97) and low RMSEP value (0.078).

However, the prediction of natural durability based on the mass loss has not always been accurate. For example, prediction of natural durability of coast redwood using NIR spectroscopy showed only moderate correlation between predicted and measured mass loss (R^2 = 0.62) and relatively low ratio of prediction to deviation (RPD) (Jones et al., 2011). Similar model performance was obtained from the NIR calibration for the natural durability of *E. cladocalyx* (Bush et al., 2011). When predicting mass loss using NIR spectroscopy, the model tries to build a relationship between chemical properties (NIR spectra) with the physical property (mass loss). This could explain the relatively low performance of the models in these studies. It would make more sense to use NIR spectroscopy to predict chemical property such as extractive content (EC) that is correlated to natural durability.

As discussed before, heartwood extractives are one of the most important factors in determining natural durability of wood (Baillères et al., 2002; Taylor et al., 2002). Measuring EC is both time-consuming and labour-intensive but it has been shown that NIRS can predict EC rapidly with strong correlation. For example, calibration of NIR for EC of *E. cladocalyx* has yielded a model with strong prediction capability(Bush et al., 2011). Furthermore, Derkyi, Adu-Amankwa, Sekyere, and Darkwa (2011) successfully calibrated the prediction model for the EC and polyphenolic content of *P. caribaea* with low ratio of RMSEc to standard deviation. Taylor, Freitag, Cadot, and Morrell (2008) discussed the superior prediction capability of the model with extractive content as

reference material compared to predicting the natural durability based on the mass loss. Their results indicated that predicting decay resistance is difficult and inaccurate when the wood showed a high resistance to the test fungus.

Spectra pre-processing techniques

NIR spectra can be significantly affected by light scattering and unwanted background information, resulting in baseline shift and tilting (Rinnan, van den Berg, & Engelsen, 2009). This can adversely affect the subsequent calibration. However, these effects can be partly removed by employing pre-processing techniques. In chemometrics modelling, two main categories of pre-processing techniques have been used: scatter-correction methods and derivatisation.

The two most common scatter correction techniques are Multiplicative Scatter Correction (MSC) (Martens & Næs, 1989) and Standard Normal Variate (SNV) (Barnes, Dhanoa, & Lister, 1989). Both serve the purposes of removing unwanted scatter effects and variations in effective path length but are performed slightly differently. MSC first estimates the correction coefficients and then corrects the recorded spectrum. This process requires a reference spectrum and in most applications the average spectrum of the whole data set is used as a reference (Rinnan et al., 2009). SNV does not require a common reference signal and each spectral record is corrected independently from the rest of the dataset. This may give SNV a practical advantage, however, there is no statistically significant difference between these two pre-processing methods in most cases Dhanoa, Lister, Sanderson, and Barnes (1994); Rinnan et al. (2009).

Another category of the spectra pre-processing methods is derivation. Derivations are applied to the spectra in order to remove additive and multiplicative effects which result from the multicollinearity of the spectra. Derivatives have been commonly used in spectral analysis. The first derivative is the slope of the tangent to the signal at each point and can remove the baseline. The second derivative is the derivative of the derivative which measures the curvature of the signal. The second derivative can remove both the baseline and linear trend and increase resolution of overlapping signals (Rinnan et al., 2009). The two commonly used derivation algorithms in chemometrics are Norris-Williams derivation (Norris & Williams, 1984) and Savitzky-Golay derivation (Savitzky & Golay, 1964). Both derivations involve a smoothing of the spectra to minimise the risk of

reducing the signal to noise ratio. Norris-Williams derivation takes the centre point between two smoothed values whereas Savitzky-Golay derivation fits a polynomial to derive a centre point. In Savitzky-Golay derivation, users can select the window size and the degree of the fitted polynomial.

PLS regression and variable selection

Partial Lease Square (PLS) regression has been used ubiquitously in chemometrics. PLS regression was developed for multivariate regression analysis in social sciences (Wold, 1996) and became popularised in chemometrics (Geladi & Kowkaski, 1986). PLS regression aims to predict a Y variable from a large number of X variables. PLS regression looks for a set of components (called *latent vectors*) in X variables which are related to the variation in the Y variable. PLS regression then carries out a simultaneous decomposition of X and Y variables in a way that the selected components explain most of the covariance between X and Y variables (Abdi, 2003). This technique is particularly useful when working with NIR spectra which contain more than a thousand variables and feature multicollinearity. Consequently, a number of studies applied the PLS regression in order to predict a parameter of interest using NIR spectroscopy.

In addition to the PLS regression, numerous studies have employed a variable selection method to enhance the prediction capability of their models. While some studies manually selected variables in the NIR spectra based on the band assignments for the wood components (da Silva et al., 2013; He & Hu, 2013), others have used variable selection algorithms such as Variable Importance in the Projection (VIP) and Selectivity Ratio (SR) (Mehmood, Liland, Snipen, & Sæbø, 2012). The recently developed significance Multivariate Correlation (sMC) algorithm (Tran, Afanador, Buydens, & Blanchet, 2014) has successfully improved the prediction model for extractive content of *E. bosistoana* and *E. argophloia* (Li & Altaner, 2017)

Introduction to the durable eucalypt project and the species

NZDFI

The NZDFI is a research organisation established in 2008 and is "a collaborative cross-sector research and development project to investigate and promote the establishment of genetically-improved naturally durable eucalypts in plantations and woodlots on drought prone and erodible pastoral land within New Zealand" (Millen, 2009, p. 2). The

NZDFI pointed out the use of tropical hardwood in New Zealand and the regulations on toxic preservatives which is becoming more stringent. New Zealand's major commodity species, radiata pine, is very susceptible to decay and requires preservatives which have traditionally been Copper Chromium Arsenic (CCA) (Schultz et al., 2007). The New Zealand wine industry has been rapidly expanding and so too has the demand for vineyard posts. Currently radiata pine posts are used, however there is a perceived risk of toxic chemicals such as chromium and arsenic leaching into the ground. High breakage rate due to the low stiffness and strength of the wood is also an issue with *P. radiata*. Durable eucalypts have a high potential of replacing radiata pine poles and fences as well as tropical hardwood railway sleepers. Also locally sourced durable eucalypts offer more benefits by: covering low-productivity dryland areas which will exhibit low profitability in other land uses; reducing soil erosion and capturing nutrient runoff, and; greatly reducing the cost of transportation, processing and treatments (Millen, 2009).

Since its establishment, the NZDFI has directed its research towards breeding programmes, site-species matching, wood quality assessment, and forest health (Ballekom & Millen, 2017). To date the NZDFI has identified the top five species which are going to be its main focus. These species are *E. bosistoana*, *E. argophloia*, *E. globoidea*, *E. quadrangulata*, and *E. tricarpa*. The breeding programmes aim to improve the various aspects of these durable eucalypts including growth and form, durability, stiffness and strength, frost and drought tolerance, and tree health. Research on site-species matching is important in determining what climatic, site, or biological factors influence the growth and survival of the species. Wood quality research looks into developing novel techniques to quickly and cost-efficiently assess wood quality which would promote fast assessment and screening of individual families.

Eucalyptus globoidea

Figure 0-1 5 years old tree of Eucalyptus globoidea in Central Hawkes Bay, New Zealand.

Eucalyptus globoidea is one of the >1500 *Eucalyptus* species native to Southeast Australia. *E. globoidea* grows in a wide range of slopes and altitudes from near sea level up to 1,100m (Boland et al., 2006). It favours warm to sub-humid climate and can tolerate low level of frosts. In terms of wood properties, *E. globoidea* wood is of higher quality compared to *P. radiata* but not as good as *E. bosistoana* (Table 1). Nonetheless, wood of *E. globoidea* is quite dense and stiff compared to numerous softwoods.

Table 0-1 Wood properties of NZ-grown E. globoidea, E. bosistoana, and P. radiata timber. Adapted from Bootle (2005); (Jones, McConnochie, Shelbourne, & Low, 2010)

Origin/species	Modulus of Rupture (MPa)	Modulus of Elasticity (MoE)	Compression Parallel (MPa)	Janka Hardness (kN)	Kiln-dry Density (kg/m^3)
E. globoidea	132	17	67	6.1	703
E. bosistoana	163	21	-	13	1,100
P. radiata	89	8.5	238	5.0	500

The strength and stiffness measurements of New Zealand-grown *E. globoidea* are slightly lower relative to the Australia-grown counterpart documented in (Bootle, 2005). This is because the Australian data were obtained using wood samples from several old-growth forests. According to the Australian Standard AS5604, *E. globoidea* is categorised into Class 2 in-ground natural durability (Standards Australia, 2005). This indicates that an

untreated timber of this species can last in the ground for 15 to 25 years. However, its resistance to lyctid and termite and above-ground durability have not been tested. Jones et al. (2010) reported the sawing of the mature trees of *E. globoidea* has been quite successful and that 55% log recovery was achieved.

Methods

Sample Collection

88 wood disc samples were collected from a variety of locations in NZ. The age of these samples ranged from 5 years to 80 years-old (Table 3-1). The samples were taken either from an established stand of single or mixed species or research breeding trials set up by NZDFI (Millen, 2009). The majority of the samples were taken from the bottom section of trees (<50 cm above the ground) apart from some samples with no information as to which part of a tree it came from.

During the sample collection, care was taken so that the samples had a wide range of ages. The calibration process benefits from a wide range of ECs. Typically, trees at young age tend to have less extractives than older trees (Taylor et al., 2002). Thus, by having a wide range of ages in the samples the prediction capability of the model should be enhanced. .

Table 0-1 Age and location of the wood disc samples of E. globoidea

Site name	Region	Age	No. Sample
Atkinson	Wairarapa	5	22
Waikakaho	Marlborough	7	4
Tai Tane	Marlborough	10	14
Waikakaho	Marlborough	10	28
McNeil	Central Hawkes bay	23	1
Satchell	Northland	16	3
Ettrick	Canterbury	20-25	7
Hocking	Rangitikei	30	7
Hillersden	Marlborough	80	2
Total			88

Sample Pre-Processing

The samples were sent to the Wood Technology Laboratory at University of Canterbury and placed in an air-conditioned room (20°C and relative humidity (RH) of 65%) for at least two weeks to homogenise the moisture content of the samples. Since some samples were collected from a stump while others were collected either from a living tree or logs left on the forest ground for some time, the condition of the cut surface was quite variable among the samples. Thus, after the conditioning, they were all sanded using a belt sander so that the surface condition would not interfere with the result.

After sanding of the surface, methyl orange ($C_{14}H_{14}N_3NaO_3S$) was applied in order to reveal the heartwood band of each sample. Samples were then re-sanded to remove the indicator. Then the heartwood was isolated by drilling at roughly 1 cm interval into the cross face using an electric drill with an 8 mm drill bit. The drill dust was collected from each sample and then milled to fine particles using Wiley Mini Mill (Thomas Scientific, USA) fitted with a 2 mm screen. The wood powder was stored in an air-conditioned room (20°C and RH of 65%) until further processing.

NIR Spectra

NIR absorbance spectra of the powder samples was taken using Bruker Tensor 37 spectrometer (BRUKER, Germany) equipped with an optic probe. NIR Spectra between 4,000 and 9,000 cm^{-1} were collected with an 8 cm^{-1} step and 32 scans from each sample three times. The three spectral measurements of each sample was then averaged and converted into matrix using R (Team, 2014). The average spectra were used for the NIR calibration.

Extractive Content

After the spectral measurements were done for all samples, the samples were placed in a paper bag and oven dried overnight at 103 °C. Weight of each sample was measured and the samples were then placed in a desiccator to keep them dry. Samples were extracted using a Thermo Scientific Accelerated Solvent Extraction (ASE) machine (Thermo Fisher Scientific, USA). Each sample was placed in a 350 ml metal extraction cell. The cells were pressurised to around 1,600 PSI and heated to 70 °C. Ethanol was injected into the cell for 15 minutes. The cell was then purged and this cycle was repeated once more so as to increase the yield of extractives.

Figure 0-1 Ethanol solution containing the extractives of E. globoidea heartwood.

The ethanol solutions containing extractives were then poured into an aluminium foil of a known mass (Fig. 3-1). The samples were then dried in a fume cupboard overnight to evaporate the solvent and then dried further using a vacuum oven overnight. EC was then calculated from the formula below:

$$EC\ (\%) = \frac{WoE}{W0} \times 100$$

Where: $W0$ is the oven dried weight of un-extracted wood powder; WoE is the oven dried weight of the extracts.

NIR Data Analysis and Model Calibration

Spectral data pre-processing

Use of several spectra pre-processing techniques was considered. The prospector package (Stevens & Ramirez-Lopez, 2014) was installed into R to carry out the spectra pre-processing techniques. The two scatter correction techniques, Standard Normal Variate (SNV) and Multiplicative Scatter Correction (MSC) were applied to the NIR spectra in order to remove the varying degree of spectral noise and background effects (Barnes et al., 1989; Martens & Næs, 1989).

NIR spectra contain overlapping molecular vibrations and overtones of various molecular bonds (Schwanninger et al., 2011). One way of reducing the effects of the multicollinearity is to calculate derivatives which can accentuate small differences and enhance spectral resolution to determine the number of bands. 1st and 2nd derivative of the average spectra were calculated using the Savitzky-Golay algorithm with a window size of 15 and polynomial order of 3 (Savitzky & Golay, 1964).

Variable selection was carried out using the sMC method in the plsVarSel package (Mehmood et al., 2012). sMC variation selection can find regions of the NIR spectra that explain much of the variance in the X variables (Tran et al., 2014).

Calibration model

Due to the high number of variables and multicollinearity in NIR spectra (n=1296), the modelling process required multivariate statistics. Spectral data pre-processing and model calibration were carried out using the Partial Least Square (PLS) regression in the pls package for R (Mevik, Wehrens, & Hovde, 2015). PLS regression is one of the most commonly used multivariate modelling methods for NIR spectra (Schwanninger et al., 2011). PLS regression develops a linear regression model between predicted and observed variables by projecting them to new spaces (Abdi, 2003). This method is particularly useful if X values have multicollinearity as it is the case with NIR spectra.

The samples were divided into two datasets. 70 samples were randomly selected to calibrate the model (i.e. calibration samples) while the remainder were used to validate the calibration model (i.e. validation samples). In the calibration process, a number of models were developed in order to determine which model and which spectra pre-processing technique(s) shows the best prediction capability. For each model, Residual Mean Square Error (RMSE) was obtained for both the calibration model and validation results (RMSEc and RMSEv, respectively). RMSE was calculated by the pls package as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(\hat{y}_i - y_i)^2}{n}}$$

Where: $\hat{y}_i$ is the predicted value of the observation i; y_i is the observed value of observation i; and n is the total number of observations.

Coefficient of determination (R^2c and R^2v) was also calculated as follows to show the level of correlation:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}}$$

Where: SS_{res} is the sum of squares of residuals; and SS_{tot} is the total sum of squares.

The optimal number of components (i.e. latent vectors) in the PLS regression was recorded for each model. The number of components in a PLS regression model influences the fit of the model to the observed values. Overfitting of data is identified by prediction parameters such as RMSE increasing with the number of components. Overfitted model can result in poor prediction performance. Thus the number of components was determined by finding the minimised RMSE.

Results and Discussion

Extractive Content

Of the 88 samples obtained, 72 were randomly selected for calibration and the remaining 18 samples were used for validation (Table 4-1). The range of extractive content was similar in both the calibration and validation sets. Overall, the samples had a mean extractive content of 3.42% and a standard deviation of 2.91 indicated that a large number of samples had relatively low extractive contents. The range of EC was comparable to that of *E. bosistoana* (3 – 12%) and *E. argophloia* (4.64 – 18.85%) (Li & Altaner, 2017; Lierde, 2013).

Table 0-1 Summary of E. globoidea heartwood ehanol-soluble extractives (EC) used for NIR calibration. (SD: Standard Deviation)

	No. of samples	Age range	Mean EC (%)	Min EC (%)	Max EC (%)	SD (%)
Calibration	72	5 - 80	3.47	0.34	13.51	2.62
Validation	18	5 - 30	3.22	0.75	11.79	3.06
All	88	5 - 80	3.42	0.34	13.51	2.91

The maximum extractive content of 13.51% was observed in a 5 year-old sample. Apart from the two 80 year-old samples, there were no samples older than 30 years, so the variability of extractive content in that age range could not be obtained. There was no relationship between extractive content and age (Fig. 4-1). The range of extractive content varied significantly within an age group. This implied that the extractive content was not primarily dependent on the age but other factors such as site, genetics and the interaction between them. However, it should be noted that the conclusion was confounded by site and genetics, so a correlation between age and extractive content might still exist. The range of extractive content was comparable to other durable eucalyptus such as *E. bosistoana* and *E. argophloia*, which exhibited Class 1 natural

durability (Li & Altaner, 2017; Standards Australia, 2005). The natural durability rating of *E. globoidea* is Class 2.

The high variability of extractive content observed in the young samples suggested an opportunity to segregate trees for higher and lower extractive content as an indicator of natural durability at an early stage. Natural durability has been shown to be partly under genetic control for species such as *E. cladocalyx* and interspecific hybrid larch (*Larch* x *eurolepsis*) (Bush et al., 2011; Paques & Charpentier, 2015). Therefore, it should be possible to breed *E. globoidea* for natural durability. However, the heritability of traits such as hardwood size and extractive content is variable between species (Bush et al., 2011; Paques & Charpentier, 2015). Thus the genetic heritability of extractive content of *E. globoidea* heartwood needs to be investigated.

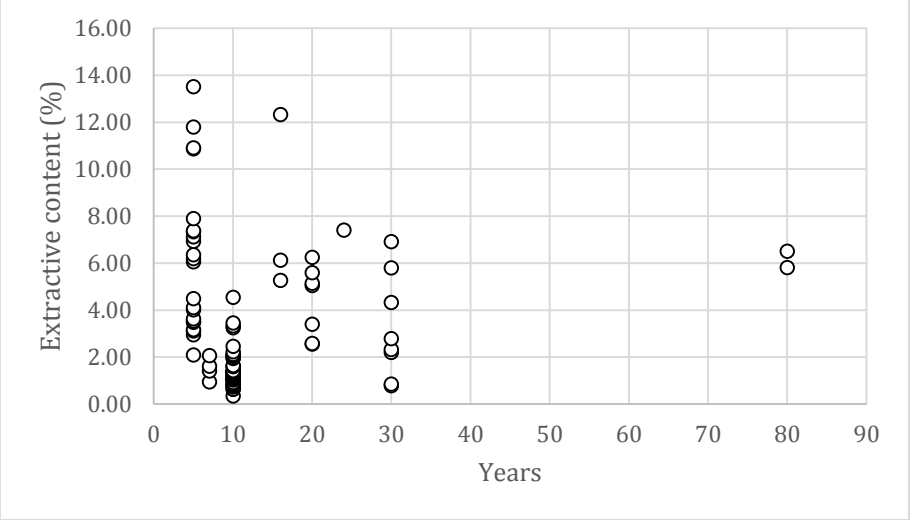

Figure 0-1 Age and extractive content distribution of E. globoidea heartwood samples of this study

Calibration of NIR for Extractive Content

Calibration without variable selections

Table 4-2 shows the performance of all models developed with all 1296 variables (i.e. wavenumbers) of NIR spectra of the different pre-processing methods. All calibration models had a strong correlation ($R^2 < 0.9$) and low residual errors (RMSEc < 1%) relative to the EC range (0.34 – 13.51%). Neither SNV nor MSC resulted in significant model improvement. However, derivation of the spectra with 1st derivative reduced the number of components in the model and also improved the validation results ($R^2v = 0.96$ and RMSEv = 0.56). The reduced number of components prevented the model from becoming over-fitted to the calibration dataset. Derivation with the 2nd derivative also reduced the

number of components in the PLS model but resulted in higher RMSEc (0.98%). Applying both the scatter correction method and the derivative did not make significant improvement to the 1st derivative model. Therefore, the 1st derivative spectra has been selected as the best calibration model. The 1st derivative of NIR spectra was also selected as the best performing model for the prediction of EC of *argophloia* (Li & Altaner, 2017). A number of studies on the prediction of EC of different species using NIR spectroscopy have achieved a similar level of performance (da Silva et al., 2013; He & Hu, 2013; Mounguengui et al., 2016; Paques & Charpentier, 2015)

Table 0-2 Performance of the calibrated PLS regression models for the extractive contents of E. globoidea heartwood with validation results. (SNV: Standard Normal Variate; MSC: Multiplicative Scatter Correction; RMSE: Resiidual Mean Square Error)

Pre-processing method	Calibration			Validation	
	R^2c	RMSEc (%)	Number of components	R^2v	RMSEv (%)
Raw Spectra	0.95	0.66	8	0.91	0.86
SNV	0.95	0.68	7	0.92	0.83
MSC	0.95	0.68	7	0.92	0.83
1st derivative	0.95	0.66	6	0.96	0.56
2nd derivative	0.92	0.81	7	0.96	0.57
SNV + 1st derivative	0.95	0.66	5	0.96	0.61
SNV + 2nd derivative	0.92	0.82	7	0.96	0.61
MSC + 1st derivative	0.95	0.66	5	0.96	0.61
MSC + 2nd derivative	0.92	0.82	7	0.96	0.58

Calibration with variable selections

Table 0-3 Performance of the PLS regression model for EC with and without the significance Multivariate Correlation (sMC) variable selection on the 1st derivative NIR spectra of E. globoidea.

Pre-processing method	Calibration			Validation	
	R^2c	RMSEc (%)	Number of components	R^2v	RMSEv (%)
All variables					
1st derivative (n=1296)	0.95	0.66	6	0.96	0.56
sMC variable selection					
1st derivative (n=138)	0.96	0.57	4	0.97	0.52

Variable selection was carried out using the sMC algorithm on the 1st derivative of the raw spectra. With the variable selection, the model performance has improved (Table 4-3). Even though the improvement of the model in terms of R^2 was not notable, the number of components reduced from 6 to 4 and the RMSEc improved from 0.66% to 0.57%. The

improvement indicated that the sMC algorithm successfully removed unnecessary variables that showed little correlation with the EC of *E. globoidea* heartwood.

Figure 4-2 shows the correlation of measured and predicted extractive content for *E. globoidea* heartwood. The residuals seemed evenly distributed and the Breusch-Pagan test for heteroscedasticity returned a P value of 0.92, indicating that there was no statistically significant heteroscedasticity present in the residuals. However, there were only few data points in the higher EC range. More data points in the higher range would give more confidence in the calibration model.

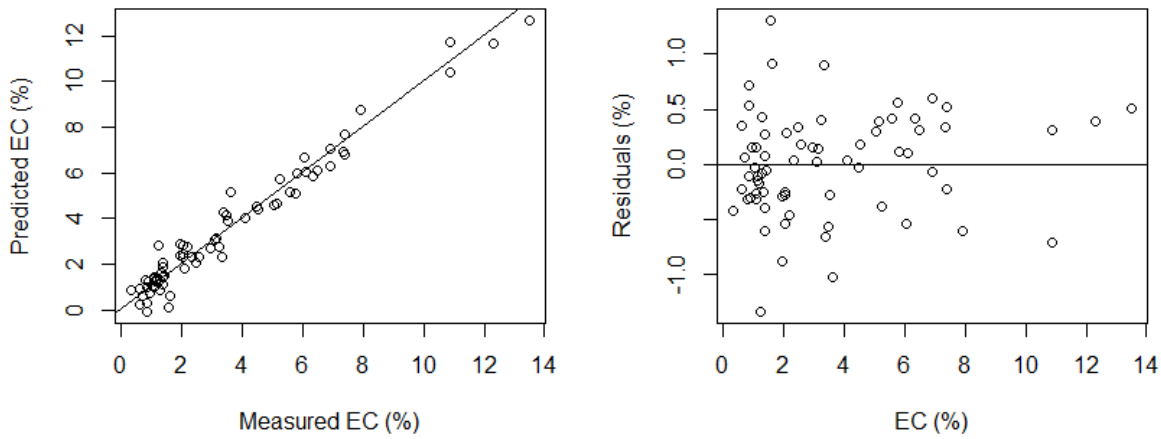

Figure 0-2 Left: Measured value of EC of E. globoidea heartwood against the predicted EC by the sMC 1st derivative model. Right: Residual plot for the predicted and measured EC of E. globoidea heartwood from the sMC 1st derivative model.

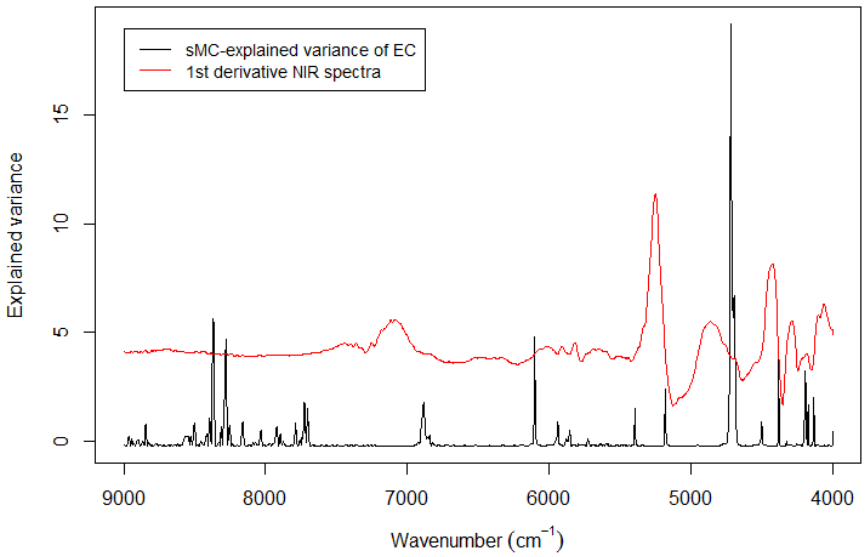

Figure 0-3 Average 1st derivative NIR spectra for E. globoidea heartwood (red line) and the variance of EC explained by each wavenumber (black line)

138 spectral variables were selected by the sMC variable selection method (Table 4-3). Much of the variance was explained by the spectral bands around 4700 cm^{-1} (2112 nm) (Fig. 4-3). In literature, the spectral bands around 4,700 cm^{-1} (2132 nm) have been assigned to the bond vibration of C_{ar}-H stretching and C=C stretching of lignin and extractives (Michell & Schimleck, 1996). This indicated that the sMC successfully selected the variables that were associated with the chemical properties of the extractives. Other spectral bands such as ~8,350 (1198 nm) cm^{-1}, ~6,100 cm^{-1} (1639nm), and ~4,400 cm^{-1} (2273 nm), were found to be significant in explaining the variance of EC of *E. globoidea* heartwood. In literature, these bands have been assigned to the vibrations of several chemical components characteristic of extractives and lignin (Alves et al., 2010; Michell & Schimleck, 1996; Schwanninger et al., 2011). The sMC methods has effectively rejected the strong absorbance peaks of water around 7,070 cm^{-1} (1414 nm) and 5,200 cm^{-1} (1923 nm) in the first derivative NIR spectra (Schwanninger et al., 2011).

The sMC selected similar spectral bands for the EC of *E. globoidea* to those selected for the EC of *E. bosistoana* and *E.* argophloia heartwood (Li & Altaner, 2017). However, the significance of the selected spectral bands differed. In the cross-species calibration of NIR for EC of these two species, much of the variance was explained by the spectral bands around 6,000 cm^{-1} and to a lesser extent by ~4,680 cm^{-1}. The difference in the spectral bands used to explain the variance indicated that a cross-species calibration may not be feasible for *E. globoidea*, even though it was successful between *E. bosistoana* and *E. argophloia*.

Conclusion

The study measured the EC of 88 wood powder samples of *E. globoidea* heartwood which ranged from as low as 0.34% up to 13.51%. Large variation of EC was observed within an age group, even at five years. This suggested that screening trees for natural durability at a relative early stage of growth might be possible. Future research should investigate the variation of EC of *E. globoidea* heartwood with different height, age, site, and genetics.

NIR spectroscopy in combination with multivariate statistical analysis was found to be an effective predictor of the EC of *E. globoidea* heartwood. The calibration was successful and the 1st derivative of the average NIR spectra was the most accurate in explaining the variance of the EC (R^2c = 0.95; RMSEc = 0.66%). The calibration model was further improved by the sMC variable selection method (R^2c = 0.96; RMSEc = 0.57%) and the number of components required in the PLS regression model was also reduced from 6 to 4. The sMC has rejected the spectral peaks of absorbed water along with other irrelevant variables and successfully selected the spectral bands assigned to the bond vibration characteristic of extractives and lignin. Now that the calibration of NIR for the EC was achieved with the high precision, in the future the model can be used to rapidly predict the EC of a large number of samples of a breeding programme.

Reference

Abdi, H. (Ed.). (2003). Partial least square (PLS) regression. Thousand Oaks, CA: Sage.

Aloui, F., Avadi, N., Charrier, F., & Charrier, B. (2004). Durability of European oak (Quercus petraea and Quercus robur) against white rot fungi (Coriolus versicolor): relations with phenol extractives. Holz Roh Werkst, 62, 286-290. doi: 10.1007/s00107-004-0489-7

Alves, A., Santos, A., Rozenberg, P., Pâques, L. E., Charpentier, M., Schwanninger, M., & Rodriggues, J. (2010). A common near infrared-based partial least squares regression model for the prediction of wood density of Pinus pinaster and larix x eurolepis. Wood Science and Technology, 46(1-3), 157-175.

Baillères, H., Davrieux, F., & Ham-Pichavant, F. (2002). Near infrared analysis as a tool for rapid screening of some major wood characteristics in a eucalyptus breeding programme. Annals of Forest Science, 59(5-6), 479-490.

Ballekom, S. V., & Millen, P. (2017). NZDFI: Achievements, constraints and opportunities Paper presented at the Durable eucalypts on drylands: protecing and enhancing value, Blenheim, New Zealand.

Bamber, R. K., & Fukazawa, K. (1985). Sapwood and Heartwood: A review. Forestry abstracts, 46(9), 567-580.

Barnes, R. J., Dhanoa, M. S., & Lister, S. J. (1989). Standard normal variate transformation and de-trending of near-infrared diffuse reflectance spectra. Applied spectroscopy, 43(5), 772-777.

Blanchette, R. A., & Shaw, C. G. (1978). Associations among bacteria, yeasts, and basidiomycetes during wood decay. Phytopathology, 68(4), 631-637.

Boland, D. J., Brooker, M. I. H., Chippendale, N., Hall, N., Hyland, B. P. M., Johnston, R. D., . . . Turner, J. D. (2006). Forest Trees of Australia (5th ed.). Melbourne, Australia: CSIRO Publishing.

Bootle, K. R. (2005). Wood in Australia. Types, properties, and uses (2nd ed.). Australia: MzGraw-Hill.

Brimmer, P. J., DeThomas, F. A., & Hall, J. W. (2001). Method development and implementation of near-infrared spectroscopy in industrial manufacturing processes. In

P. C. Williams, Norris, K.H. (Ed.), Near-infrared technology in the agricultural and food industries. (2nd ed., pp. 199-214). St. Paul, MN: American Association of Cereal Chemists.

Brown, M. E., & Chang, M. C. (2014). Exploring bacterial lignin degradation. Current opinion in chemical biology, 19, 1-7.

Brunner, A., & Kimmins, J. P. (2003). Nitrogen fixation in coarse woody debris of Thuja plicata and Tsuga heterophylla forests on northern Vancouver Island. Canadian Journal of forest research, 33(9), 1670-1682.

Bush, D., McCarthy, K., & Meder, R. (2011). Genetic variation of natural durability traits in Eucalyptus cladocalyx (sugar gum). Annals of Forest Science, 50(4), 1057-1066.

CEN. (1989). EN252. Field test method for determining the relative peotective effectivenes of a wood preservative in ground contact. Brussels, Belgium: European Committee for Standardisation.

CEN. (1994). EN 350-1 Durability of wood and wood-based products. Natural durability of solid wood. Part !. guide to the principles of testing and classification of the natural durability of wood. Brussels, Belgium: European Committee for Standardisation.

CEN. (1996). EN 113 Wood preservatives. Test method for determining the protective effectiveness against wood destroying basidiomycetes. Determination of the toxic values. Brussels, Belgium: European Committee for Standardisation.

Clausen, C. A. (1996). Bacterial associations with decaying wood: a review. International Biodeterioration & Buidegradation, 37(1-2), 101-107.

da Silva, A. R., Pastore, T. C. M., Braga, J. W. B., Davrieux, F., Okino, E. Y. A., Coradin, V. T. R., . . . do Prado, A. G. S. (2013). Assessment of total ohenols and extractives of mahogany wood by near infrared spectroscopy. Holzforschung, 67, 1-8.

Derkyi, N. S. A., Adu-Amankwa, B., Sekyere, D., & Darkwa, N. A. (2011). Rapid prediction of extractives and polyphenolic contents in Pinus carriage bark using near infrared reflectance spectroscopy. International Journal of Applied Science, 2(1), 2011.

Dhanoa, M. S., Lister, S. J., Sanderson, R., & Barnes, R. J. (1994). The link between multiplicative scatter correction (MSC) and standard normal variate (SNV) transformations of NIR spectra Journal of Near Infrared Spectroscopy, 2(1), 43-47.

Eaton, R. A., & Hale, M. D. C. (1993). Wood: decay, pests, and protection. London, UK: Chapman & Hall.

Edlund, M. L., Evans, F., & Henriksen, K. (2006). NT TR 591: Testing durability of treated wood according to EN252 interpretation of data from Nordic test fields

Esteves, B., & Pereira, H. (2008). Quality assessment of heat-treated wood by NIR spectroscopy. European Journal of Wood and Wood Products, 66(5), 323-332.

Feldhoff, R., Huth-Fehre, T., & Cammann, K. (1998). Detection of inorganic wood preservatives on timber by near infrared spectroscopy. Journal of Near Infrared Spectroscopy, 6(A), A171-A173.

Flæte, P. O., & Haartveit, E. Y. (2004). Non-destructive prediction of decay resistance of Pinus sylvestris Heartwoood by near infrared spectroscopy. Scandinavian Journal of Forest Research, 19(5), 55-63.

Gao, B. C. (1996). NDWI—A normalized difference water index for remote sensing of vegetation liquid water from space. Remote sensing of environment, 58(3), 257-266.

Gartner, B. L. (Ed.). (1995). Plant stems: Physiology and functional morphology. San Diego, CA: Academic Press. Inc.

Geladi, P., & Kowkaski, B. (1986). Partial least square regression: A tutorial. Analytica Chemica Acta, 35, 1-17.

Gierlinger, N., Jacques, D., Schwanninger, M., Wimmer, R., Hinterstoisser, B., & Pâques, L. E. (2003). Rapid prediction of natural durability of larch heartwood using Fourier transform near-infrared spectroscopy. Canadian Journal of Forest Research, 3(9), 1727-1736.

He, W., & Hu, H. (2013). Rapid prediction of different wood species extractives and lignin content using near infrared spectroscopy. Journal of Wood Chemistry and Technology, 33(1), 52-64. doi: 10.1080/02773813.2012.731463

Hills, W. E. (1987). Heartwood and tree exudates. Berlin, Germany: Springer-Verlag Berlin Heidelberg.

Hoffmayer, P., & Pederson, J. G. (1995). Evaluation of density and strength of Norway spruce wod by near infrared reflectance spectroscopy. Holz Roh Werkst, 53, 165-170.

Johnston, S. R., Boddy, L., & Weightman, J. (2016). bacteria in decomposing wood and their interactions with wood-decay fungi. FEMS Microbiology Ecology, 92(11), 1-12.

Jones, G. T., McConnochie, R. M., Shelbourne, T., & Low, C. B. (2010). Sawing and Grade recovery of 25-year-old Eucalyptus fastigata, E. globoidea, E. muelleriana and E. pilularis. New Zealand Journal of Forestry Science, 40, 19-31.

Jones, G. T., Meder, R., Low, C. B., O'Callahan, D., Chittenden, C. M., Ebdon, N., . . . Riddell, M. (2011). natural durability of the heartwood of coast redwood [Sequoia semperviens (D.Don) Endl.] and its prediction using near infrared spectroscopy. Journal of Near Infrared Spectroscopy, 19, 381-389.

Kleist, G., & Schmmit, U. (1999). Evidence of accessory comnpounds in vessel walls of Spaelli heartwood (Entandrophragma cylindricum). Holz Roh Werkst, 57, 93-95.

Li, Y., & Altaner, C. (2017). Improving heartwood quality of durable eucalypts. Paper presented at the Durable Eucalypts on Drylands: Protecting and enhancing value, Blenheim, New Zealand.

Lierde, J. J. (2013). What causes natural durability in Eucalyptus bosistoana timber? (Dissertation). University of Canterbury, Christchurch, New Zealand.

Martens, H., & Næs, T. (1989). Multivariate Calibration. Chichester, United Kingdom: John Wiley & Sons.

Maynard, D. S., Crowther, T. W., King, J. R., Warren, R. J., & Bradford, M. A. (2015). Temperate forest termites: ecology, biogeography, and ecosystem impacts. Ecological Entomology, 40(199-210). doi: 10.1111/een.12185

Mehmood, T., Liland, K. H., Snipen, L., & Sæbø, S. (2012). A review of variable selection methods in partial least squares regression. Chemometrics and Intelligent Laboratory Systems, 118, 62-69.

Messner, K., Facker, K., Lamaipis, P., Gindl, W., Srebotnik, E., & Watanabe, T. (2003). Overview of white-rot research: where we are today. In B. Goodell, D. B. Nicholas & T. P. Schultz (Eds.), Wood deterioration and preservation: advances in our changing world. Washington DC: American Chemical Society.

Mevik, B., Wehrens, R., & Hovde, L. (2015). Partial Least Squares and Principal Component Regression. R package version 2.5-0.

Meyer, L., Brischke, C., Melcher, E., Brandt, K., Lenz, M. T., & Soetbeer, A. (2014). Durability of English oak (Quercus robur L.) - Comparison of decay progress and resistance under various laboratory and field conditions. International Biodeterioration & Biodegradation, 86(B), 79-85.

Michell, J. A., & Schimleck, L. R. (1996). NIR spectroscopy of woods from Eucalyptus globulus. Appita Journal, 49(1), 23-26.

Millen, P. (2009). NZ Dryland Forests Initiative: A market focused durable eucalypt R&D project

Monika, S., & Altaner, C. (2017). New Zealand grown eucalypts for rotary peeled venner production. Paper presented at the Durable eucalypts on drylands: Protecting and enhancing values, Blenheim, New Zealand.

Mounguengui, S., Tchinda, J. B. S., Ndikontar, M. K., Dumarcay, S., Atteke, C., Perrin, D., . . . Gerardin, P. (2016). Total phenolic and lignin contents, phytochemical screening, antioxidant and fungal inhibition properties of the heartwood extractives of ten Congo Basin tree species. Annals of Forest Science, 73, 287-296.

Norris, K. H., & Williams, P. C. (1984). Optimization of mathematical treatments of raw near-infrared signal in the measurement of protein in hard red spring wheat. I. influence of particle size. Cereal Chemistry, 61, 158-165.

Osborne, B. G., Fearn, T., & Hindle, P. H. (1993). Practical NIR spectroscopy with applications in food and beverage analysis. Harlow, England: Longman Scientist and Technical.

Paques, L. E., & Charpentier, J. P. (2015). Perspectives for genetic improvement in hardwood size and extractive content in relation to natural durability and aesthetics is interspecific hybrid larch (Larix x eurolepis). European Journal of Forest Research, 135(5), 857-868.

Peters, B. C., Creffield, J. W., & Eldridge, R. H. (2002). Lyctine (Coleoptera: Bostrichidae) pests of timber in Australia: A literature review and susceptibility testing protocol. Australian Forestry, 65(2), 107-119. doi: 10.1080/00049158.2002.10674861

Pfautsch, S., Macfarlane, C., Ebdon, N., & Roger, M. (2012). Assessing sapwood depth and wood properties in Eucalyptus and Corymbia spp. using visual methods and near infrared spectroscopy. Trees, 26, 963-974.

Preston, A. F. (2000). Wood preservation. Forest products journal, 50(9), 12.

Rinnan, Å., van den Berg, F., & Engelsen, B. (2009). Review of the most common pre-processing techniques for near-infrared spectra. Trends in Analytical Chemistry, 28(10), 1201-1222. doi: 10.1016/j.trac.2009.07.007

Ryvarden, L., & Gilbertson, R. L. (1993). European Polypores. Part 1. Synopsis Fungorum, 6, 1-387.

Salekin, S., Morgenroth, J., & Mason, E. (2017). Site characterisation and growth modelling for durable eucalypts: a case study in Marlborough, New Zealand. Paper presented at the Durable eucalypts on drylands: Protecting and enhancing value, Blenheim, New Zealand.

Savitzky, A., & Golay, M. J. E. (1964). Smoothing and differentiation of data by simplified least squares procedures. Analytical chemistry, 36(8), 1627-1639.

Schenzel, K., & Fischer, S. (2001). NIR FT Raman spectroscopy - a rapid analytical tool for detecting the transformation of cellulose polymorphs. Cellulose, 8(1), 49-57.

Schimleck, L. R., Evans, R., Ilic, J., & Matheson, A. C. (2002). Estimation of wood stiffness of increment cores by near-infrared spectroscopy. Canadian Journal for forest research, 32, 129-135.

Schimleck, L. R., Michell, A. J., Raymond, C. A., & Muneri, A. (1999). Estimation of basic density of Eucalyptus globulus using near-infrared spectroscopy. Canadian Journal for forest research, 29(2), 194-201.

Schink, B., Ward, J. C., & Zeikus, J. G. (1981). Microbiology of wetwood: importance of pectin degradation and Clostridium species in living trees. Applied and environmental microbiology, 42(3), 526-532.

Schmidt, O. (2006). Wood and tree fungi - biology, damage, protection, and use. Heidelberg: Springer-Verlag Berlin Heidelberg.

Schultz, T. P., Harms, W. B., Fisher, T. H., McMurtrey, K. D., Minn, J., & Nicholas, D. D. (1995). Durability of angiosperm heartwood: The importance of extractives. Holzforschung, 49, 29-34.

Schultz, T. P., Nicholas, D. D., & Preston, A. F. (2007). A brief review of the past, present and future of wood preservation. Pest Management Science, 63, 784-788.

Schwanninger, M., Rodrigues, J. C., & Fackler, K. (2011). A review of band assignments in near infrared spectra of wood and wood components. Journal of Near Infrared Spectroscopy, 19, 287-308.

Shenk, J. S., Workmann, J. J., & Westerhaus, M. O. (1992). Application of NIR spectroscopy to agricultural products. In D. A. Burns, & Ciurczak, E.W. (Ed.), Handbook of Near Infrared Analysis (pp. 383-431). New York: Marcel Dekker.

Standards Australia. (2005). Australian Standard Timber - Natural durability ratings (Vol. AS 5604 - 2003). Sydney: Standards, Australia.

Stevens, A., & Ramirez-Lopez, L. (2014). An introduction fo the prospectr package (Version R Package Vignette, Report No.: R Package version 0.1).

Taylor, A. M., Freitag, C., Cadot, E., & Morrell, J. J. (2008). Potential of near infrared spectroscopy to assess hot-water-soluble extractive content and decay resistance of a tropical hardwood. Holz Roh Werkst, 66, 107-111.

Taylor, A. M., Gartner, B. L., & Morrell, J. J. (2002). Heartwood formation and natural durability - a review. Wood and Fiber Science, 34(4), 587-611.

Team, R. C. (2014). R: A language and environment for statistical computing. . Vienna, Austria: R Foundation for Statistical Computing.

Thumm, A., & Meder, R. (2001). Stiffness prediction of radiata pine clearwood test pieces using near-infrared spectroscopy. Journal of Near Infrared Spectroscopy.

Tran, T. N., Afanador, N. L., Buydens, L. M. C., & Blanchet, L. (2014). Interpretation of variable importance in partial least squares with significance multivariate correlation (sMC). Chemometrics and Intelligent Laboratory Systems, 138, 153-160.

Ulyshen, M. D. (2016). Wood decomposition as influenced by invertebrates. Biological Reviews, 91, 70-85. doi: 10.1111/brv.1258

Üner, B., Karaman, İ., Tanrıverdi, H., & Özdemir, D. (2011). Determination of lignin and extractive content of Turkish Pine (Pinus brutia Ten.) trees using near infrared spectroscopy and multivariate calibration. Wood Science Technology, 45, 121-134.

Wold, H. (Ed.). (1996). Estimation of principal components and related models by iterative lesat squares. NY: Acedemic Press.

Workmann, J. J., & Weyer, L. (2012). Practical guide and spectral atlas for interpretive near-infrared spectroscopy. NY: CRC Press.