Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

Stability of Organo-mineral Complexes in Soils with Andic Properties as Influenced by Land Use Intensification

A thesis presented in partial fulfilment of the requirements for the degree of

Master of Agricultural Science

in

Soil Science

at Massey University, Palmerston North, New Zealand

RITHA KOV

2017

ABSTRACT

Soils with andic properties are characterised by having abundant reactive Al in the form of short-range-order Al constituents and organo-Al complexes, which facilitate the accumulation of soil organic matter (SOM) through the formation of the so-called organo-mineral complexes. Recent studies on New Zealand pastoral systems, however, have reported the loss of C from soils with andic properties. This has been attributed to management practices such as liming and urine deposition and associated hydrolysis reactions that un-stabilise the associations of SOM with reactive Al. but mechanistic studies to prove this have not been carried out. The objective of this study has been to compare soils under different land uses and management intensification regimes so that the influence of these on the organic and inorganic chemistry and the stability of organo-mineral complexes of soils with andic properties can be inferred. For this, soil samples under a pine stand (Forest) and two paddocks differing in the degree of intensification (Paddock 1 < Paddock 2) were taken. Major soil chemical properties were determined, including pH, total C and N content, reactive inorganic and organic Al fractions, and SOM molecular fingerprinting. Soil pH in Forest (pH-H_2O, 5.3) was significantly lower ($P<0.05$) than that in Paddock 1 (pH-H_2O, 5.7), which was itself significantly lower ($P<0.05$) than pH in Paddock 2 (pH-H_2O, 6.1). Soil C and N concentrations were significantly higher in the soils under pasture than under pine (63.8 g C kg^{-1}), and C in Paddock 2 (96.0 g C kg^{-1}) was significantly lower ($P < 0.05$) than that in Paddock 1 (101.7 g C kg^{-1}). While allophane content was shown to increase (from 5.1 to 7.9 to 10.5 %) with intensification (i.e. Paddock 2 compared with Paddock 1 and Forest), organo-Al complexes, as estimated with sodium pyrophosphate (Al_p), were shown to decrease (Forest, 6.6 g kg^{-1}; Paddock 1, 6.8 g kg^{-1}; Paddock 2, 5.7 g kg^{-1}). At the molecular level, SOM under pine had a higher relative contribution of microbially processed organic matter than that under pasture, whereas the latter had a larger contribution of N-containing and aliphatic compounds. We proposed that the increase in pH on intensification weakened the ability of organic ligands to compete with OH^- for reactive Al and thus the potential of inorganic short-range-order constituents to chemically protect SOM through the formation of organo-mineral complexes. The study thus provided evidence of how different land uses and management intensification influence soil chemistry and SOM stocks in soils with andic properties as well as SOM molecular composition.

ACKNOWLEDGEMENTS

First, I would like to dedicate this thesis to my late father, who died during my two years in New Zealand. Although he could not finish his high school education during his time, he was very positive about education. It was also the way that I was raised, that is, to be educated. Being born to an uneducated family, I would not be here today without his efforts to persuade the rest of the family to support my studies. Also, I am very thankful to my mother and siblings for allowing me time for whatever studies I was interested in.

Second, I also acknowledge my prospective bride, Mak Mealiny, for her encouragement, although it was hard for her. She is a great and inspiring example of human kindness, and is inherently helpful and generous to everybody.

Third, I would like to specially acknowledge my two supervisors, A/Prof. Marta Camps-Arbestain and Dr Roberto Calvelo Pereira, who have shown great support and patience during my studies. When I enrolled at Massey University, I realized that I had so huge a gap in knowledge to fill that I did not know where to start. With their advice and after discussions with them, I have gained a great deal of knowledge. It formed the basis of my understanding not only about soil science, but also about the universe and its continuum. Here, I want to highlight that their comments on my work have been so helpful and critical that I know how accurate researchers and scientists would like to be. Particularly, I thank Marta for creating a relaxed environment for something difficult and the push for the coming publication of my study, and I thank Roberto for his help with advanced statistical analyses and helpful instructions to do so. His reachable assistance during the weekend is especially highlighted here.

Fourth, I am also thankful to Qinhua Shen for her guidance on laboratory procedures, chemical extractions, and running machines (MP-AES ☺), especially when Marta and Roberto were away. I also thank Manuel Suárez-Abelenda for his enormous help with molecular characterization of SOM, and I acknowledge Barney and Janine Wright for kindly allowing the sampling to be done on their farm.

Fifth, I would like to thank the Ministry of Foreign Affairs and Trade (MFAT) for the New Zealand ASEAN Scholars (NZAS) Award. Without this scholarship, my studies in New Zealand would not have been possible. I also appreciate the help of people at the International Student Support Office, who oversee NZAS awardees.

Finally, I appreciate the help and friendship of friends from different parts of the planet: Spencer, Yulfia, Toulie, Lovisha, Sandrine, Khadija, May, Yada, Grace and Stanislav. They are very good people, who are open to sharing knowledge and helpful with emotional support.

Table of Contents

List of Figures

Picture

List of Tables

1. General introduction

1.1. Background

Soil organic matter (SOM) represents a continuum from recently deposited plant material to more decomposed products (Blume *et al.*, 2016). It has a key role in soil functions, given that it (i) provides nutrients necessary for plant growth including N, P and S (Haider and Schäffer, 2009) as well as energy supply (Wild *et al.*, 2014) to the soil food web through the oxidation of soil organic carbon (SOC); (ii) helps retain nutrients at exchange sites; (iii) contributes to retain plant-available water due to its influence on soil structure and porosity; and (iv) stores SOC.

SOM levels are a function of inputs (mostly from plants) and outputs (mostly through mineralization to carbon dioxide – CO_2) (Lehmann and Kleber, 2015). During decomposition of organic detritus, carbon (C) is released through soil respiration to the atmosphere in the form of CO_2, a greenhouse gas, closing the cycle that was initiated with photosynthesis. Soil contains twice the amount of C of the atmosphere and three times that in aboveground biomass (Eswaran *et al.*, 1993). Therefore, a small change in soil C stock can profoundly influence atmospheric CO_2 and its climate feedback by acting as either a net sink or a net source. Temporally, the level of SOM stock depends on the interlinked interactions between climate, soil physical, chemical and biological processes (Fenton *et al.*, 1999; Goh, 2004), as they influence both inputs and outputs. At a microsite, SOM is preserved through several mechanisms including physical, chemical and biological protection (Sollins *et al.*, 1996; Six *et al.*, 2002). Physically, soil particles assemble as microaggregates and macroaggregates, which limit the access of SOM to microbes (Six *et al.*, 2000). Chemically, interactions with minerals, short-range-order constituents, and polyvalent cations (Al^{3+} and Fe^{3+}) exert a protective effect on SOM against decomposition (Goh, 2004). And biologically, SOM may persist because it contains compounds as charcoal, which contains condensed aromatic structures that require larger activation energy for microbes to decompose than common soil organic constituents (Lehmann and Joseph, 2015). Knowledge of how the different mechanisms are affected by land use change and management practices may help inform those management practices most suitable to maintain and, if possible, increase soil C stocks.

In particular, soils with andic properties, which when fully developed soils are classified as Andisols/Andosols, possess a higher capacity of accumulating SOM than any other mineral soil orders (Brady and Weil, 2008). The accumulation of SOM has been attributed mainly to

adsorption of SOM on the surface of short-range-order constituents, such as allophane and imogolite (Matus *et al.*, 2014), physical protection within allophane clusters (Chevallier *et al.*, 2010), as well as the formation organo-aluminium (Al) complexes (Takahashi and Dahlgren, 2016). However, these protection mechanisms are vulnerable to chemical perturbations as a result of land use and management practices. For example, Parfitt (2009) suggested that SOM protection in these soils is enhanced at low pH values, and Miyazawa *et al.* (2013) reported that applying liming materials weakened the bonds between Al and organic molecules, thus exposing these to microbial degradation. Verde *et al.* (2005), studying a chrono-sequence (space-for-time substitutions) of andic soils developed from non-volcanic materials that differ in the time elapsed since conversion from native vegetation, reported the loss of andic soil properties within 30 years following land use change and management practices.

Recently, Schipper *et al.* (2007) and Schipper *et al.* (2014) working with soils from New Zealand pastures reported that Allophanic Soils (Andisols) and Gley Soils, but not other soil orders, lost some SOM over a period of two to four decades. However, these authors did not offer any reasons for the losses, although they suggested alkalinization caused by lime and urine deposition and subsequent hydrolysis reactions as potential causes for some C loss, and, more specifically, for those from the Allophanic soils. A full understanding of this phenomenon is critically important for future management of these soils.

1.2. Research objective

The study aimed to investigate whether the type of land use and degree of management intensification in soils with andic properties affects the chemistry and SOM stability, especially organo-mineral complexes of the soils. The study involved the sampling of soils of a Taranaki farm under different land uses (pine forest and pasture) and pasture under different management intensification regimes.

2. Literature Review

2.1. Introduction

Soils with andic properties develop from weathering of tephra and other parent material containing a significant content of volcanic glass (Soil Survey Staff, 2006). These soils are characterized by low bulk density, high anion storage capacity (ASC), and a certain degree of weathering (Soil Survey Staff, 2006). When these conditions are either fully displayed or there is a large amount of glass, the soils are classified as Andisols (Soil Survey Staff, 2006) or Andosols (IUSS, 2014). Soils with andic soil properties can also develop from non-volcanic materials, such as igneous and metamorphic rocks containing highly weatherable minerals under high leaching conditions (Garcia-Rodeja *et al.*, 1987). The term "andic soils" is derived from Japanese, in which Ando means black soil (Mohammad *et al.*, 1998; Takahashi and Shoji, 2002; Chesworth, 2008). These soils possess many unique properties, and are known to accumulate large amount of SOM, compared with other soils (Takahashi and Dahlgren, 2016). In this document the term Andisol is adopted, but Andosol may be included alongside where necessary.

2.2. Distribution and Development of Andisols

2.2.1. Andisols and Distribution

Even though it is now included in many soil classification systems, this group of soils has only been globally recognized in the last half century (Soil Survey Staff, 1960). The failure to recognize these soils earlier is probably related to their relatively small coverage worldwide, around 1% of the global surface area, which is equivalent to roughly 963,000 km^2 or 124 million ha (Soil Survey Staff, 1999). Beside the official recognition, the existence of these soils had been known by local soil scientists, but their names are country specific. For example, they are known as either Humic Allophane soils or Kuroboku soils in Japan (Mizota and Van Reeuwijk, 1989), Soapy hill in West Indies, Trumao soils in Chile, Brown Earth soils in Antilles, Black Dust soils and High Mountain soils in Indonesia, Txindurru lurre in the Basque Country, Spain (Verde Vilanova, 2009), and Allophanic and Pumice Soils in New Zealand (Mizota and Van Reeuwijk, 1989).

The global recognition of these soils did not happen by chance, but due to their paramount importance in crop production and their unique properties compared with other soils. These soils represent a landmass that accommodates a disproportionally large number of the global

population (Takahashi and Shoji, 2002; Chesworth, 2008), which is why some soil scientists even use the term “high human-carrying capacity” (Takahashi and Dahlgren, 2016) to describe the fertility of these soils. For instance, the proportion of Andisols in the United States of America is relatively small, but it constitutes important wheat and timber production areas and, similarly, Andisols in South America are known to be the best farm land in several countries including Chile, Ecuador, and Colombia (Brady and Weil, 2008). In the Pacific Ring of Fire, especially in cool and high elevation regions under an udic moisture regime Andisols are intensively cultivated, supporting a dense population in Japan (Brady and Weil, 2008). The significance in agriculture is due to their unique properties that include highly stable aggregates (Shoji *et al.*, 1994), excellent tilth, high water-holding capacity, low bulk density, and high natural fertility (Brady and Weil, 2008). Although the high phosphate (P) retention capacity of Andisols is well known (Pigna and Violante, 2003), this limitation can generally be overcome by adequate agricultural management practices (Brady and Weil, 2008).

As the soils form primarily from volcanic ash, volcanoes mostly dictate the elevation of Andisols but their formation can take place at any elevation of the landscape as the ashes can be transported downwind (Soil Survey Staff, 1999). Formation of Andisols occurs at all moisture and temperature regimes (Soil Survey Staff, 1999), from cool and humid Alaska to subtropical Kyushu to tropical Hawaii (Mizota and Van Reeuwijk, 1989), although those developed from non-volcanic materials only form in high leaching environments (Garcia-Rodeja *et al.*, 1987). Similarly, these soils form under a wide range of vegetation from desert shrub in arid regions to dense coniferous forests in humid tundra at different altitudes and elevations (Buol *et al.*, 2011).

Given that these soils represent early stages of weathering, volcanoes that originate in the Holocene and late Pleistocene have been important determinants of their distribution (Buol *et al.*, 2011). Geographically, these soils are distributed worldwide, including Africa (Rwanda, Madagascar, Tanzania, Ethiopia, Cameroon, Canary Islands, Sudan, Zaire), America (Guatemala, Alaska, British Colombia, Washington, Oregon, California, Costa Rica, Panama, Honduras, El Salvador, Nicaragua, West Indies, Ecuador, Colombia, Peru, Chile, Argentina, Bolivia, Mexico), Asia and the Pacific Islands (China, Papua New Guinea, Hawaii, Aleutian Islands, Kamchatka, Japan, Korea, Micronesia, Indonesia, Solomon Islands, Vanuatu, Fiji, Samoa, Tonga, Philippines), as well as Oceania (Australia, New Zealand) (Leamy, 1984;

Takahashi and Shoji, 2002; Lowe and Palmer, 2005), with a dominance in those areas along the Pacific rim.

2.2.2. Development of Andisols

Compared with other soil orders, Andisols are relatively young, their age usually within the range of 5,000–10,000 years, which is similar to that of Entisols and Inceptisols (Brady and Weil, 2008). However, in the case of New Zealand, younger and older Andisols have also been reported. Lowe and Palmer (2005) categorized New Zealand Andisols into three groups based on age of development: (1) weakly developed or 'Entic' Cryands or Udands (<1,000 years old near the Taranaki volcano and Tongariro Volcanic Centre and 1886 AD near Tarawera); (2) weakly weathered Vitrands around Taupo (232 AD) and around Karahoa (c. 1342 AD); and (3) weakly to moderately weathered Udands around Taranaki-Ruapehu region, King Country-Western Waikato, Bay of Plenty, and Auckland-Northland (c. 26,500 years old).

These soils develop mostly from materials linked to volcanic eruptions, which include pyroclastic materials, volcanic ash, pumice, cinders, lahars, volcanic alluvium, loess, and other volcanic ejecta of all compositions (Neall *et al.*, 1985; Mizota and Van Reeuwijk, 1989). In this case, volcanic ash refers to materials with a diameter of < 2 mm blown out of the crater during eruptions (Buol *et al.*, 2011). Given the high weatherability of the minerals in these materials, mineral alteration is generally faster than that of crystallisation (Brady and Weil, 2008; Chesworth, 2008), leading to the formation of short-range-order constituents precipitate (e.g. allophane; Figure 1, see below), which have a high surface area. In the surface horizon, SOM then becomes stabilised with these constituents. Organo-Al complexes also form. The predominance of allophane vs organo-Al complexes is highly dictated by soil pH and, thus, by soil leaching conditions. When pH is below 4.9, organo-Al complexes predominate at the expense of short-range-order aluminosilicates, as organic acids become stronger ligands than silicic acid. These processes are collectively referred to as andosolization (Duchaufour, 1977; Chesworth, 2008).

The degree of Andisol development is dependent on environmental conditions. The deficiency of water affects the hydrolytic reaction of the parent material and thus, the formation of short-range-order components (Buol *et al.*, 2011). Parfitt and Wilson (1985) investigated the development of Andisols in different precipitation regimes and found that,

with fine-grained rhyolitic tephra as parent material, Andisols containing allophane were overwhelmingly found in high rainfall areas (although still not high enough to decrease the pH < 4.9) while halloysite dominated in low rainfall regions.

The formation of Andisols requires a sufficiently thick layer of volcanic ash (Brady and Weil, 2008). The proximity to the point of eruption may be an important determinant of the thickness of materials, as the further away from the crater the less material is deposited. The relatively thick layer of materials found at proximal sites may bury the antecedent surface and form multiple buried profiles while a thinner layer of materials at medial and distal deposits from successive eruptions form composite or aggrading profiles (Lowe and Palmer, 2005).

As indicated above, some Andisols may develop from a parent material other than volcano-related matter, and these soils are often referred to as "non-volcanic" Andisols (Soil Survey Staff, 1999). Garcia-Rodeja *et al.* (1987) studied the properties of well-drained soils developed from gabbros, amphibolites, and schists under udic moisture and mesic temperature conditions, and found that these soils had similar characteristics to those of "non-allophanic Andisols". Similarly, soils with andic properties (but not Andisols *senso stricto*) developed from mica schist with quartzite beds and quartz veins have been described in east central Bhutan (Bäumler *et al.*, 2005). In the New Zealand South Island, soils with andic properties (but not Andisols *senso stricto*) also developed from quartzo-feldspathic sandstones and siltstones have been reported to be dominated by Al-rich allophane (Lowe and Palmer, 2005).

2.3. Classification of Andisols

2.3.1. International Classification Systems

Currently, there are several well-known classification systems for these soils. These include the Soil Taxonomy (Soil Survey Staff, 2006), in which they are referred to as Andisols, and the World Reference Base (WRB), jointly devised by the Food and Agriculture Organization (FAO), the International Soil Reference and Information Centre (ISRIC) and International Society of Soil Science (ISSS) (FAO *et al.*, 1998), in which these soils are known as Andosols. In addition, the soil classification systems of New Zealand and Japan are also known to complement the former two. This may be due to the wide coverage of volcanic soils in these countries.

Since the establishment of the Andisol soil order resulting from a proposal by Smith (1978), its classification has been modified several times, following breakthroughs of research on these soils. In Smith's proposal, there were only 6 suborders for the Order Andisols, which included Aquands, Borands, Xerands, Ustands, Tropands, and Udands (Shoji *et al.*, 1994). Later, the suborder Tropands was omitted while the suborder Borands was changed to Cryands. In subsequent modifications, the suborder Vitrands was included (Soil Survey Staff, 1999) and lately another suborder, Gelands, was added to the system (Brady and Weil, 2008). In total, Andisols of the Soil Taxonomy (2006) now consist of 8 Suborders including Aquands, Gelands, Cryands, Torrands, Xerands, Vitrands, Ustands, and Udands, and their respective Great Groups are detailed in Table 1.

Table 1: Suborders and Great Groups of Andisols in Soil Taxonomy

Suborder	Great Groups	Definition
Aquands	Gelaquands	In gelic temperature regime
	Cryaquands	In cryic temperature regime
	Placaquands	Having placic horizon within 100 cm of mineral surface
	Duraquands	Having cemented layer of 70% or more within 100 cm
	Vitraquands	At 100 kPa, having water retention <15% in dried sample
	Melaquands	Having a melanic epipedon
	Epiaquands	Having episaturation
	Endoaquands	Other Aquands (having endosaturation)
Gelands	Vitrigelands	Including all Gelands now
Cryands	Duricryands	Having upper boundary of cemented layer within 100 cm
	Hydrocryands	At 1,500 kPa, air-dried sample has water retention <15%
	Melanocryands	Having a melanic epipedon
	Fulvicryands	Having chroma and value <3, with melanic requirements
	Vitricryands	At 100 kPa, air-dried soil has water retention <15%
	Haplocryands	Other Cryands
Torrands	Duritorrands	Having upper boundary of cemented layer within 100 cm
	Vitritorrands	At 100 kPa, air-dried sample has water retention <15%
	Haplotorrands	Other Torrands
Xerands	Vitrixerands	At 100 kPa, air-dried sample has water retention <15%
	Melanoxerands	Having a melanic epipedon
	Haploxerands	Other Xerands

Vitrands	Ustivitrands	Under an ustic soil moisture regime
	Udivitrands	Under audic soil moisture regime
Ustands	Durustands	Having upper boundary of cemented layer within 100 cm
	Haplustands	Other Ustands
Udands	Placudands	Having a placic horizon within 100 cm of mineral surface
	Durudands	Having upper boundary of cemented layer within 100 cm
	Melanudands	Having a melanic epipedon
	Hydrudands	At 1,500 kPa, air-dried sample has water retention <15%
	Fulvudands	Having requirements of a melanic epipedon
	Hapludands	Other Udands

Source: Soil Survey Staff (2006)

For both the Soil Taxonomy (Soil Survey Staff, 2006) and the WRB (FAO *et al.*, 2014), the consideration of Andisols/Andosols is based on a set of criteria for the fulfilment of andic soil properties, which include phosphate retention, bulk density, and degree of parent material weathering, which is in turn reflected in the amount of oxalate-extractable aluminium (Al_o) and iron (Fe_o). Both classification systems define andic properties by two sets of these criteria, which correspond to well developed and poorly developed Andisols/Andosols (Table 2 describes those specific of the Soil Taxonomy).

Table 2: Definition of andic properties

To be considered as having andic properties, soil materials must contain less than 25% organic C by weight and meet one or both of the following criteria:	
1. In the fine-earth fraction, the following criteria must be met:	• Ammonium oxalate-extractable Alo + ½ Feo ≥ 2%, and • At 33 kPa water retention, bulk density ≤ 0.9 g/cm^3, and • Phosphate retention ≥ 85%; or
2. In the fine-earth fraction, with phosphate retention ≥ 25%, 0.02 – 0.2 mm fraction ≥ 30%, and one of the following must be met:	• Ammonium oxalate-extractable Al_o + ½ Fe_o ≥ 0.4%, and volcanic glass ≥ 30% in 0.02 – 0.2 mm fraction; or • Ammonium oxalate-extractable Al_o + ½ Fe_o ≥ 2%, and volcanic glass ≥ 5% in 0.02 – 0.2 mm fraction; or • Ammonium oxalate-extractable 0.4% < Al_o + ½ Fe_o< 2%, and volcanic glass between 5 and 30% in 0.02 – 0.2 mm fraction.

Source: Soil Survey Staff (2006)

As shown in Table 2, Definition 1 (for glass-poor Andisols) requires that the soil must have the bulk density 0.9 g/cm^3 or less and the phosphate retention of 85% or more. In addition, that soil must have a considerable amount of short-range-order constituents, as reflected by the sum of ammonium oxalate-extractable Al + ½ Fe of 2% (w/w) or more. On the other hand, in Definition 2 (for glass-rich Andisols), these conditions are less accentuated, given the lesser degree of weathering, and as reflected by the presence of volcanic glass in the 0.02 – 0.2 mm fraction (Table 2).

The definitions above solely emphasize the chemical and mineralogical requirements. In addition, Andisols must also meet some other criteria on profile basis, in which the soil must have andic properties in 60% of the top 60 cm, as detailed in Table 3.

Table 3: Definitions of Andisols by profile of Soil Taxonomy

Other soils that possess andic properties 60% or more of the thickness either:	
1. Within 60 cm either of the mineral soil surface or of the top of an organic layer with andic properties, whichever is shallower,	Without: • A duripan, • A densic layer, • A lithic or paralithic contact, • Or petrocalcic horizon within the depth; or
2. Between either the mineral surface or the top of an organic layer with andic properties, whichever is shallower,	With: • A densic layer, • A lithic or paralithic contact, • A duripan, or • A petrocalcic horizon.

Source: Soil Survey Staff (2006)

In contrast, the classification of volcanic soils in New Zealand is intended to ease management purposes. New Zealand volcanic soils were originally classified into 5 orders including Allophanic Soils, Pumice Soils, Granular Soils, Recent Soils, and Podzols (Hewitt, 1989; Shoji *et al.*, 1994). In the most recent classification by Hewitt (2010), volcanic soils that are equivalent to Andisols/Andosols are classified under Allophanic Soils and Pumice Soils for glass-poor and glass-rich Andisols, respectively. The Allophanic Soils are equivalents of Aquands, Cryands, and Udands, while Pumice Soils are Vitrands equivalents of the Soil Taxonomy's Andisols. In New Zealand, these two soil orders cover 7% and 6%, respectively; Pumice Soils may weather to form Allophanic soils (Hewitt and Dymond,

2013). The inorganic constituents of Allophanic Soils are dominated by allophane (Figure 1), imogolite and ferrihydrite, which do not possess the crystalline lattice structure, whereas Pumice Soils considerably contain a dominance of moderately-weathered pumice or pumice sand (Hewitt, 2010). In addition, young volcanic soils in New Zealand are included in the Recent order, which classify as Andic Dystrudepts in the Soil Taxonomy (Lowe and Palmer, 2005). In contrast to other soils, Granular Soils are highly weathered volcanic soils older than 50,000 years, and are mainly dominated by kaolin clay minerals and associated vermiculites as well as hydrous interlayer vermiculites (Shoji *et al.*, 1994).

2.3.2. Allophanic and Non-allophanic Andisols

In the systems above, Andisols are classified based on the presence of diagnostic horizons, and their properties vary depending on degree of weathering, soil moisture regime, temperature regime, and content of SOM. However, for the purpose of management, Andisols are sometimes classified as allophanic Andisols (dominated by allophane, imogolite and ferrihydrite) and non-allophanic Andisols (dominated by organo-Al complexes) (Takahashi and Dahlgren, 2016). In general, non-allophanic Andisols exhibit larger acidity and Al toxicity to plants while these become attenuated in allophanic Andisols (Takahashi *et al.*, 2008). The WRB classifies them as sil-andic Andosols and alu-andic Andosols, respectively (FAO *et al.*, 2014).

There are several parameters that lead to the development of one vs. the other type of Andisol. These are leaching regime – directly linked to environmental acidity – supply of organic ligands, and the existence or absence of 2:1 phyllosilicates (Buol *et al.*, 2011). During the pedogenic transformation, the threshold pH value of 4.9 was described by Dahlgren *et al.* (2004) as the turning point that distinguishes the two pathways for development of either allophanic or non-allophanic Andisols.

In these soils, at pH values above 4.9 (and thus organic acidity is low), Al and Si released during the weathering of aluminosilicates tend to polymerize and precipitate to form short-range-order aluminosilicates such as allophane and imogolite (Dahlgren *et al.*, 2004). In some cases, ferrihydrite, a short-range-order oxyhydroxide of Fe, also forms alongside (Bigham *et al.*, 2002). Henmi and Wada (1976) identified the basic unit of allophane as a hollow spherule with a diameter of 3.5 – 5 nm (Figure 1) whereas that of imogolite was documented to be a hollow tubule with the wall thickness of 0.7 nm and the outer diameter of roughly 2.1 nm

(Parfitt, 2009). A single unit of allophane is composed of an inner layer of silica sheet and an outer layer of gibbsite sheet (Figure 1). Generally, these minerals are collectively referred to as “allophane group” (Lal, 2006). Under some conditions, poorly crystalline smectites are the first products of weathering, and desilication of these weathering products induce the formation of allophane and imogolite (Southard and Southard, 1989). These short-range-order aluminosilicates are subject to subsequent transformations, in which dehydration, structural arrangement, and weak desilication produce halloysite, whereas severe desilication produces gibbsite (Churchman, 2000), although the latter already deprives a horizon of andic properties. Allophane forms under a high rainfall regime (Parfitt and Wilson, 1985), whereas halloysite forms under a low rainfall regime (Parfitt and Wilson, 1985; Lowe, 1986; Churchman, 2000). The formation of allophane may be accelerated by the human-enhanced dissolution of volcanic glass shards, like that induced by the application of acidifying fertilizers such as phosphate (Taylor *et al.*, 2016).

Mineralogically, allophane is categorized into three groups, which are based on the richness of Al and Si, and where this soil constituent is found: Al-rich allophane (Al:Si ratio of ~2); Si-rich allophane (Al:Si ratio of ~1); and stream-deposit allophane (Al:Si ratio of 0.9 – 1.8) (Parfitt, 1990, 2009). It should be noted that allophane (and imogolite) may also be found in non-tephric soils and sediments (Parfitt, 2009), and where favourable environmental conditions permit the synthesis of short-range-order minerals from weathering products of non-volcanic parent materials (Mizota and Van Reeuwijk, 1989).

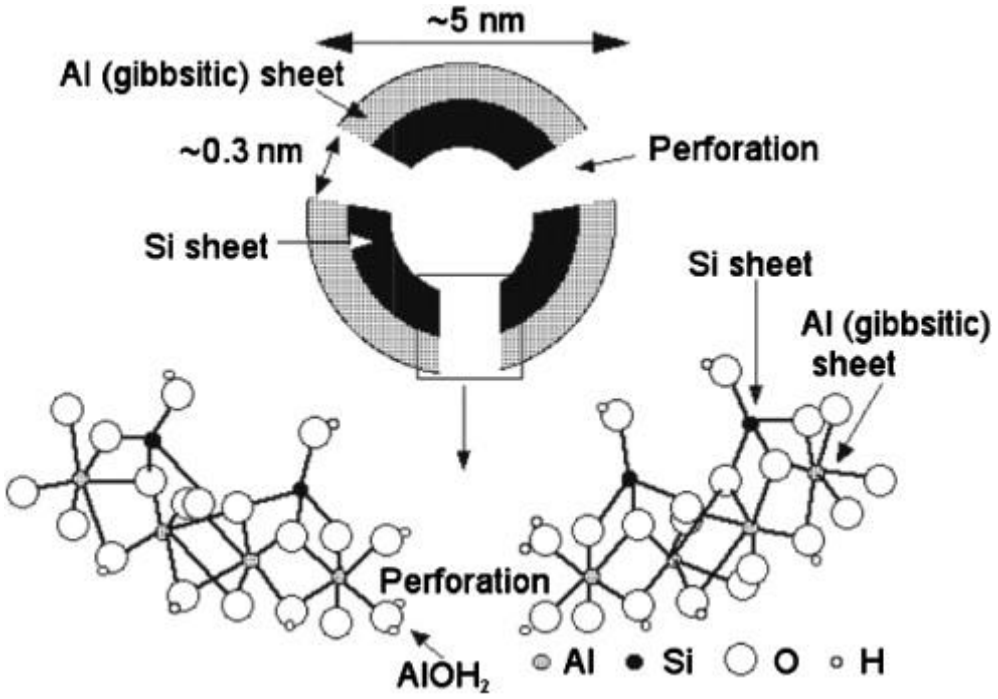

Figure 1: Diagram representing composition and structure of an allophane spherule, from Hashizume and Theng (2007).

The second pathway of formation, leading to formation of non-allophanic Andisols, occurs when the pH value is below 4.9 and organic ligands are abundant. A base-poor volcanic glass, such as rhyolitic, dacitic and andesitic deposits, could be the underlying cause of such an acidic environment (Takahashi and Dahlgren, 2016), but not necessarily, as a high leaching environment may also lead to similar chemical conditions, as well as organic acidity produced from SOM decomposition (Buol *et al.*, 2011). When the pH is below 4.9 organic acids control the pH of the soil, since carbonic acid can only bring the pH down to between 5.1 and 5.5 (Dahlgren *et al.*, 1993). As pH increases, organic acidity decreases, and the pH is then dictated by carbonic acid (p*K*a=6.3) (Dahlgren *et al.*, 1993).

As result of volcanic material weathering, the concurrent release of Si and Al, and the supply of SOM induce a competition between Si and SOM to bind with Al (and Fe) (Dahlgren *et al.*, 2004). At pH values below 4.9, a portion of acid functional groups of organic acids will still be un-neutralised by base cations, and thus facilitating complexation with Al and Fe ions, the concentrations of which increase as pH lowers (Dahlgren *et al.*, 1993). In such circumstances, organo-Al complexes form preferentially, which consequently reduces the availability of Al for co-precipitating with Si in order to form short-range-order minerals like allophane and imogolite (Takahashi and Dahlgren, 2016). Given that the complexation of Al by organic ligands impedes the precipitation of allophane (and imogolite), the formation of organo-Al

complexes is sometimes termed the ‘anti-allophanic effect’, which also broadly includes the incorporation of Al into hydroxyl-Al interlayer of 2:1 phyllosilicates (Dahlgren *et al.*, 1993). Sometimes, the formation of organo-Fe complexes may also occur, but the presence of these tends to be limited, given the high affinity of Fe^{3+} for hydroxyls (Dahlgren *et al.*, 1993).

These two soil types (allophanic and non-allophanic Andisols) are commonly classified based on the relative abundance of Al_p and Al_o. When $Al_p/Al_o < 0.5$, the WRB (FAO *et al.*, 2014) refers to it as sil-andic Andosols, whereas the opposite occurs with alu-andic Andosols. Allophane dominates in the former and organo-Al complexes do so in the latter. Recently, Takahashi and Higashi (2015) proposed the use of sulphate adsorption as the criterion to classify these two soil types. The proposition is derived from the fact that sulphate is preferentially adsorbed by hydrous Al/Fe such allophane, but not by organo-Al complexes. In accordance with the WRB system, they found that all alu-andic (non-allophanic) soils retained sulphate poorly (<60%).

2.4. Properties of Andisols

Andisols possess several distinctive properties compared with other soil orders, some of which are beneficial to agricultural productions but others constitute agricultural production challenges. As already highlighted in the definition of andic properties, these soils have a high ASC, low bulk density, high OM content, stable aggregation, variable charge, thixotropy, high fertility, excellent tilth, high water-holding capacity, and in some instances, acidity and Al toxicity. The unique physical and chemical properties are ascribed to the non-crystalline colloidal constituents and the relatively high OM of the soils (Ugolini and Dahlgren, 2002).

2.4.1. Phosphate Retention

Andisols, by definition, have phosphate retention greater than 85%, which is due to the presence of a colloidal fraction dominated by variable-charge constituents. These are allophane, imogolite, and organo-Al complexes in allophanic Andisols while organo-Al complexes are dominant in non-allophanic soils; ferrihydrite may dominate in both soil types (Takahashi and Dahlgren, 2016). Allophane is able to adsorb 2–8 P oxyanions per spherule, and, as P oxyanions covering the surface increases, the additional P ions will become weakly adsorbed (Parfitt, 2009). Mechanistically, adsorption occurs through the binding of P oxyanions to the Al-OH/Fe-OH via ligand exchange reactions (Harsh *et al.*, 2002) at defect

sites on the allophane spherule surface (Parfitt, 2009). Similarly, the ligand exchange reactions that are responsible for P adsorption also happen between orthophosphate anions and Al associated to organo-Al complexes (Appelt *et al.*, 1975). Comparatively, non-allophanic Andisols retain more P than allophanic Andisols (Parfitt, 2009) due to the relative abundance of reactive Al-OH groups in organo-Al complexes (Dahlgren *et al.*, 2004).

As a consequence of sorption reactions, P concentration in soil solution is relatively low, limiting plant-available P forms (Buol *et al.*, 2011). This represents a challenge for agricultural production. Several management methods are carried out to overcome this barrier, including fertilizer application (adequate dose, timing, and selection of fertilizer) and liming. The utilization of P fertilizer in the form of large pellet superphosphate has been found to improve P fertilizer efficiency (Buol *et al.*, 2011). By increasing the soil pH, phosphate becomes a weaker ligand compared with hydroxyls. These tend to precipitate with Al forming Al hydroxides thus ameliorating P deficiency (Takahashi and Dahlgren, 2016).

2.4.2. Low Bulk Density

Low bulk density is another typical characteristic of Andisols/Andosols. In both Soil classification systems (Soil Survey Staff, 2006) and WRB (IUSS, 2014), the bulk density is set to be at most 0.9 g/cm^3. This bulk density is the lowest of all mineral soils and only organic soils have lower bulk density than Andisols (Nanzyo, 2002). In some cases, a bulk density as low as 0.3 g/cm^3 has been reported (Mizota and Van Reeuwijk, 1989). Such a bulk density is due to the presence of well-structured aggregates of short-range-order constituents and SOM (Nanzyo, 2002). Since allophane has a particle density as high as other phyllosilicate minerals (Wada, 1989), the low bulk density of these soils is only explained by the presence of porous clusters of allophane spherules (Asano and Wagai, 2014; Huang *et al.*, 2016) and their close association with SOM (Nanzyo, 2002). As the formation of short-range-order constituents progresses, there is a relative decrease in macropores and a concomitant increase in micropores (Nanzyo, 2002). Due to this physical property, Andisols/Andosols are known to possess excellent tilth and sustain high live weight loadings.

2.4.3. SOM Accumulation

Andisols/Andosols contain large amounts of SOM, with C concentration of up to 200 g C/kg soil (Nanzyo, 2002). Compared with other mineral soil orders, Andisols have the potential to accumulate the highest amount of SOM (Dahlgren *et al.*, 2004). SOM in these soils is

considered to have a longer mean residence time than other mineral soils (Takahashi and Dahlgren, 2016). Globally, these soils covers only 0.8% of the land mass, but they contain around 1.8% of the OM stocks (Takahashi and Dahlgren, 2016). The relatively high SOM observed in these soils has an interdependent relationship with their widely-recognized high fertility. As plants can grow well in Andisols, the vegetation returns large amount of detritus input back in the form of plant litters (Dahlgren *et al.*, 2004). This, in turn, tends to be chemically stabilised through interactions with short-range-order constituents (Yuan *et al.*, 2000) and also physically protected within the porous structure (Chevallier *et al.*, 2010). In addition, the burial of surface layers of a precedent soil by fresh volcanic materials from new eruptions buries topsoil rich in SOM, and this contributes to the slow down its decomposition (Ugolini and Dahlgren, 2002). Similarly, grassland fire, common in Japanese Andisols, further contributes to C stabilisation through the formation of charcoal, which gives the dark colour of the A horizon of these soils (Ugolini and Dahlgren, 2002). In terms of the chemical composition of SOM, Buurman *et al.* (2007) revealed that allophanic Andisols had a large fraction of microbially processed SOM. Similar results have been reported in non-allophanic Andisols (Suárez-Abelenda *et al.*, 2011).

2.4.3.1. Chemical Protection of SOM

In many instances, the chemical protection of SOM involves complexation reactions of organic ligands with Al cation and adsorption of these ligands onto reactive surfaces, dominated by Al-OH (Nanzyo, 2002; Ugolini and Dahlgren, 2002) and are referred to as reactive Al. Reactive Al includes Al in short-range-order aluminosilicates such as allophane and imogolite, interlayer hydroxy-Al ions in phyllosilicates, and organo-Al complexes and exchangeable Al ions on phyllosilicates (Wada, 1980). Interaction of reactive Al with organic ligands could occur not only through the formation of inner-sphere complexes (ligand exchange), but also through that of outer-sphere complexes (including proton and other cations bridging), and van der Waals type of interactions (Kleber *et al.*, 2015). The adsorption of organic ligands on allophane occurs at the OH groups of silanol and aluminol in defect surfaces, which are referred to as acid centres, and unsaturated Al^{3+} at coordination spots (Filimonova *et al.*, 2016). At low pH values, inner-sphere complexes are formed, whereas as pH increases, weaker outer-sphere complexes may dominate (Kleber *et al.*, 2015), suggesting that protection of SOM by this mechanism is less effective (Huygens *et al.*, 2005; Matus *et al.*, 2009; Verde *et al.*, 2010).

The sorption of negatively charged organic ligands onto the surface of allophane has been shown to increase the negative surface charge of the mineral (Parfitt, 2009), thus the cation exchange capacity of the soil (Fig. 2a; Yuan *et al.* (2000). Also, these organo-Al interactions protect SOM from microbial attack (Tokashiki and Wada, 1975; Ugolini and Dahlgren, 2002), mostly due to the increase of energy needed to be invested by microbes to break the organo-Al bonds (Boudot *et al.*, 1989), as well as the fact that the complexation renders organic-containing functional groups more condensed, and therefore, less susceptible to microbial mineralization (Baldock and Nelson, 2000). Monomeric Al (i.e. Al^{3+}) can also impair microbial decomposition of SOM (Miyazawa *et al.*, 2013), but its toxicity decreases once complexed with organic ligands.

SOM content of these soils tend to relate linearly to Al extractable with pyrophosphate (Al_p) instead of clay (Percival *et al.*, 2000; Nanzyo, 2002). This reagent extracts Al that is found complexed by organic ligands. The degree of saturation of OM with Al is inferred from the molar ratio of Al_p to C_p (Blakemore *et al.*, 1987; Matus *et al.*, 2008), which tends to be between 0.1 and 0.2 at its maximum capacity (Higashi, 1983; Buurman, 1985). For most A horizons of Andisols, the molar ratios of Al_p:C_p have been reported to be between 0.05 and 0.2, and the molar (Al_p + Fe_p)/C_p ratios range between 0.1 and 0.2 (Inoue *et al.*, 1988; Dahlgren *et al.*, 1993). Higher values suggest the presence of polymeric Al (Camps Arbestain *et al.*, 2003).

2.4.3.2. Physical Protection of SOM

Conceptually, soil aggregation and aggregate arrangement based on the aggregate hierarchy model developed by Oades and Waters (1991), are known to limit access of OM decomposers (Gregorich and Janzen, 2000). However, in the past decades, the mechanism of protection in Andisols has been questioned, given that the aggregate hierarchy model did not work adequately with these soils (Paul *et al.*, 2008; Candan and Broquen, 2009). The puzzle has been partially solved by Asano and Wagai (2014), who found that in Andisols, aggregates followed the hierarchy model at micron and submicron levels. This has been supported by the results of Huang *et al.* (2016) and Chevallier *et al.* (2010). The latter proved the fractal pore structure (Figure 2c) of allophane clusters and the associated pore system responsible for entrapping and stabilising SOM. Filimonova *et al.* (2016), using xenon isotope and nuclear magnetic resonance technology (^{129}Xe NMR), proposed the presence of four types of pores in the system to be important for SOM adsorption: *pore type I or micropores* (pores between

primary allophane nanospherules; 0.92 nm in diameter); *pore type II or meso- or macropores* (pores between allophane aggregates); *pore type III or ultra-micropores* (pores of allophane wall perforations; 0.6 nm in diameter); and *pore type IV* (interiors of primary allophane spherule) (Figure 2b), although the latter is quite unlikely (Benny Theng, Landcare Research, per. comm.).

2.4.3.3. Other Mechanisms of SOM Protection

Additional mechanisms of SOM protection include sorption and deactivation of exoenzymes (Saggar *et al.*, 1994; Matus *et al.*, 2014), and the presence of recalcitrant charcoal, which, as above-mentioned, is common in Japanese Andisols under grasslands (Shindo *et al.*, 2002). Andisols tend to have a relatively smaller microbial biomass C out of total C, because the fraction of SOM that is available to microbes out of total SOM is lower than that of other soils. Additional factors contributing to this may include their low pH, Al toxicity, low phosphate status, and low base cation content. Interestingly, and also as indicated above, SOM in these soils tends to be more decomposed than in other soils, as a greater fraction of the organic molecules have been microbially processed (Buurman *et al.*, 2007).

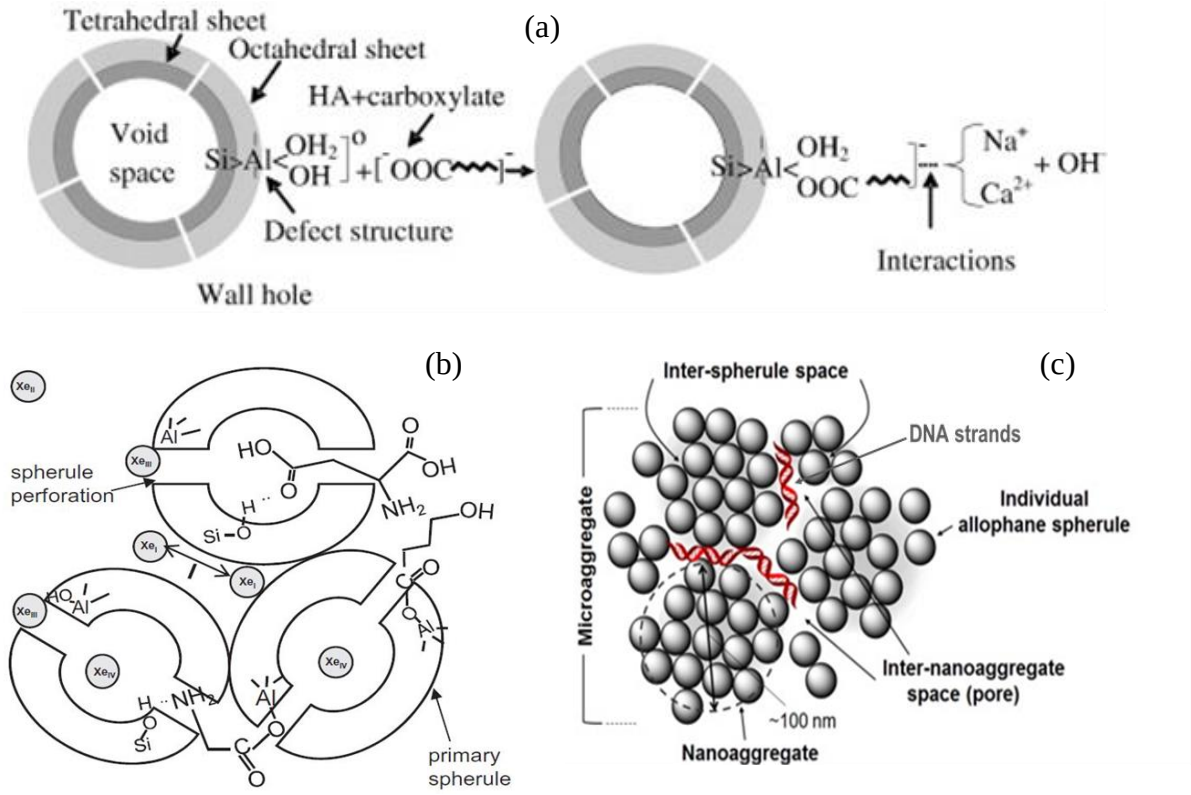

Figure 2: Diagrams showing (a) A transversal view of a hypothetical allophane spherule and organic substances with carboxylate groups (COOH) show a ligand exchange mechanism and Na^+ or Ca^{2+} electrostatic interactions, from Matus et al. (2014); (b) schematic illustration of adsorption model of allophanic soil by ^{129}Xe nuclear magnetic resonance showing pore type I (Xe_i), pore type II (Xe_{ii}), pore type II (Xe_{iii}) and pore type IV (Xe_{iv}), from Filimonova et al. (2016); and (c) adsorption of DNA in fractal pore structure of allophane spherules, from Huang et al. (2016).

2.4.4. Aggregate Stability

Compared with other soil orders, Andisols are resistant to soil erosion because of the presence of stable aggregates that gives the soil high permeability and thus rapid surface water percolation (Buol *et al.*, 2011).

2.5. Changes in Soil Properties due to Land Use Intensification

The effect of land use on Andisols/Andosols properties is still poorly understood. On the one hand, it has been proposed that, compared with other mineral soils, these soils are physically very resilient due to highly stable aggregates and to their ability to stabilize SOM (Saggar *et al.*, 1994; Parfitt *et al.*, 1997b); Matus *et al.* (2014) hypothesized that land use changes had little impact on the SOM stabilization capacity of these soils. On the other hand, results from an increasing number of studies (Johnson-Maynard *et al.*, 1997; Verde *et al.*, 2005; Verde *et al.*, 2010) in which changes in Andisols/Andosols properties have been monitored following medium-term land use conversion and management practices do not support the above assumptions. Verde *et al.* (2005) found that conversion of Andisols under forest land use to agricultural use decreased SOM by 50% and increased soil pH significantly as a result of liming and fertilization practices. Aluminium in the forms of complexes (extracted by $CuCl_2$ and sodium pyrophosphate), and poorly crystalline and crystalline inorganic constituents (extracted by oxalate and NaOH, respectively) also decreased significantly. Their results suggested that these soils can lose some of andic properties after land use change. A study by Takahashi *et al.* (2006) also agreed that liming reduced organically complexed and exchangeable Al, thus increasing the cation exchange capacity (CEC) associated with variable charge constituents. Further, a study on forest alu-andic Andosols by Verde *et al.* (2010) observed that simulated “agricultural management practices” such as tillage, liming, fertilization, and higher temperature fluctuations associated with the absence of plant cover led to the attenuation of some soil andic properties, especially by decreasing SOM content and organo-Al complexes. These findings suggest that Andisols/Andosols properties are not as stable as previously thought, and that their colloidal fraction is affected on conversion from forest to agricultural land use.

At the colloidal level, allophane and organo-Al complexes can coexist in the soil profile of Andisols/Andosols. In nature, the colloidal Al fraction generally forms a continuum from pure allophane to pure organo-Al complexes (Takahashi and Dahlgren, 2016). Compared with deeper horizons, topsoil is exposed to plant residue accumulation, to the detriment of

allophane formation. This explains why it is not unusual to observe that organo-Al complexes co-exist with allophane in the A horizon of Allophanic soils, with allophane increasing in the B horizon (Takahashi and Dahlgren, 2016). Similarly, in non-allophanic soils, allophane may also be found in lower horizons (Dahlgren *et al.*, 2004).

Allophanic Andisols can evolve to non-allophanic Andisols and vice versa. This transformation depends much on the chemical environment of the soil, in which pH plays a prominent role. Such change can be caused by land use change and management. Takahashi *et al.* (2008) reported the conversion of allophanic to non-allophanic soils of a tea garden, where the alleyway became acidified upon application of ammonium fertilizer, causing an increase in organo-Al complexes at the expense of allophane. These changes are not only confined to the application of chemical substances, but may also be induced by plants. Johnson-Maynard *et al.* (1997) observed a similar transformation 30 years after the establishment of bracken ferns (*Pteridium aquilinum* L.) on allophanic soils in a site where native grand fir (*Abies grandis* L.) forest was originally grown.

The content of SOM is one of the most important properties of Andisols/Andisols that become affected following land use change to a more intensive system. Based on the studies described above, it can be understood that the stability of SOM, and that of short-range-order constituents and organo-Al complexes, is strongly influenced by chemical changes in the soil system, which may be induced either by application of soil amendments or by changes in vegetation type.

2.6. C Sequestration, C input belowground, and Properties Changes in the Rhizosphere

Photosynthetic C is ultimately the primary source of soil C. Pedospheric SOM can act either as a source or sink of C (Fernandes *et al.*, 1997). An increase in the amount and persistence of SOM, and thus in its mean residence time, would contribute to mitigating CO_2 emissions. Studies are being conducted worldwide – as part of the concerted effort of the international community to combat global warming and address food security (Sweeney *et al.*, 2011) – to better understand how SOM is stabilized in soils and how management practices can help build up SOC stocks.

2.6.1. C Sequestration from a New Zealand Perspective

Dairy farming has become the dominant primary livestock industry sector in New Zealand and also the largest source of GHG emissions nationally. Efforts are being made to reduce nitrous oxide and methane emissions from pastoral systems, but current evidence suggests soil C sequestration as a feasible short-term option to mitigating GHG emissions from the New Zealand dairy sector (Lawrence-Smith *et al.*, 2015). New Zealand soils are generally rich in SOM (Schipper *et al.*, 2010; Schipper *et al.*, 2014). Release of CO_2 from soil to the atmosphere through adverse management or environmental changes would contribute to further losses. It may be possible to increase C stocks through a better understanding of the mechanisms involved in stabilising C in these soils.

Historically, surface horizons have gained C on conversion from native forest to legume-based grassland, triggered by the application of plant-limiting nutrients to the system (Guo and Gifford, 2002) and the C input from the dense rooting system of pasture species. However, losses of some C from grassland soils – especially from those with the largest C stocks (e.g. Allophanic soils) – have recently been reported (Schipper *et al.*, 2014).

As pastures nationwide are commonly covered by mixtures of white clover (*Trifolium repens* L.), perennial ryegrass (*Lolium perenne* L.) and a variety of other forage species, the understanding of how these species contribute to the sequestering of soil C is of paramount importance. Much has been said of the role played by their root systems in aggregating soil particles, thus protecting SOM, and as the source of SOM *per se*. In an experiment intended to compare the relative contribution of root systems from both species to soil aggregation, Tisdall and Oades (1979) found that perennial ryegrass was more effective than white clover in stabilizing soil aggregates due, in part, to mycorrhizae contribution. The authors also reported that polysaccharides from mycorrhizal hyphae contributed to soil aggregation. However, this study fell short of reporting the relative contributions of these two species to SOM content.

2.6.2. C Input Belowground and Rhizodeposition

It has been recently demonstrated that soil C is mostly root-derived (as opposed to aboveground materials) (Rasse *et al.*, 2005), and therefore in order to increase soil C, a better understanding of root C contribution to SOM is needed. The architecture of root systems (Nielsen *et al.*, 1994; Warembourg *et al.*, 2003) and the depth that roots can reach (Dodd *et*

al., 2011) have a clear influence on C allocation below ground. The use of deep-rooting plant species has in fact been proposed as an alternative to enhance soil C storage (Crush and Nichols, 2010; Powlson *et al.*, 2011), although some work has shown that the supply of SOM in a deeper layer may accelerate decomposition of ancient SOM (Fontaine *et al.*, 2007). The interest in growing roots at depth lies in the fact that soil is generally less C-saturated deep in soil than the surface horizon (Hassink, 1997; Six *et al.*, 2002).

Dodd *et al.* (2011) measured root mass contribution of mixed New Zealand pasture species and found that at a 0 – 7.5 cm depth, root mass was significantly greater in non-allophanic soils (Te Kowhai silt loam) than in allophanic soils (Horotiu silt loam). Moreover, root mass of non-allophanic subsoils was significantly higher in plots without N fertilizer than in those where fertilizer was added. The study concluded that the soil layer from 0 to 10 cm is a viable zone for manipulating OM, either by choosing the most suitable pasture species or by modifying soil properties. In this regard, compared with white clover roots, ryegrass roots are a prominent source of OM in pastures, at least on root mass basis. For a long-lasting C preservation, however, root C will need to become stabilised through chemical and physical protection mechanisms in the soil.

There is an increasing interest in investigating the chemistry of the compounds released by plants in the rhizosphere (Table 4). The rhizosphere concept was first developed by Hiltner (1904), who defined it as the zone close to the root, recognized by intense microbial activity and now known as the "volume of soil affected by the presence of living roots", which usually extends from 1 to 2 mm from the root (Gregory, 2007). As the definition suggests, salient features of the zone are marked by the many interlinked and complex interactions between the root and the microenvironment, especially the release of C compounds from the plant.

Table 4: Organic compounds exuded into rhizosphere

Group	Compounds
Sugar and polysaccharides	Arabinose, fructose, galactose, glucose, maltose, mucilage of various compositions, oligosaccharides, raffinose, ribose, sucrose, xylose
Amino acids	α-Alanine, β-alanine, γ-aminobutyric, arginine, aspartic, citrulline, cystathionine,

	cysteine, cystine, deoxymugineic, 3-epihydroxymugineic, glutamine, glutamic, glycine, homoserine, isoleucine, leucine, lysine, methionine, mugineic, ornithine, phenylalanine, praline, serine, threonine, tryptophane, tyrosine, valine
Organic acids	Acetic, aconitic, ascorbic, benzoic, butyric, caffeic, citric, p-coumaric, ferulic, fumaric, glutaric, glycolic, glyoxilic, malic, malonic, oxalacetic, oxalic, p-hydroxy-benzoic, propionic, succinin, syringic, tartaric, valeric, vanillic
Fatty acids	Linoleic, linolenic, oleic, palmitic, stearic
Sterols	Campesterol, cholesterol, sitosterol, stigmasterol
Growth factors	p-Amino benzoic acid, biotin, choline, N-methyl nicotinic acid, niacin, pantothenic, vitamins B1 (thiamine), B2 (riboflavin) and B6 (pyridoxine)
Enzymes	Amylase, invertase, peroxidase, phenolase, phosphatases, polygalacturonase, protease
Flavonones	Adenine, flavonone, guanine, uridine/cytidine
Miscellaneous	Auxins, scopoletin, hydrocyanic acid, glucosides, unidentified ninhydrinpositive compounds, unidentified soluble proteins, reducing compounds, ethanol, glycinebetaine, inositol and myo-inositol-like compounds, Al-induced polypeptides, dihydroquinone, sorgoleone

From Uren (2007)

Usually, these compounds are collectively termed “rhizodeposits”, which include low-molecular weight, water-soluble compounds released without involving metabolic pathway

(e.g. glucose), high-molecular weight secreted by metabolic pathway (e.g. polysaccharide mucilage and enzyme), lysates of sloughed-off root cells, and gases (e.g. CO_2, ethylene and hydrogen cyanide) (Gregory, 2007). Usually, gases – despite their key role in root and microbial respiration – are not considered because they are emitted to the atmosphere, although the high solubility of CO_2 in solution contributes to charge balance mostly as HCO_3^- and to solution pH. Organic compounds induce chemical, physical, and biological changes surrounding the roots (see below) (Mimmo *et al.*, 2014), and the alterations subsequently affect ecosystem functioning and plant productivity (Philippot *et al.*, 2013). Organic substances deposited belowground may also be classified based on their chemical composition or function, but generally these classifications attempt to cover sloughed-off root cap and border cells, mucilage, and exudates (Figure 3).

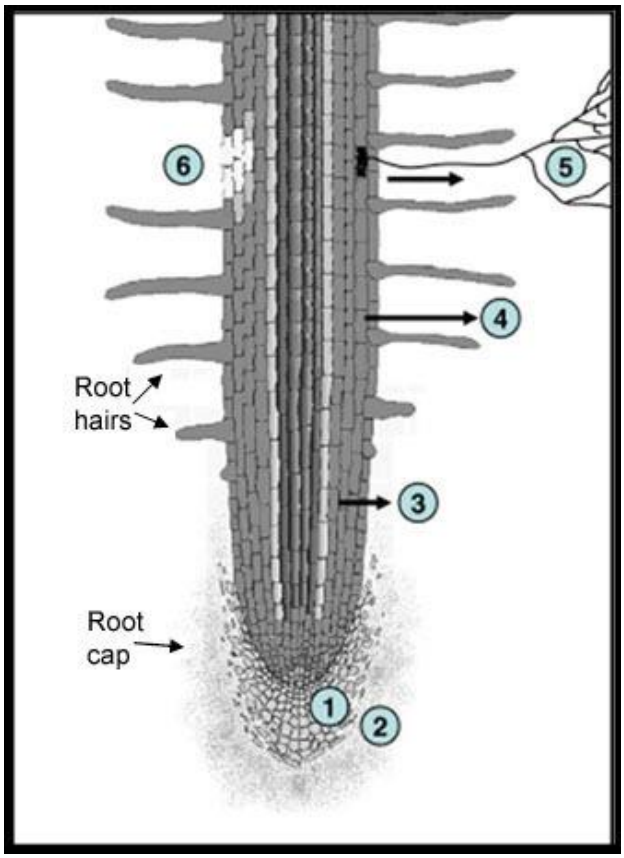

Figure 3: Illustration of a root showing major regions of rhizodeposits. 1) loss of cap and border cells, 2) loss of insoluble mucilage, 3) loss of soluble root exudates, 4) loss of volatile organic compounds, 5) loss photosynthates to symbionts, and 6) loss of death and lysis of root epidermal, from McNear Jr (2013).

In general, plants exude a large amount of photosynthetically fixed C into the soil. Typically, rhizodeposition makes up 40–60% of C assimilated from the atmosphere (Lynch and Whipps,

1991; Högberg *et al.*, 2001; Keiluweit *et al.*, 2015). Studying the C allocation of wheat, barley, maize, mustard, tomato, and pea belowground, Lynch and Whipps (1991) estimated that 40–90% of C translocated belowground was lost as rhizodeposition and respiration of roots and associated microbes. In a field experiment, Keith *et al.* (1986) found that wheat rhizodeposits were equivalent to 1.3 tonnes C/ha annually. The exudation of these organic compounds was reported to be higher in mycorrhizal than non-mycorrhizal plants, but the C cost to the plant was compensated for by the benefits provided by this symbiotic relationship, which enhances photosynthesis (Reid *et al.*, 1983; Lynch and Whipps, 1991; Barber, 1995; Allen, 2007). Merckx *et al.* (1985) observed that C exudates released from wheat roots were incorporated into microbial biomass, but Kuzyakov and Cheng (2001) found that only some of this C was assimilated into microorganisms and that most of the exuded compounds were microbially respired. These findings are consistent with a study on cereals by Nguyen *et al.* (1999), who found that out of the fixed C that was transferred to belowground tissues, 10–30% built up in roots, 10-20% was microbially respired in the rhizosphere, while only 1–5% was assimilated into organic materials and microbial biomass in the rhizosphere. Although C contribution to microorganisms is relatively small, this C pool can be hypothesized to increase in response to enhanced root exudation as the exudates are an important substrate for these organisms (Gregory, 2007).

The type of plant species also has an influence on rhizodeposition and C allocation, which is in turn dependent on stages of development. Warembourg *et al.* (2003) conducted a study on C partitioning in the rhizosphere of 12 plant species in different families, which involved grasses (Poaceae), legumes (Fabaceae), and non-legume forbs (Asteraceae, Rosaceae and Lamiaceae), and included annual, biannual, and perennial species. Consistent with the studies discussed above, this research reported that C transferred belowground varied from 41% to 76% of that fixed from the atmosphere. Out of the total biomass, root C was significantly lower in legumes (35%) than in grasses and non-legume forbs (43%). Annual plants translocated 70% C belowground, compared with 69% for biennials and 59% for perennials. This contrasts with the results of Lynch and Whipps (1991), who reported that perennial plants invested more primary products in roots than annual plants in order to survive prolonged stress, and also in line with the research by Van Veen *et al.* (1991). However, Warembourg *et al.* (2003) was aware of the anomaly and pointed out that the discrepancy might be due to the exclusion of respiration and exudation (rhizosphere losses) in those studies, and the variable C partitioning by plants at different stage of development.

Warembourg and Estelrich (2001) found that the C lost through respiration and exudation in the rhizosphere was greater in annuals than in slow-growing perennials. The relatively high C allocated belowground by annuals found by Warembourg *et al.* (2003) seems to explain the larger C loss in the rhizosphere of annuals than perennials (Warembourg and Estelrich, 2001).

Some research has been specifically conducted on the below-ground C allocation of legume and ryegrass. Compared with other systems, clover-grass pastures augment SOM through a dense fine root systems, high rhizodeposition, and low disturbance by agricultural machinery (Tisdall and Oades, 1979). For rhizodeposition, de Neergaard and Gorissen (2004) reported that ryegrass (*Lolium perenne* L.) allocated up to 52% of fixed C to belowground tissues, compared with just 36% by clover (*Trifolium repens* L.), and that root-derived compounds from clover decomposed more rapidly than those from the grass. The finding is consistent with a study by Minchin *et al.* (1981), who reported that 30–50% of net C fixed by legumes was transferred to roots, of which 63–79% was lost. Clover exudates were found to become rapidly converted from incorporation in microbial biomass to soil whereas those of ryegrass were retained longer within microbial cells (de Neergaard and Gorissen, 2004). However, the longevity of root exudates of these two species in the soil is not yet known.

In summary, it is known that plants release many organic compounds into the rhizosphere and that, in order to understand the substrate flow in the rhizosphere, rhizodeposits have to be analysed (Lynch and Whipps, 1991). These authors also highlighted the difficulties of budgeting the rhizosphere C due to the many interactions of different C pools, as priming effects are common (Kuzyakov, 2010; Kuzyakov and Blagodatskaya, 2015). These effects result from the enlarged overall microbial activity associated with the higher available energy and nutrients in fresh OM (Fontaine *et al.*, 2003), which triggers the decomposition of native SOM (Fontaine *et al.*, 2003; Paterson, 2003; Keiluweit *et al.*, 2015). This has been shown to be influenced by the type of plant species and the C:N ratio of the exudates (Keiluweit *et al.* (2015).

2.6.3. Biological and Chemical Changes in the Rhizosphere

The rhizosphere is recognized as having clearly distinct biological, physical and chemical properties compared with the bulk soil. While the biological and chemical properties of the rhizosphere are often studied, this is not the case for rhizosphere physical properties

(Gregory, 2006), despite their important implications for water and solute movement (Gregory and Hinsinger, 1999).

2.6.3.1. Biological Characteristics of the Rhizosphere

From the biological aspect, the rhizosphere is a relatively active site where microbial activity is especially stimulated compared with the bulk soil, and some researchers refer to it as "microbial seed bank" (Lennon and Jones, 2011; Philippot *et al.*, 2013). This is critical for both SOM stability and plant mineral nutrition, as (i) intense microbial activity and associated enzymes will accelerate SOM decomposition (Das and Varma, 2010) and (ii) the secretion of exudates, such as phytosiderophores, increases the availability of nutrients to plants and microbes (Mimmo *et al.*, 2014). In a study on the microbial community structure in the root zone of ryegrass and white clover, Sarathchandra *et al.* (1997) found that their rhizospheres were dominated by r-strategists, compared with the dominance of K-strategists in the rhizoplane, which is defined as the external surface of the root. Fontaine *et al.* (2003) defined r-strategists microorganisms as those whose growth is very responsive to the availability of fresh OM (FOM), and K-strategists as those that can feed on bulk SOM. Sarathchandra *et al.* (1997) concluded that bacterial communities inhabiting the rhizoplanes of ryegrass and white clover might be unique and utilize specific compounds exuded from the roots.

2.6.3.2. Chemical Characteristics of the Rhizosphere

The rhizosphere is characterised as having several distinctive chemical properties, including gradients in ionic concentrations and pH changes (Gregory and Hinsinger, 1999).

2.6.3.2.1. Ionic Concentration Changes in the Rhizosphere

Large differences in ionic concentration between bulk and rhizosphere soil have been reported, these being element specific. In the case of nutrients such as calcium and magnesium, a relatively high concentration of these elements was observed in the rhizosphere of radish compared with that of the bulk soil of sandy loam (Lorenz *et al.*, 1994), whereas potassium in a sandy and silt loam study (Claassen and Jungk, 1982), nitrogen (N) in a study involving a wide range of soil texture (Scherer and Ahrens, 1996), and phosphorus (P) in nutrient media (Trolldenier, 1992) were reported to be depleted in the area surrounding roots. Camps Arbestain *et al.* (2003) investigated the rhizosphere chemistry of acid forest soils and compared it with that of the bulk soil and found key differences in elemental concentrations.

2.6.3.2.2. pH Changes in the Rhizosphere

The most well-known factor that determines pH in the rhizosphere is the ionic form of nutrients absorbed by plants, especially that of N. For example, it is widely observed that when plants take up more cations (e.g. NH_4^+) than anions (NO_3^-), the rhizosphere is acidified, but it is alkalinized when more anions are absorbed, given the charge the balance needed for these processes occurring (Gregory, 2007). In the case of legumes, more cations than anions are taken up, thus acidifying rhizosphere despite the fact that electrically neutral, negative and positive forms of N may be assimilated (McLay *et al.*, 1997; Tang *et al.*, 2001). In an experiment involving phosphate rocks, N sources and plant species (ryegrass, *Lolium rigidum* L. and clover, *Trifolium subterraneum* L.), Hinsinger and Gilkes (1997) found that the rhizosphere of both species was slightly acidified when nitrate was supplied, but when fed with ammonium, the drop of rhizosphere pH was more accentuated. The authors also reported that for the ammonium treatment, the acidification was more pronounced in ryegrass rhizosphere than in clover. It can be concluded that both species and forms of supplied nutrients are factors influencing rhizosphere pH adjustment.

Furthermore, changes in rhizosphere pH can also be caused by organic anions being released from the root, but the net effects of these are complex to evaluate. Due to the relatively low dissociation constants of organic acids compared with the circumneutral pH in the root cell cytosol, their base conjugates are released instead of the corresponding acid forms. This triggers an electrical balance by an influx of OH^- or an efflux of H^+, thus acidifying the rhizosphere (Hinsinger *et al.*, 2003). In contrast, the rhizosphere is alkalinized if organic anions are protonated at the root-soil interface (Jones and Darrah, 1994). However, this is a simplified explanation, given that in some instances the efflux of protons can be associated with organic anions (e.g. citrate) (Dinkelaker *et al.*, 1989). Overall, organic anions make an important contribution to the rhizosphere cation–anion balance.

Another factor that influences soil pH is carbon dioxide (CO_2). Concentration of CO_2 in soil is 30 to 100 times that is in the atmosphere (Norstadt and Porter, 1984; Hinsinger *et al.*, 2003), as a result of root respiration and microbial decomposition of SOM (Hinsinger *et al.*, 2003). The CO_2 molecule dissolves and reacts with water to form carbonic acid (H_2CO_3), which tends to deprotonate at the pH values of most soils. The acidity generated will tend to be balanced by cation exchange reactions and mineral dissolution (Oh and Richter, 2004). If these are subsequently leached out of the system, the soil is acidified (Oh and Richter, 2004).

The acidity contribution by CO_2 to very acidic soils is negligible, however, as H_2CO_3 will be formed (Hinsinger *et al.*, 2003) and organic acids then become the dominant pH buffers.

Redox reactions are also of paramount importance in rhizosphere pH. Soil redox potential is the measurement of electron availability in the soil system (DeLaune and Reddy, 2005). During redox reactions, protons may either be produced or consumed, thus modifying soil pH. A well-known redox reaction in soil is the reduction of mineral iron, which is proton-consuming. In this phenomenon, a Fe^{3+}-bearing mineral such as goethite (FeOOH) is reduced with a concomitant consumption of 3 moles of protons per mole goethite reduced (Hinsinger *et al.*, 2003), thus alkalinizing the microsite. The alkalinization resulting from such redox processes may be neutralised by protons released from the roots, and/or soil pH-buffering mechanisms.

2.7. Conclusion and Research Gap Identified

In summary, from the review above, it is recognised that Andisols/Andosols, due to their high natural fertility, contain a large C stock compared with other mineral soils, which allows plants to grow well along with the presence of reactive surfaces able to increase the persistence of organic molecules in soil. Mechanistically, SOM in these soils is protected by complexation with metals (Al and, to a lesser extent, Fe), adsorption onto short-range-order constituents (i.e. allophane and imogolite), and entrapment within soil aggregates. SOM and andic soil properties are vulnerable to chemical perturbations and management practices. A recent study found that New Zealand Allophanic Andisols (along with Gley soils) under pasture land use, but not other soil orders, are losing some SOM, and the losses have been suggested to be caused by chemical changes associated to their use (Schipper *et al.*, 2014).

The current study aimed to investigate whether types of land use and degrees of management intensification in Andisols have an effect on their chemistry and SOM stability, with special attention to that of organo-mineral complexes. The study involved the sampling of soils of a Taranaki farm under different land uses (pine forest and clover-ryegrass pasture) and pasture under different management intensification regimes. It was hypothesized that the addition of amendments such as effluents, fertiliser, and lime causes changes in the chemistry of Andisols/Andosols, affecting the stability of organo-mineral complexes, and this has implications to soil C stability.

3. Materials and Methods

3.1. Soil Sampling

The soil sampling was carried out on February 9, 2016 in a farm located in Hawera, Taranaki, New Zealand (39°35'18.0"S and 174°21'54.2"E) (see map in Photo 1). The site is on the Ngarino uplifted marine bench and the soils are Egmont loam soils formed on andesitic tephra. The samples were taken at 0–7 cm depth from three different locations (less than 500 m apart) in the same farm: (1) pine forest stand (*Pinus radiata* L.) (*Pine*); (2) pasture located far away from the milking shed (*Paddock 1*); and (3) pasture located closer to the milking shed (*Paddock 2*). Both paddocks received farm effluents, but Paddock 2 was under a more intense management regime and received effluent a few weeks before sampling. Ideally, soil under native forest should have been sampled instead of soil under pine, as the two paddocks were originally converted from native forest, but this was not possible. In the current study, the *Pine* soil represented a non-intensified site. As the pine stand occupied a small surface area at the edge of the road (*Pine* stand, 1 ha; *Paddock 1*, 8 ha and *Paddock 2*, 3 ha) only five soil samples were taken – for this, pine litter was removed before sampling. In the two pastures, seven sites were sampled along a transect. At each site, separate soil blocks (7 cm × 20 cm × 20 cm) under perennial ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) were taken. Soils were then transported intact from the field to the laboratory and stored in a cool room < 4℃ before processing.

Photo 1: Map of the farm showing the three sampling sites (Google Earth).

3.2. Rhizosphere Separation

Bulk and rhizosphere soils were separated from fresh samples following the procedures of (Chung and Zasoski, 1994; Camps Arbestain *et al.*, 2003). Briefly, above-ground stems were used to track living roots in the sample block ($7 \times 20 \times 20$ cm^3); these were then taken with tweezers and shaken to eliminate the soil loosely attached to them. Roots were then air-dried and thereafter shaken gently in a plastic bag to obtain the rhizosphere soil. Root fragments that came off with rhizosphere soil while shaking were removed manually using tweezers. All rhizosphere soil particles could pass through the 850-µm sieve. The amount of rhizosphere soil recovered was in some instances less than 2 g per site, and, in such cases, samples were pooled with others taken from the same site and under the same pasture species (e.g. clover). In such cases, the corresponding bulk soils (air-dried subsamples) were also pooled following the same mass ratio as the rhizosphere samples pooled. At the end, 48 samples were obtained (24 bulk and 24 rhizosphere soils). Air-dried samples were used in the chemical analyses unless otherwise indicated.

3.3. Chemical Characterisation of Bulk and Rhizosphere Soils

The measurement of pH was done in both deionized H_2O (DI water) and 1 M KCl using the 1:2.5 ratio of soil to solution (Blakemore *et al.*, 1987). Total carbon (TC) and total nitrogen (TN) were determined using a vario MACRO cube CHNS elemental analyser (Elementar Analysensysteme GmbH, Hanau, Germany). Aluminium and iron complexed with OM (Al_p, Fe_p) were extracted by sodium pyrophosphate (Blakemore *et al.*, 1987). Briefly, 20 ml of 0.1 M sodium pyrophosphate was added to 200 mg of air-dried sample, and the solution was shaken at 50 rpm in an end-over-end shaker overnight (16 h). With 1 drop of 0.2% superfloc added, the solution was centrifuged at 15,000 rpm for 40 min, and the supernatant was read for Al_p and Fe_p by microwave-plasma atomic emission spectroscopy (4200 MP-AES, Agilent Technologies, Singapore). The extract was also analysed for dissolved organic C (i.e. C_p) by Total Organic Carbon Analyser (TOC-LCSH, Shimadzu, China). Aluminium, iron and silicon present in short-range-order minerals (Al_o, Fe_o, Si_o) were extracted by acid oxalate (Blakemore *et al.*, 1987). A volume of 20 ml of 0.2 M acid oxalate was added to 200 mg of air-dried sample, and the solution was shaken in the dark in an end-over-end shaker at 50 rpm for 4 h. The solution was filtered with a Whatman No. 42 filter paper, and the supernatant was analysed by atomic emission spectrometry. The concentrations of Al_p, Al_o and Si_o were used to calculate the content of allophane following a relationship developed by Parfitt and Saigusa (1985).

Water soluble cations and anions were extracted by DI water following the method by Chinu *et al.* (2016). Briefly, 5 ml of water was added to 0.5 g of sample, and the slurry was incubated in 50°C hot water for 24 h with 1–2 h periodic shaking. It was then centrifuged at 3,000 rpm for 15 min and filtered by suction with a 0.45 µm filter. Cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+}) in the extract were analysed by 4,200 MP-AES (Agilent Technologies, Singapore) whereas anions (F^-, Br^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) were analysed by Ion Chromatography (Dionex Aquion, USA). The concentration of NH_4^+ was analysed by NH_4^+/NO_3^- Technicon auto-analyser, and that of bicarbonate (HCO_3^-) was determined by titrating 0.01 M H_2SO_4 against 5 ml of subsample with an auto–titrator (TIM 865 Titration Manager, Radiometer Analytical).

3.4. Additional Chemical Characterization of Bulk Soils

The concentration of Olsen P of only bulk soil was determined following the method by Olsen *et al.* (1954). For this, 20 ml of 0.5 M $NaHCO_3$ were added to 1 g of air-dried 2 mm sieved soil, and the slurry was shaken in an end-over-end shaker for 30 min. The solution was centrifuged at 8,000 rpm for 10 mn and filtered through Whatman No. 5 filter paper. Accurately, 10 ml of the Murphy and Riley reagent was added to 4 ml extract aliquot, and absorbance was read by a UV/VIS Spectrophotometer (PU 8625, Bioscientific Lab Ltd, England).

Dissolved organic carbon (DOC) in water extracts was determined for bulk soil following Chinu *et al.* (2016), and the method has already been detailed above. The concentration of DOC in the extracts was analysed by Total Organic Carbon Analyser.

Subsamples of field-moist bulk soil were air-dried (AD) until constant weight. Other subsamples of field-moist bulk soil were supercritically dried (SD). For SD, the soil sample was soaked for 24 h in absolute ethanol and several steps were taken to ensure complete dehydration. The alcohol was then replaced by CO_2 slightly above the critical point (31 °C and 7.4 MPa). This was executed using a Polaron E3000 series II critical point drying apparatus (Quorum Technologies, East Sussex, UK).

After SD and AD, specific surface area (SSA) was measured by adsorption of N_2 gas at 77 K using a TriStar 3000 analyser (Micromeritics Instrument Corp., Norcross, GA, USA). Samples were outgassed at 120 °C overnight before SSA determination. A total of 49 adsorption points, in the relative pressure range between 0.025 and 0.995, were collected. The

SSA was determined from 5-point adsorption isotherms in the relative pressure range between 0.05 and 0.30 by applying the Brunauer–Emmett–Teller (BET) equation (Brunauer *et al.*, 1938).

3.5. Molecular Fingerprinting of Bulk SOM

The molecular fingerprint of bulk SOM was characterized by pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS). A representative soil aliquot was treated with 2% hydrofluoric acid (HF) to concentrate organic material prior to Py-GC-MS. Briefly, ~3g of soil were mixed with 30 ml of 2% HF and shaken in an end-over-end shaker overnight. The soil suspensions were then centrifuged at 14,000 rpm for 10 min and the supernatant was removed by aspiration. The process was repeated 6 times. Finally, samples were thoroughly rinsed with DI water (at least 6 times; until supernatant liquid showed pH ~5) to remove residual acid. Afterwards, the soil residues were re-suspended with DI water, transferred into pre-weighted plastic bottles and dried at 45 °C in an oven until constant weight. The HF-treated soils were manually ground (<500 μm) for Py-GC-MS characterisation and C and N determination as described above.

Pyrolysis of HF-treated soils was carried out using a Multi-Shot Pyrolyser (EGA/PY-3030D, Frontier Lab). Depending on the C content of the HF-treated soil, between 0.5 and 3 mg of sample was pyrolysed at 550 °C for 12 s. The pyrolysis unit was connected to a GC-MS unit (GCMS QP2010 Ultra, Shimadzu, Japan). Injection was done in split mode (split ratio, 1:30). The pyrolysis products were separated on a stainless-steel capillary column [SH-Rxi-5ms (Crossbond® 5% diphenyl / 95% dimethyl polysiloxane): 30 m, 0.25 mm internal diameter, with a film thickness of 0.50 μm, Shimadzu]. High purity He was used as carrier gas (flow rate: 1 ml min^{-1}). The initial oven temperature was 40 °C and held for 12 s (same as the pyrolysis time), and then ramped up to 300 °C at a rate of 5 °C min^{-1}. The final column temperature was 300 °C and held for 16 min. The temperature of interface between GC and MS was 270 °C and that of ion source was 230 °C. The ionisation energy was set as 70 eV, mass change m/z 45–650 and cycle time 0.5 s.

A total of 213 pyrolysis compounds were identified using the internal NIST library and published sources such as Buurman *et al.* (2007), Suárez-Abelenda *et al.* (2011), Suárez-Abelenda *et al.* (2015) and Wang *et al.* (2016). Quantification of the pyrolysis products was achieved using the GCMS solution version 2.17 software (Shimadzu, Japan) provided with the equipment.

3.6. Statistical Analyses

Statistical analyses were conducted with Statistica version 8 software package (Stat Soft. Inc., Tulsa, OK, USA). Statistical analysis for the different variables related with the soil and soil solution chemistry were planned to disentangle the effect of: (i) land use intensification (i.e. pine Forest stand < Pasture 1 < Pasture 2); (ii) pasture type (i.e. predominance of either ryegrass or legume as plant species dominant in both Pasture 1 and Pasture 2); and (iii) the soil components (i.e. rhizosphere and bulk soil).

A factorial ANOVA considering the fixed effect of land use intensification (i.e. Paddock 1 and Paddock 2), pasture species type (i.e. ryegrass and legume) and the interaction between land use intensification and pasture species type was conducted for each soil type independently, concluding that, in general, the effect of pasture species type was negligible (at $P < 0.05$) for most of the parameters tested. Consequently, the average values (i.e. for both ryegrass and legume) for most parameters were included in tables, figures and subsequent statistical analysis, unless otherwise indicated.

Thereafter a factorial ANOVA test was applied to averaged variables related with the soil and soil solution chemistry. The model included the fixed effect of land use intensification (i.e. Forest, Paddock 1 and Paddock 2), soil type (i.e. rhizosphere and bulk), and the interaction between land use intensification and soil components.

For the data obtained by Py-GC-MS, the sum of the total quantified peak area (TQPA) of major fragment ion(s) (*m/z*) was set to 100% providing the relative contribution of each pyrolysis product. The relative proportions of pyrolysis products were subjected to factor analysis.

Finally, relationship between variables was also explored graphically and both correlation and linear regression were applied.

4. Results

4.1. Changes in Soil Chemical Properties across Land Uses

4.1.1. Soil C and N

For the bulk soils, mean TC concentration values of top 7 cm soils under pasture (Paddock 1, 101.7 g C/kg; Paddock 2, 96.0 g C/kg) were higher than that of the soil under pine (63.8 g C/kg) (Figure 4a). Differences in TC concentrations were detected between the two pasture sites, with Paddock 1 having a higher mean value than that of Paddock 2. Mean N concentration values followed a similar pattern, as expected (Figure 4b), but with differences between pasture and forest soils being more accentuated than for TC. Mean C/N ratio (range: 9.4 to 9.6) was lower in pasture soils than in that under pine (average: 11.9) (Figure 4c). Similar trends of TC and TN values were observed for the corresponding rhizosphere soil, although these were significantly greater ($P < 0.001$) than those of the bulk soil. Differences between bulk and rhizosphere soils under pine were however not as accentuated as under pasture, which explains the site x soil interaction ($P < 0.05$) detected (Figure 4). Differences in C/N ratios between the rhizosphere and the bulk soil were only evident in the soil under pine, again explaining the site x soil significant interaction ($P < 0.05$) detected.

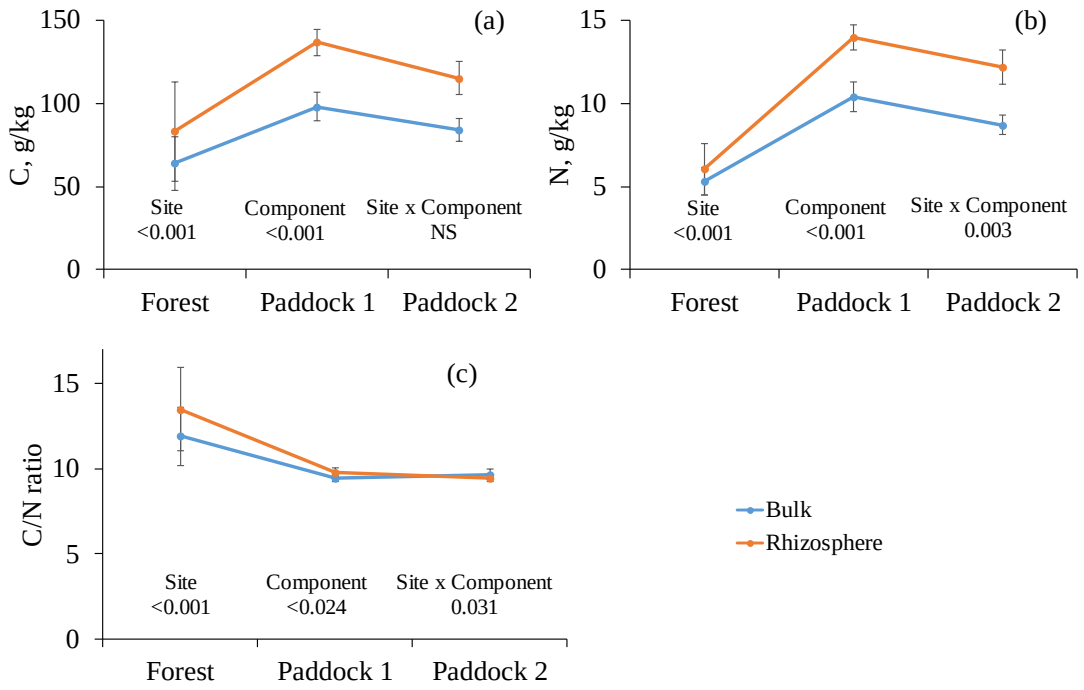

Figure 4:Average and standard error of the mean (SEM) values of (a) total C, (b) total N, and (c) C/N ratio of top 7 cm samples obtained at different sites (i.e. pine Forest, pasture Paddock 1 and pasture Paddock 2) and soil components (i.e. rhizosphere and bulk soil). Results (P value) from factorial ANOVA considering the main effect of Site, Soil and the interaction between Site and Soil are also presented. NS, differences between means not significant at P<0.05.

Root density in soil at each site was determined by the ratio of root mass to soil mass. This was significantly lower ($P < 0.01$) in forest soils (3.2 mg/g) than those in the two paddocks (Paddock 1, 11.2 mg/g; Paddock 2, 12.7 mg/g), but between Paddock 1 and Paddock 2 no statistical differences were detected (Figure 5). Also, root density of ryegrass (Paddock 1, 16.0 mg/g; Paddock 2, 19.2 mg/g) was significantly higher ($P < 0.001$) than that of clover (Paddock 1, 6.5 mg/g; Paddock 2, 6.3 mg/g).

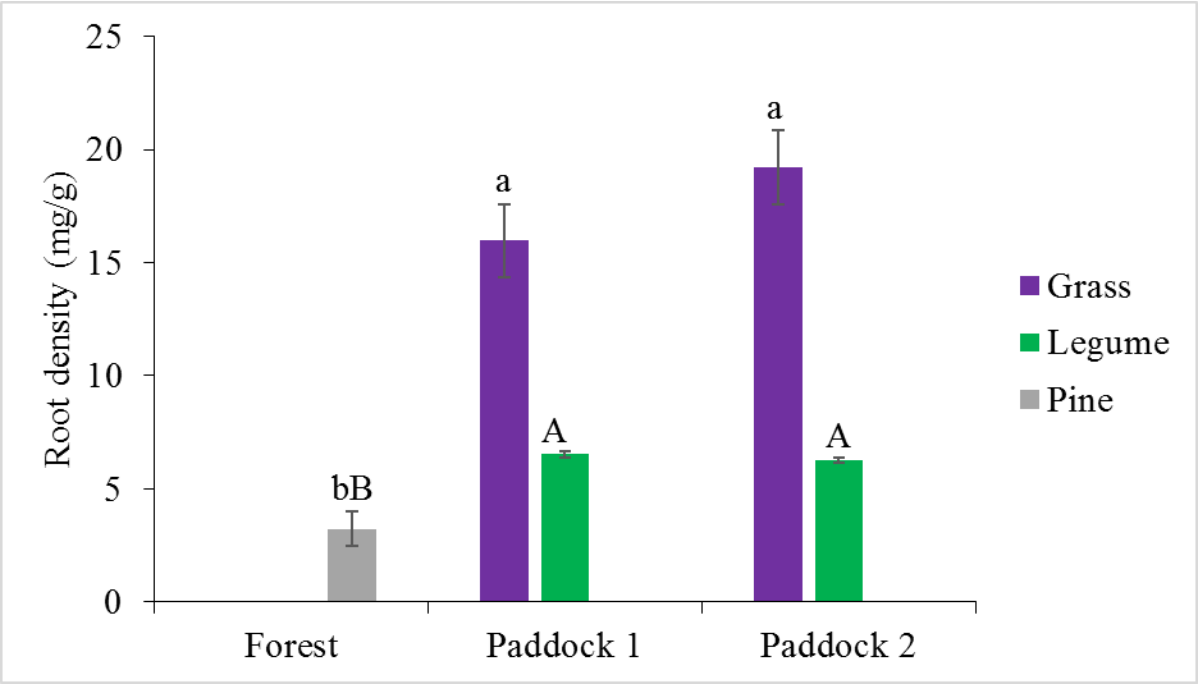

Figure 5: Root density of top 7 cm soils under Forest (pine), in Paddock 1 (grass and legume) and Paddock 2 (grass and legume). Bars represent standard deviation of means. Significant differences in root density are indicated by letters: small letters compare density of pine and that of grass, whereas capital letters compare density of pine and that of legume.

4.1.2. Soil pH

Mean pH-H_2O of 5.3 was smaller than the corresponding mean pH-H_2O values under pasture species (5.7 for Paddock 1 and 6.1 for Paddock 2) (Figure 6a). There were also differences in pH-H_2O ($P < 0.05$) between paddocks. Values of pH-KCl (Figure 6b) followed a similar pattern to those of pH-H_2O, but the former were always smaller (pine, 4.4; Paddock 1, 4.9; Paddock 2, 5.4), reflecting the displacement of Al cations from exchange sites by K^+, which favoured hydrolysis and thus decreased the solution pH. The drop in pH was larger as the acidity of the soil increased (i.e., soil under pine). There were significant differences ($P < 0.05$) in mean pH-KCl values between paddocks ($P < 0.01$), and also between type of pasture species, with values being significantly ($P < 0.05$) smaller under legume (Paddock 1, 4.8; Paddock 2, 5.2) than under ryegrass (Paddock 1, 5.0; Paddock 2, 5.5) (see Figure S 1 in Supplementary Information). Mean pH-H_2O values of the bulk and rhizosphere soils under

pine were similar, but higher values were observed for the rhizosphere soils under pasture compared to their corresponding bulk soils, with these differences becoming greater as intensification increased (Figure 6a); these different patterns are consistent with the site x soil significant interaction ($P < 0.05$) detected.

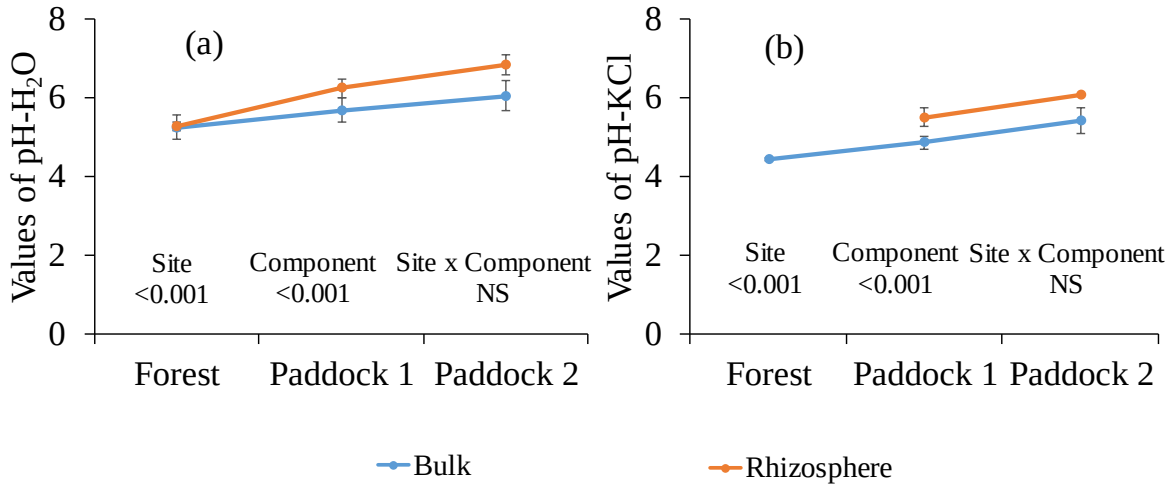

Figure 6: Average and standard error of the mean (SEM) values of (a) pH-H2O and (b) pH-KCl from samples obtained at different sites (i.e. pine Forest, pasture Paddock 1 and pasture Paddock 2) and soil components (i.e. rhizosphere and bulk soil). Results (P value) from a factorial ANOVA considering the main effect of Site, Soil and the interaction between Site and Soil are also presented. NS, differences between means not significant at P < 0.05.

4.1.3. Reactive Al and Fe

All soil samples but one, of them (23 out of 24 samples) fulfilled the requirements for classifying as Andisols (Al_o+½Fe_o > 20 g/kg) (Figure 7a). Overall, mean Al_o+½Fe_o values of the three sites were significantly different ($P < 0.001$) between them, with the highest value found in Paddock 2 (35.7 g/kg), followed by that of Paddock 1 (30.5 g/kg), and that under Forest (22.1 g/kg). No significant differences in Al_o +½Fe_o values were found between rhizosphere and bulk soils.

The concentrations of Al_p of the bulk soils were found to be significantly smaller ($P < 0.001$) in Paddock 2 (5.7 g/kg) than in the other two sites (Paddock 1: 6.8 g/kg; under pine: 6.6 g/kg (Figure 7b), and a similar pattern was observed in the rhizospheric soil, although values in the latter were significantly ($P < 0.05$) smaller than in the bulk soil. For both bulk and rhizospheric soils of Paddock 1, mean Al_p value of soils under legume was significantly higher ($P < 0.05$) than that under grass, whereas no significant effect was found between species in Paddock 2 (see Figure S 2 in Supplementary Information).

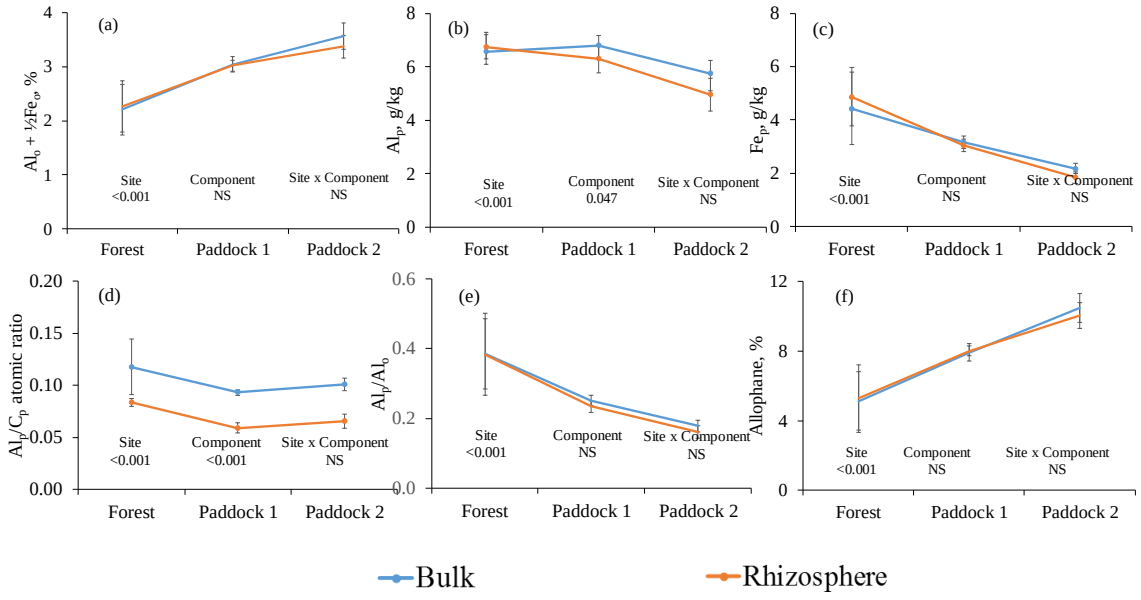

Figure 7: Average and standard error of the mean (SEM) values of (a) Al_o +½ Fe_o, (b) pyrophosphate-extractable aluminium (Al_p)and (c) pyrophosphate-extractable iron (Fe_p), (d) the atomic ratio between aluminium and C extractable with pyrophosphate (Al_p/C_p), (e) the ratio between aluminium extractable with pyrophosphate to that extractable with oxalate (Al_p/Al_o) and (f) allophane from samples obtained at different sites (i.e. pine Forest, pasture Paddock 1 and pasture Paddock 2) and soil components (i.e. rhizosphere and bulk soil). Results (P value) from a factorial ANOVA considering the main effect of Site, Soil and the interaction between Site and Soil are also presented. NS, difference between means not significant at P < 0.05.

Iron complexed with OM, as estimated by Fe_p, was significantly different ($P < 0.001$) between the three sites, this being the highest under pine (4.4 g/kg) and the lowest in Paddock 2 (2.2 g/kg) (Figure 7c). Land use intensification thus halved the content of organo-Fe complexes, whereas for organo-Al complexes the pattern was less accentuated. The trends observed in the Fe_p values in the rhizosphere were similar to those of the bulk soil, there being no significant differences between them (Figure 7c).

The saturation of Al with OM was estimated by the atomic ratio of Al_p to C_p (Figure 7d). The molar Al_p/C_p ratio under pine (0.11) was significantly higher ($P < 0.05$) than those of the two paddocks (0.09 and 0.10), which was to some extent unexpected, it is possible that C_p of pasture soils has included some water-soluble C that is not necessary complexed with Al. A similar pattern was observed in the rhizospheric soils. Here, this ratio was significantly smaller ($P < 0.001$) in the rhizosphere soil (0.07) than in the bulk soils (0.10), as expected. Again, the contribution of some water-soluble C not necessarily complexed with Al might explain these differences.

The relative dominance of organo-Al complexes vs. short-range-order aluminosilicates was assessed using the ratio between Al_p and Al_o (Figure 7e). Values showed a significant decrease in the Al_p/Al_o ratio ($P < 0.01$) from Forest (0.39) to Paddock 1 (0.25) to Paddock 2

(0.18), reflecting the dominance of short-range-order aluminosilicates. Consistently, the trend of allophane followed the opposite pattern, with a significant increase ($P < 0.01$) from Forest (5.1%) to Paddock 1 (7.9%) to Paddock 2 (10.5%; Figure 7f). Interestingly, there was no rhizosphere effect either for the Al_p/Al_o ratio or the allophane content.

4.1.4. Olsen P concentration

Concentrations of Olsen P were affected by land use, with Olsen P concentrations of pine Forest (7.3 mg/kg) were lower than those in Paddock 1 (34.1 mg/kg) and Paddock 2 (32.0 mg/kg) (Figure 8). The latter two values were not significantly different.

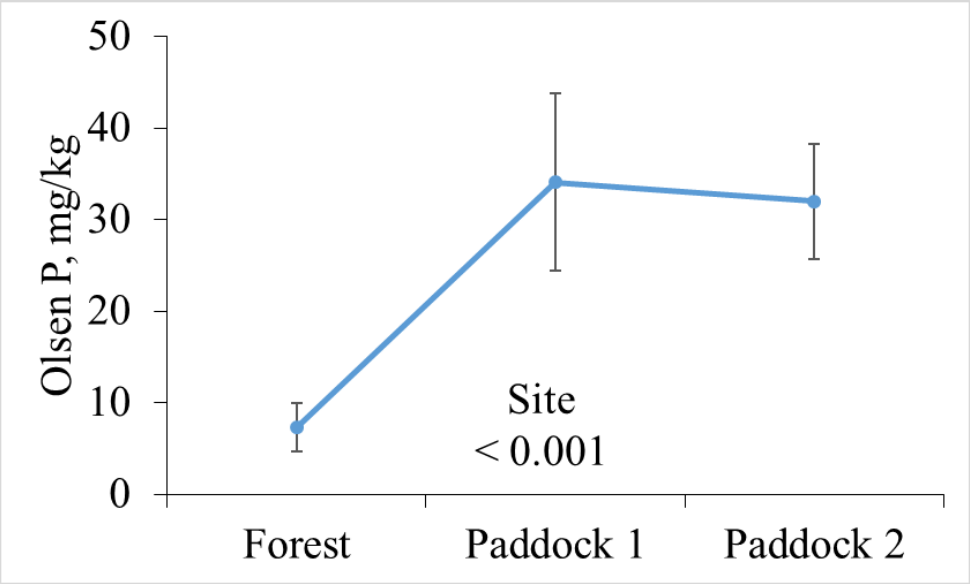

Figure 8: Average Olsen P values of bulk fraction obtained at different sites (i.e. pine Forest, pasture Paddock 1 and pasture Paddock 2).

4.1.6. Specific Surface Area

Specific surface area (SSA) of a representative sample from each site was measured after it was treated with supercritical drying (SD) (Figure 9). The SSA values of samples treated with supercritical drying decreased from the least intensively managed system (Forest soil, 42.9 m^2/g) to soil in Paddock 1 (13.2 m^2/g) to soil in Paddock 2 (8.4 m^2/g), despite the increase in allophane content observed in this sequence. It is possible that the 120 °C drying of the samples prior the BET measurements might have caused the collapse of the allophane clusters, despite the supercritical drying pre-treatment.

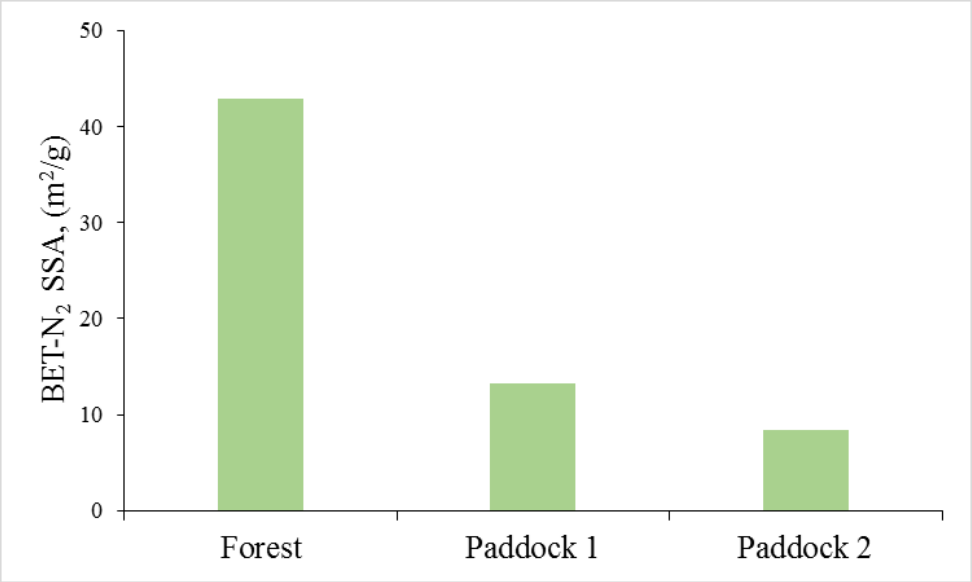

Figure 9: BET-N_2 SSA (m^2/g) obtained at different sites (i.e. Forest, Paddock 1 and Paddock 2) after supercritical-drying (SD).

4.2. Soil Solution Composition

The chemical composition of the soil solution was found to be influenced by land use and management (Figure 10). Specifically, for the bulk soil, there were significantly greater ($P < 0.05$) contents of Na^+, Fe^{2+}, Cl^-, Br^-, and SO_4^{2-} in solution under pine than under pasture, whereas the opposite pattern was observed for NH_4^+, $Ca^{2+}$and F^- (Figure 10a). The concentrations of K^+ and HCO_3^- under pine were significantly smaller ($P < 0.05$) than in Paddock 2, but not that in Paddock 1, whereas Al^{3+} concentration under pine was significantly greater ($P < 0.05$) than that in Paddock 2, but not that in Paddock 1. No significant differences in the concentrations of other ions (Mg^{2+} and PO_4^{3-}) were detected between sampling sites.

The ionic total concentration (moles of charge basis) in the rhizospheric soil was 1.5- to 3.7-fold that of the bulk soil, this effect being more accentuated in Paddock 2 (Figure 10b). The increase in ionic concentration was mostly caused by an increase in plant nutrient cations, such as Ca^{2+}, K^+, and NH_4^+, with the charge being predominantly balanced by HCO_3^- (Figure 10b). Overall, the concentration of Ca^{2+}, Fe^{2+}, K^+, Mg^{2+}, Al^{3+}, Na^+, NH_4^+, Cl^-, Br^-, and HCO_3^- was significantly greater ($P < 0.01$) in the rhizosphere than in bulk soil.

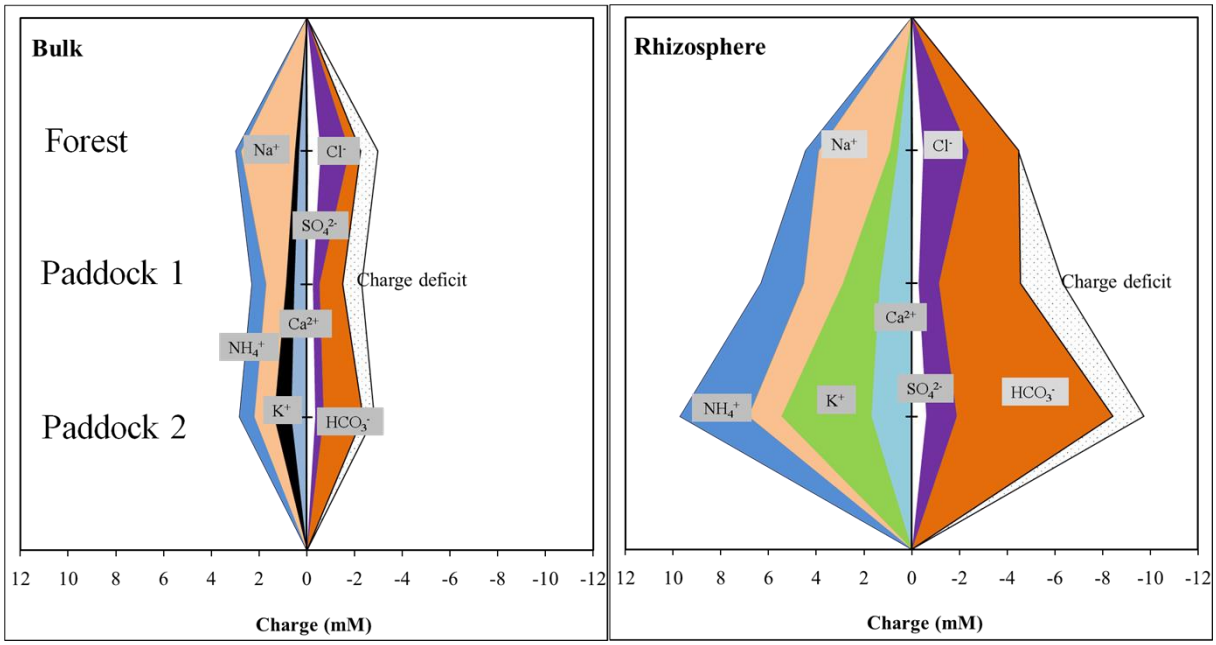

Figure 10: Charge balance of bulk and rhizosphere fractions of Forest (Pine), Paddock 1 (Grass, Legume) and Paddock 2 (Grass, Legume). It should be noted that, when considering the charge of Al^{3+} and PO_4^{3-} species, they were considered to be dominantly present as monovalent species, i.e. $Al(OH)_2^+$ and $H_2PO_4^-$ species, based on the pH range of these soils.

Except for the rhizosphere of the pine soil, the charge deficit was always negative (Figure 10), suggesting the contribution of dissolved organic C (DOC) to that charge. Under pine, it is possible that most of DOC charges were balanced by Al cation, given the more acidifying conditions of the pine forest system. DOC was also directly measured (Figure 11a) and mean values were found to be significantly different ($P < 0.05$) between Forest (0.64 g/kg) and pasture soils (Paddock 1, 0.96 g/kg; Paddock 2, 0.92 g/kg), following a parallel trend to that of TC. Figure 5b shows that charge balance is weakly correlated with DOC ($P < 0.05$), suggesting some contribution of DOC charge to the charge deficit.

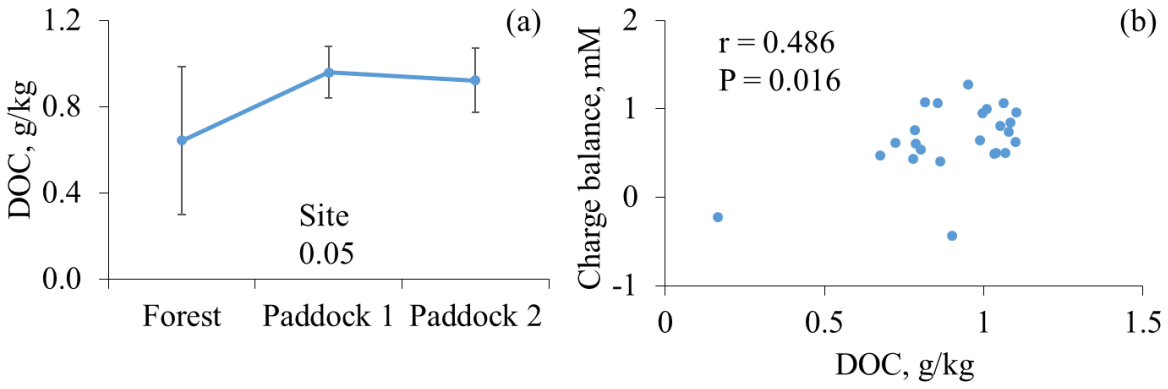

Figure 11: (a) Average and standard error of the mean (SEM) values of DOC from bulk soil obtained at different sites (i.e. pine Forest, pasture Paddock 1 and pasture Paddock 2). "P" refers to the significance level of correlation analysis whereas "r" is the correlation coefficient; (b) relationship between charge balance and DOC.

4.3. Molecular Fingerprint of SOM[1]

4.3.1. General description of pyrolysis products

The pyrolysis products were grouped according to probable source or chemical structure: (i) polysaccharide products, (ii) lignin-related products, (iii) N-containing compounds, (iv) aliphatic components, and (v) other groups, including phenols, monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs).

4.3.1.1. Polysaccharides

Polysaccharides were the most abundant compound class, comprising on average 51% of TQPA (Table 5). These may derive from either plant material (Nierop *et al.*, 2005; Poirier *et al.*, 2005) or microbial activity (Sáiz-Jiménez and De Leeuw, 1986; Buurman and Roscoe, 2011). Total relative abundances of polysaccharides tended to be high under pine (Forest) than under pasture (Paddock 1 and Paddock 2). Levosugars [i.e. levogalactosan (Ps38), levomannosan (Ps41) and levoglucosan (Ps42), markers of cellulose; (Stuczynski *et al.*, 1997)] accounted the half of the signal assigned to polysaccharides, this being an indicative of a relatively fresh SOM for all studied soils (Stuczynski *et al.*, 1997; Poirier *et al.*, 2005). Levoglucosan (Ps42) and levomannosan (Ps41) accounted for higher relative proportion of TQPA under pine than under pasture (with levomannosan being significantly higher; $P < 0.05$); levogalactosan (Ps38) was more abundant (at $P < 0.01$) under pasture than under pine. 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (Ps18), which is a hemicellulose marker, was largely dominant under pasture, especially in Paddock 2.

Other plant-derived polysaccharides such as 1,4:3,6-Dianhydro-alpha-D-glucopyranose (Ps32) and pyranones (Ps18, Ps19, Ps27 and Ps28; Table S 1 in Supplementary Information) were found in higher amount in pine than in pasture ($P < 0.05$), while dianhydrorhamnose (Ps22) and some non-identified sugars (e.g. Ps29. Ps39 or Ps40), which may indicate a likely source from cellulose and hemicellulose, were more abundant under pasture ($P < 0.05$).

SOM fingerprint obtained from soils under pine was characterised by the presence of degraded polysaccharides [e.g. benzofurans (Ps17, Ps24-26, Ps31, and Ps33) and cyclopentenes (Ps20-21); Table S 1]. Such contribution of degraded polysaccharides might

[1] Dr. Suárez Abelenda carried out the identification of peaks and helped with interpretation.

indicate (i) larger microbial decay and/or (ii) a higher (residual) accumulation of degraded polysaccharides compared to that of soils under pasture.

Table 5: Average relative abundances (% TQPA) of pyrolytic compounds grouped according to their possible origins obtained at different sites (i.e. Forest, Paddock 1 and Paddock 2) with contrasted dominant plant (i.e. Pasture type: legume and ryegrass) for bulk soil. Relevant indices and ratios described in text are included. MAHs, monocyclic aromatic hydrocarbons; PAHs, polycyclic aromatic hydrocarbons.

Group	*% of TQPA*	Forest	Paddock 1		Paddock 2	
			Legume	Grass	Legume	Grass
Polysaccharides		51.7	50.1	50.4	50.6	50.0
Lignin		7.03	5.06	5.07	5.72	5.92
N-containing	Non-chitin	8.85	9.67	9.37	9.55	9.43
	Chitin	3.78	4.65	4.47	4.35	4.17
Aliphatic structures	n-alkenes	3.41	4.12	4.32	3.70	3.74
	n-alkanes	4.42	6.40	6.57	5.61	5.75
	Fatty acids	3.73	3.33	3.44	3.43	3.67
	Methylketones	1.30	1.85	1.90	1.59	1.59
	Other aliphatics	0.37	0.37	0.35	0.37	0.37
Other compounds	Phenols	8.24	7.50	7.40	7.96	8.09
	MAHs	6.82	6.65	6.49	6.82	6.95
	PAHs	0.35	0.27	0.27	0.28	0.28
Indices	*Units*					
Lignin indices						
G^1 units	% of total Lignin	70.8	59.1	59.7	58.7	58.7
S^2 units	% of total Lignin	6.01	15.9	16.0	16.6	17.0
H^3 units	% of total Lignin	23.2	25.1	24.3	24.8	24.2
(C3-S/total S)/(C3-G/total G)[4]	Ratio	1.49	2.28	2.39	2.00	2.12
4-acetylguaiacol (Lg13)/total G	Ratio	0.12	0.09	0.09	0.08	0.08

vanillic acid (Lg16)/total G	Ratio	0.17	0.13	0.12	0.10	0.10
4-acetylsyringol (Lg19)/total S	Ratio	0.28	0.18	0.19	0.17	0.16
CPI[5]						
n-alkenes	$((C_{19}-C_{29})+(C_{21}-C_{31}))_{odd}/2(C_{20}-C_{32})_{even}$	2.70	2.99	2.27	2.28	1.77
n-alkanes	$((C_{19}-C_{31})+(C_{21}-C_{33}))_{odd}/2(C_{20}-C_{34})_{even}$	5.60	6.01	4.94	4.97	3.37
Acetamide ratio[6]						
	Acetamide compounds (N21+N25+N26+N28 / Acetamide (N3)	0.48	0.47	0.52	0.51	0.53

[1] G, guacyl units; [2] S, syringyl units; [3] H, hydrophenyl units; [4] ratio between C3-side chain (well-preserved) syringols and C3-side chain guaiacols (Schellekens *et al.*, 2009); [5] CPI, C preference index ((Nierop and Jansen, 2009); (Schellekens and Buurman, 2011)); [6] unpublished.

4.3.1.2. Lignin

Lignin moieties were detected in all samples, with total lignin signal being higher under pine (7% of TQPA) than under pasture (around 5% of TQPA). The general composition of lignin signal detected reflects the different chemistry of plant material (pine vs grass). Guaiacyl (G) units (e.g. Lg1, Lg2, Lg4, Lg5; 68% of total lignin signal) were dominant in the SOM from soils under pine, followed by hydrophenyl (H) moieties (Lg3, Lg6, 26% of total lignin signal), and syringyl (S) moieties (e.g. Lg7, Lg10, Lg 15; 6% of total lignin signal). The sum of syringyl units increased in soils under pasture (up to 16% of total lignin signal), with a corresponding decrease for the contribution of guaiacyl (~59% of total lignin signal) and hydrophenyl units (~25% of total lignin signal). The dominance of guaiacyl over syringyl units in soils under pine management (S/G ratio < 0.10) reflects the non-biosynthesis of syringols in conifers [gymnosperm lignin is mainly constituted by guaicayl and cynmanyl units; angiosperm lignin presents equal proportions of syringyl and guaiacyl units (Lewis and Yamamoto, 1990)]. S/G ratio for soils under pasture (> 0.25; similar for Paddock 1 and Paddock 2) was significantly larger than for soils under pine (at $P < 0.01$).

The ratio between C_3-side chain (well-preserved) syringols (i.e. Lg17, Lg18 and Lg21) and C_3-side chain guaiacols (i.e. Lg8, Lg10, Lg12, Lg14, Lg20, and Lg22), calculated as (C_3-S/total S)/(C_3-G/total G) is used to assess the state of preservation of lignin (i.e. a large value equals to high preservation of lignin . This ratio followed a decreasing trend from Paddock 1 (2.3) > Paddock 2 (2.1) > Forest (1.5). Similar ratios were used to assess the macromolecular degradation of lignin [e.g. (i) 4-acetylguaiacol (Lg13)/total G; (ii) vanillic acid (Lg16)/total G; and (iii) 4-acetylsyringol (Lg19)/total S], which reflect the shortening and oxidation of side chains to produce formyl-side chain (acetyltated) methoxyphenols, and agreed in assigning a more degraded lignin in the following order Forest > Paddock 1 > Paddock 2 (data not shown).

4.3.1.3. N compounds (including diagnostic chitin markers)

N-containing compounds represented the 12–15% of TQPA (higher values found in soils under pasture) and included pyridines (N1, N4, N7, N9, N11, N13, N18), pyrroles (N2, N5, N6, N8, N10, N12, N14–16), indoles (N23–24), dikedipyrrole (N29), benzonitrile (N20), diketopiperazine derivatives (N30-33) along with an amalgam of chitin-derived pyrolysis products [e.g. acetamide-containing compounds (N3, N21, N25, N26 and N28), pyrrolidone (N27) and others (e.g. N15–19, N22)], which are typically derived from fungi or arthropods

(Stankiewicz *et al.*, 1996). Diketodipyrrole (N29), indoles (N23-24) and diketopiperazine (N31-33) were assigned to proteins and chitin-entangled proteins (Gutiérrez *et al.*, 1995; Suárez-Abelenda *et al.*, 2015), while pyrroles and pyridines have an unspecific origin. Chitin markers, accounting on average for approx. 43% of the signal for the fraction of N-containing compounds, were relatively more abundant in soils from Paddock 1 (Table 5).

The ratio acetamide-containing compounds (N21, N25, N26, N28) to acetamide (N3) (Suarez Abelenda, personal communication) would indicate the decomposition degree of chitin (decaying conditions promotes degradation of acetamide-containing compounds into acetamide, which produces strong peaks of acetamide at m/z 59). This ratio would indicate that chitin is more degraded in soils under pine (value of 0.48) than in pasture (average ratio: 0.51; Table 5).

4.3.1.4. Aliphatic structures: n-alkenes, n-alkanes, other aliphatics, n-fatty acids, n-methyl ketones

The sum of aliphatic compounds (i.e. n-alkenes, n-alkanes, n-fatty acids, n-methyl ketones and other alkenes; see Table S 1 in Supplementary Information) ranged between 13% and 16% of TQPA. Contributions of total n-alkenes (3.4 – 4.3% of TQPA), total n-alkanes (4.4 – 6.6% of TQPA) and n-methylketones (1.3 – 1.9% of TQPA) followed a decreasing trend: Paddock 1 > Paddock 2 > Forest. Whereas other aliphatics did not provide any information to this set of samples. *n*-Alkenes, n-alkanes, and n-fatty acids gave an insight on the degree of perseveration of SOM.

Straight chain n-alkanes and n-alkenes doublets may be derived from several sources as plant tissues [e.g. cuticular waxes (Eglinton and Hamilton, 1967)], cutin and cutan (Tegelaar *et al.*, 1989), and suberin and suberan of roots (Nierop, 1998). In this study, long chain n-alkenes ($C_{19:32}$) and n-alkanes ($C_{19:35}$) were more dominant in soils under pasture, whilst the shorter moieties ($C_{10:18}$) were relatively more abundant ($P < 0.01$) in soils under Forest. Moreover, CPI [C Preference Index; ; Schellekens and Buurman (2011)] values reflected the higher dominance of odd over even chain length of n-alkanes in soil under pasture when compared with soil under pine ($P < 0.01$), indicating a better preservation of these moieties in both Paddock 1 and Paddock 2.

n-Fatty acids (3.3-3.7% of TQPA) were more abundant in soils under pine than under pasture. The contribution of long chain fatty acids (FA12-18) to the TQPA was higher in soils

under pine, which likely reflects that they originate from pine needle waxes (Tegelaar *et al.*, 1989). A small fraction of n-fatty acids including iso and anteiso C_{15} and C_{17} n-fatty acids, (FA15i, FA15a, FA16i, FA17a; ca. 5% of total n-fatty acids) are used as bacterial biomarkers (Grimalt and Sáiz-Jiménez, 1989; Chefetz *et al.*, 2002). This microbial fraction of n-fatty acids was found in higher contributions ($P < 0.05$) under pasture than under pine soils, which indicated a relevant decaying activity.

4.3.1.5. Other groups: phenols, monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs)

Phenolic compounds (including phenols and catechols) account between 7.4% and 8.2% of TQPA, and they were in higher proportion in soils under pine. They originated either from lignin, tannins or protein (Stuczynski *et al.*, 1997). MAHs (mostly benzenes, indenes and alkylated forms) comprise 6.5 and 7.0% of TQPA and (if excluding toluene, which is abundant in e.g. proteinaceous biomass; (Tsuge and Matsubara, 1985)) were predominant in pine soils ($P < 0.01$), probably from non-aromatic phenolic compounds, as charring traces were not detected. PAHs i.e. naphathalene compounds comprised a small proportion of TQPA (< 0.35%) and may be analytical artefacts (Sáiz-Jiménez, 1994) but also derivatives of terpenes (Suárez-Abelenda *et al.*, 2014).

4.3.2. Distribution of soil samples and chemical compounds after factor analysis

4.3.2.1. Factor analysis including pine (Forest) and pasture (Paddock 1 and Paddock 2) soils

Four extracted factors explained 72% of the variation of all pyrolysis products, while Factor 1 and Factor 2 together explained 53%. The following description focuses on the F1–F2 factor space. Three main populations of samples occur in different regions of the factor scores plot (Figure 12a), each corresponding to the main groups identified (i.e. from left to right, Forest, Paddock 2, and Paddock 1). Soils under pine had overall negative loadings in both F1 and F2 axis, whereas soils under pasture (with no clear separation between legume and grass) plotted towards the positive side of F1-F2 space, with those samples from Paddock 1 contained higher loadings than those from Paddock 2 (Figure 12a). This distribution stressed the differences between soils under pine and soils under pasture.

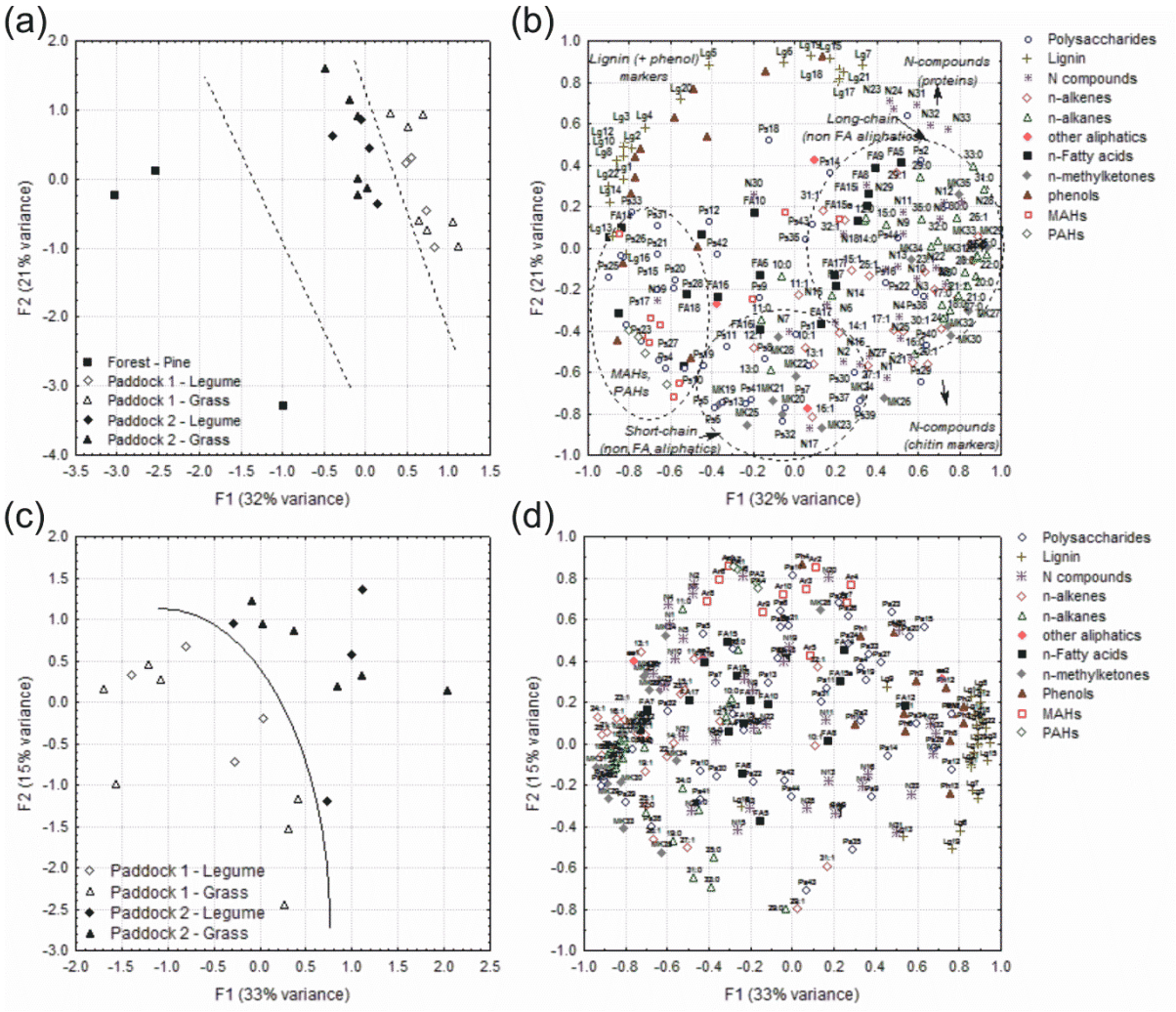

Figure 12: (a) factor scores of Forest, Paddock 1 (legume and grass) and Paddock 2 (legume and grass) samples in the F1–F2 space obtained from all soil samples; (b) factor loadings in F1–F2 space that underlay Figure 12a; (c) factor scores of Paddock 1 (legume and grass) and Paddock 2 (legume and grass) samples in the F1–F2 space obtained using only soil samples under pasture; (d) factor loadings in the F1–F2 space that underlay Figure 13c. Relevant pyrolysis compounds are included; codes correspond to those in Table S 1.

The factor loading's plot (Figure 12b) illustrated which pyrolytic products or groups of products were responsible for the arrangement of the sample point in Figure 12a. Overall, lignin signal spread out between the central (F2) left (F1) side [containing acetyltated methoxyphenols as 4-acetylguaiacol (Lg13) and vanillic acid (Lg16), an indication of oxidised lignin] towards the top (F2) central (F1) area (including syringol units as Lg7, Lg 15, and syringol-related – as well oxidised moieties as 4-acetylsyringol, Lg19 – that were characteristic in soils under pasture). This reflected the importance of a predominantly guaiacyl (and more oxidised) lignin signal in soils under pine when compared with soils under pasture (Figure 12a,b; Table 5).

Polysaccharide compounds tended to distribute all over the space F1–F2, but especially clustering in the lower side of the F2 axis, distributed along F1 axis (Figure 12b). Those polysaccharide-markers associated with sugars (e.g. Ps29. Ps39 or Ps40) were plotted in the lower right side of the factor space (Figure 12b), and thus were characteristic of soils under pasture. Both MAHs and PAHs pyrolysis products clustered close to a number of products of degradation of carbohydrates such as acetylfuran (Ps11), cyclopentenones (Ps20–21) along with all the benzofurans (Ps17, Ps25–26, Ps31;lower left side; Figure 12b), which might reflect the relative contribution of degraded polysaccharides to the pyrolysis fingerprint in soils under pine (Figure 12a).

N-containing compounds tended to plot towards the right side of the F1 axis, with a contrasted distribution based on the F2 axis: on the positive side of F2, protein markers (N23–24, N31–34) concentrated, whereas those markers associated with chitin (e.g. N3, N18, N21–22, N27) were distributed along the F2 axis towards the lower right side of the plot (Figure 12b).

Aliphatic compounds tended to cluster in the right side of the diagram, opposite to lignin markers along F1 axis, and distributed from upper to lower F2 axis (Figure 12b). Short-chain n-alkenes, n-alkanes and n-methyl ketones tended to be arranged around the upper right side, whereas those of long-chain were clustered around the lower left side (Figure 12b). n-fatty acids were distributed along the F1 axis, from the lower left (long-chain FA predominating, e.g. FA14, FA16, FA18) towards the upper right side (short-chain FA predominating, e.g. FA5, FA8–9). Those n-fatty acids associated with microbial activity (iso and anteiso C15 and C17 n-fatty acids, FA15i, FA15a, FA16i, FA17a) were concentrated in the right side of the F1–F2 factor space, which reflected their importance in soils under pasture.

4.3.3. Factor analysis of only soils under pasture (Paddock 1 and Paddock 2)

When factor analysis was applied to those soils under pasture (i.e. Paddock 1 and Paddock 2 alone), four extracted factors explained 68% of the variation of all pyrolysis products, while Factor 1 and Factor 2 together explained 48%. Paddock 1 soils and Paddock 2 soils showed a contrasted distribution in the F1–F2 space (Figure 12c). Paddock 2 soils plotted in the upper right side of factorial space, whereas Paddock 1 soils had negative loadings (or close to zero) along the F1 axis (Figure 12c), and a more dispersed distribution along the F2 axis. This distribution stressed the differences between soils from Paddock 1 and Paddock 2,

independently of the plant source (i.e. legume vs grass). The factor loading's plot (Figure 12d) illustrated which pyrolytic products or groups of products were responsible for the arrangement of the sample point in Figure 12c. Relative arrangement of the main compound groups was similar to that already described in Figure 12a and Figure 12b.

5. Discussion

5.1. Soil C, N Stocks and Fertility

The current study supports the generally common pattern observed in New Zealand in forest and pasture topsoils, where lower amounts of soil organic C (and N) (ca 40% less) accumulate under forest compared with soils under pasture. Scott *et al.* (1999) analysed the National Soils Database of New Zealand for organic C content in soils under pasture and forest in different soil types including Allophanic soils and found that, in the top 10 cm, soil C content was 20–40% lower under pine compared with pasture in all soils except those with high clay activity, in which no significant difference detected. Similarly, Davis (2001) investigated soil properties under pasture and pine forest and reported that soil organic C concentrations under pine forest were significantly lower than those under pasture in yellow-brown earth soils (Allophanic Soils), but not in yellow-grey earth soils (Brown Soils). This has generally been attributed to fertilisation and liming practices in soils under pasture (Conant *et al.*, 2001; Batlle-Bayer *et al.*, 2010) as well as to the fact that pasture species have a dense rooting system (Tate, 1987), thus having a greater root C input. In fact, in this study, the ryegrass root density was 6-fold that of pine, and the root density of clover root was twice that of pine. These ratios are not paralleled by a similar increase in soil C, indicating that under pasture a large amount of C from decaying roots barely interacts with the mineral fraction and quickly decomposes.

The greater root input and SOM decomposition in pasture soils is also consistent with the results from the pyrolysis-GC/MS analyses, which reflect greater abundance of long-chain aliphatic compounds in pasture soils. This reveals an important contribution of fresh SOM and also a higher abundance of bacterial markers (such as the iso/ante-iso isomeric form of branched C_{15} and C_{15} fatty acids (Grimalt and Sáiz-Jiménez, 1989; Chefetz *et al.*, 2002), suggesting also a high degradation activity. The results contrast with the fingerprints of SOM found in soils under forest, in which there was a smaller fraction of "fresh" organic constituents, but a preferential accumulation of degradation products of polysaccharides, aliphatic compounds (with poorer odd over even chain length dominance), and oxidized lignin, as inferred by the greater abundance of acetylated forms [as 4-acetylguaiacol (Lg13) and vanillic acid (Lg16)]. Interestingly, pyrolysis-GC/MS makes it possible to distinguish the different source of lignin, with pine being enriched with guaiacyl (G), and pasture having an increase in the fraction of syringyl (S). Legume and grass litter have equal contents of

guaiacols and syringols (Lewis and Yamamoto, 1990), whereas syringols are less relevant in pine litter (Baldock and Nelson, 2000; Kögel-Knaber, 2002). Hedges *et al.* (1985) reported that the differences in S/G ratio influences lignin degradation as syringyl units are more susceptible to microbial attack.

The generally lower C:N ratio of the soils under pasture compared with those under forest, as found in the present study, results not only from a greater N input from N fixation but also from an accelerated decomposition (caused by the presence of a more palatable OM and overall more eutrophic conditions). Hedley *et al.* (2009) reported that converting pine and eucalyptus forests to pasture in volcanic soils increased C and N, decreased the C:N ratio. Again, the data generated from pyrolysis-GC/MS support a greater microbial activity in soils under pasture. N-compounds were more abundant in these soils, consistent with a lower C:N ratio (when compared with soils under pine). This fraction had an important contribution of chitin, and proteins and chitin-entangled proteins (Figure 12b). The dominance of these two N fractions indicate a strong re-assimilation of OM by fungal and arthropods. However, as these fractions are extremely palatable (i.e. susceptible to strong decomposition and net removal from soil), the relatively high chitin signal found might be related to either high production, a high preservation in these soils with andic properties, or a combination of both processes.

5.2. pH and Soil Solution Composition

The pH data in the current study showed that pine soils were relatively acidic, and there was an increasing trend of pH with the trend of management intensification. The low pH of soils under pine compared with pasture was reported to be caused by pine needles, which are naturally acidic (Ghani *et al.*, 1994; Davis, 2001), whereas the application of lime into pastures (Hedley *et al.*, 2009) would increase the pH of pasture soils. Urine deposition and urea hydrolysis in pasture has also been hypothesized to increase pH of the system (Schipper *et al.*, 2014), although further nitrification reactions will tend to drop the pH unless buffered by the soil system. In addition, the pH of the rhizosphere soils under pasture was significantly higher than that of bulk soils (Figure 6), which can be explained by the dominance of NH_4^+ and K^+, strong bases, and HCO_3^-, a weak acid, in the rhizosphere (Figure 10) – this being more accentuated in Paddock 2. It should be noted that the contribution of both dominant chemical species was about 4 times higher in the rhizosphere than in bulk soils. Longhurst *et*

al. (2017) has recently reported averaged compositional values of farm dairy effluents, these being predominantly enriched in K^+ (0.29 kg/m^3), N (0.19 kg/m^3 of which 0.13 are mineral N), and Ca^{2+} (0.07 kg/m^3), values consistent with the nutrient enrichment pattern observed in the paddocks, and more specifically in the one that had a recent effluent addition (Paddock 2). The composition of the soil solution under the pine stands showed the dominance of ions as Na^+ and Cl^- in soils, which can be explained by the entrapment of sea salts (and subsequent transfer) by pine forest (Giddens *et al.*, 1997; Parfitt *et al.*, 1997a; Davis, 2001).

5.3. Reactive Al and Fe

Reactive Al increased following the sequence Forest < Paddock 1 < Paddock 2, and this was mostly associated with an increase in the content of allophane at the expense of Al complexed with organic ligands (Al_p) and Al in micro-gibbsite (Al_n-Al_o). This, in turn, was paralleled by the above-described increase in soil pH. A more alkaline system would weaken the stability of organic ligands and favour the formation of allophane (Dahlgren *et al.*, 2004), while the addition of phosphate fertiliser may have caused an accelerated weathering (due to the increase in phosphate and fluoride ligand concentrations) also contributing to allophane formation (Taylor *et al*., 2016), although the contribution of soils' natural variability to these patterns cannot be disregarded. As for Al complexes with organic ligands, Fe associated with organic compounds decrease as intensification management/use increases following the sequence Forest < Paddock 1 < Paddock 2, as that of Al; although for Fe the trend was more accentuated. This could be explained by the fact that as pH increases Fe^{3+} cations preferably bind to OH^- ions in detriment to organic ligands (Dahlgren *et al.*, 1993), although as for Al, the contribution of soil's natural variability to these patterns cannot be disregarded.

The C accumulation in soil was not related to the allophane content, as already noted by Percival *et al.* (2000) and Matus *et al.* (2006). Also, the trend of TC concentrations at the three sites could not be explained by that of SSA (Figure 9). This indicated that adsorption of SOM on the surface of allophane (Torn *et al.*, 1997; Parfitt, 2009) was not the controlling factor of SOM stabilization in these soils. While this seems to contradict the well-known relationship between allophane and OM content, this could be explained as follows. Management practices that contribute to both increasing the soil pH and soil fertility of these soils with andic properties, will, on the one hand, tend to positively influence the formation of allophane (i.e. less acidity in the system) and, on the other hand – especially after conversion from pine to pasture, will increase the organic C input into the soil. This boost in organic C

input will enhance the formation of organo-Al complexes and the associations between allophane and organic ligands (that is, the formation of organo-mineral complexes), as well as the content of particulate organic matter. However, as the pH of the system keeps increasing with management intensification, the ability of reactive Al to interact with organic ligands will become weaker, given that outer-sphere complexes will preferentially form at the expense of inner-sphere complexes (Kleber *et al.*, 2015) – thus organic matter will not be as strongly protected. Moreover, Al in organo-Al complexes will tend to be precipitated with OH-ions forming crypto-gibbsite, freeing organic ligands that were previously chemically protected in this process (Verde *et al.*, 2010). In fact, Miyazawa *et al.* (2013) found that liming non-allophanic Andisols weakened the bonds of organo-Al complexes and promoted mineralization of OM, which was measured by CO_2 in respiration. Along with liming materials, these authors also observed that adding N and P also accelerated mineralization, but the effect exerted by the former was more pronounced. This could explain the lower organic C content of Paddock 2 compared with Paddock 1, as well as the trends described by Schipper *et al.* (2014) when monitoring the C and N stocks changes in New Zealand pasture soils over two to four decades, in which some C losses were detected in Allophanic (and Gley) Soils, but not in other soil orders. Although these authors could not fully explain the reasons behind the losses, they linked them to the higher pH values in paddocks as a result of liming and urine deposition and hydrolysis, which altered the protection of labile C pools.

This accelerated decomposition of OM in the most intensified system, i.e. Paddock 2 compared with Paddock 1, was also reflected at the molecular level, as the latter had a greater relative aliphatic signal, containing higher relative contributions of chain n-alkanes and n-alkenes doublets, with a predominance of large over short-, and odd over even-C numbers, as described by CPI ratios, along with long-chain n-fatty acids, derived from plant cuticules, and products of n-alkane degradation, i.e., n-methyl-ketones. In addition, soil samples from Paddock 1 were characterised by a relevant presence of plant polysaccharides (i.e. cellulose and hemicellulose markers, Ps38, Ps41–42, Ps18), as well as gluco-pyranose (Ps32) and other palatable sugars (e.g., Ps29–30, Ps39–40). This abundance suggested that fresh litter input was remarkable in soils under Paddock 1. In addition, the SOM fingerprint in soils from Paddock 1 showed a large contribution of chitin markers (N2, N21, N25–26 and others) and unspecific N compounds, mostly pyridines and pyrroles, which was consistent with a larger presence of fresh (and digestible) SOM.

Contrastingly, those soil samples from Paddock 2 showed a less relevant contribution of long-chain n-fatty acids, as well as a relative predominance of short-chain n-alkanes and n-alkenes, along with a less remarkable dominance in the odd over even C number, which may be an indication of less fresh SOM input than that found in Paddock 1. Another feature of soils from Paddock 2 was the important contribution from unspecific polysaccharides [e.g. pyranones (Ps18–19, Ps27–28), pyrandiones (Ps9) and furanones (Ps7, Ps9, Ps12, and others)] along with both (i) degraded polysaccharides: benzofurans (as Ps17, Ps24–26) and cyclopentenones (Ps20–21); and (ii) high loads or aromatics (i.e. MAHs and PAHs). This assembly of polysaccharide markers and aromatics, along with the aliphatic signal described above corresponding to a less fresh SOM input, stressed a stronger decaying state of the SOM in Paddock 2 when compared with that in Paddock 1.

Moreover, diketopiperazines and protein especially N compounds, i.e. indoles, were clearly dominating in Paddock 2, which would be attributed to some extent to recent rich N/proteinaceous farming effluents. On the other hand, these soils (especially under graminoids) were rich in pyrolysates derived from lignin (i.e. all methoxyphenols mentioned previously, and lignin phenols: including phenols and catechols; Table S 1; Figure 12; Figure 12c,d), which would indicate lignin persistence upon decay whether compared with plant polysaccharides, though it is considered that lignin is highly palatable in aerobic conditions (Buurman *et al.*, 2007).

6. Conclusions

The findings of this study suggest that an increase in management intensification in Andisols promoted the formation of short-range-order constituents. Studies have suggested that fluoride in phosphate fertilisers accelerate the weathering of tephra. Also, an increase in pH favours the formation of allophane compared with that of organo-Al complexes. However, we could not fully discard the contribution of the natural variability of soils to the differences observed between sampling sites. In this regard, more research is needed to confirm this aspect.

The increase in short-range-order constituents was not paralleled by an increase in soil C, although soils under the two paddocks had greater C content than that under pine in agreement with their greater fertility and the fine and dense rooting system of pastures, which are the primary source of C to these soils. It was hypothesised that increasing pH values above a specific threshold weakens the stability of organo-mineral complexes, which subsequently exposes SOM to microbial attack. This might explain why Paddock 2 had less C than Paddock 1, despite having greater content or short-range-order constituents.

The greater root input and microbial activity in pasture soils was revealed by the abundance of long-chain aliphatic compounds (fingerprints of fresh SOM) and that of microbial markers (suggesting a high degradation activity). The results contrasted with the fingerprints of SOM under forest, where there was a smaller fraction of "fresh" organic constituents, but a preferential accumulation of degraded products of polysaccharides, aliphatic compounds, and lignin.

The type of pasture species (ryegrass vs. clover) had little effect on the soil properties investigated. Particularly, the effect was only observed for pH and Al_p. The type of soil considered, rhizosphere vs. bulk soil, had a greater effect, especially in soil TC, TN, C:N ratio, pH, Fe_p, Al_p/C_p, soil solution composition, and charge balance.

The acidity of the soil under pine could be attributed not only to the lack of amendments but also to the fact that this forest stand had an acidifying effect (i.e. acidic pine needle) on the soil. Future studies are needed so that native forest can be compared with pasture paddocks.

The findings of the current study have offered an insight into how reactive surfaces in soils with andic properties and other soil chemical properties (such as soil pH and nutrient fertility) relate to SOM quality and quantity in soils under different land use and/or degree of intensification. The results suggest the existence of a Critical Threshold of Grassland Intensification for SOM preservation, above which the chemical conditions that stabilise soil organic matter are no longer effective. More research is needed to support this hypothesis.

References

Allen, M.F., 2007. Mycorrhizal Fungi: Highways for Water and Nutrients in Arid Soils All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Vadose Zone Journal 6, 291-297.

Appelt, H., Coleman, N., Pratt, P., 1975. Interactions between organic compounds, minerals, and ions in volcanic-ash-derived soils: II. Effects of organic compounds on the adsorption of phosphate. Soil Science Society of America Journal 39, 628-630.

Asano, M., Wagai, R., 2014. Evidence of aggregate hierarchy at micro-to submicron scales in an allophanic Andisol. Geoderma 216, 62-74.

Baldock, J.A., Nelson, P., 2000. Soil organic matter. In: Sumner, M.E. (Ed.), Handbook of Soil Science. CRC Press, Boca Raton, FL.

Barber, S.A., 1995. Soil nutrient bioavailability: a mechanistic approach. John Wiley & Sons.

Batlle-Bayer, L., Batjes, N.H., Bindraban, P.S., 2010. Changes in organic carbon stocks upon land use conversion in the Brazilian Cerrado: A review. Agriculture, Ecosystems & Environment 137, 47-58.

Bäumler, R., Caspari, T., Totsche, K.U., Dorji, T., Norbu, C., Baillie, I.C., 2005. Andic properties in soils developed from nonvolcanic materials in Central Bhutan. Journal of Plant Nutrition and Soil Science 168, 703-713.

Bigham, J., Fitzpatrick, R.W., Schulze, D., Dixon, J.B., 2002. Iron oxides. Soil mineralogy with environmental applications, 323-366.

Blakemore, L.C., Searle, P.L., Daly, B.K., 1987. Methods for Chemical Analysis of Soils. NZ Soil Bureau Scientific Report 80.

Blume, H.-P., Brümmer, G.W., Fleige, H., Horn, R., Kandeler, E., Kögel-Knabner, I., Kretzschmar, R., Stahr, K., Wilke, B.-M., 2016. Soil Organic Matter. Scheffer/SchachtschabelSoil Science. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 55-86.

Boudot, J.P., Bel, H., Brahim, A., Steiman, R., Seigle-Murandi, F., 1989. Biodegradation of synthetic organo-metallic complexes of iron and aluminium with selected metal to carbon ratios. Soil Biology and Biochemistry 21, 961-966.

Brady, N.C., Weil, R.R., 2008. The Nature and Properties of Soils. Prentice Hall.

Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. Journal of the American chemical society 60, 309-319.

Buol, S.W., Southard, R.J., Graham, R.C., McDaniel, P.A., 2011. Soil genesis and classification. John Wiley & Sons.

Buurman, P., 1985. Carbon/sesquioxide ratios in organic complexes and the transition albic-spodic horizon. Journal of Soil Science 36, 255-260.

Buurman, P., Peterse, F., Almendros Martin, G., 2007. Soil organic matter chemistry in allophanic soils: A pyrolysis-GC/MS study of a Costa Rican andosol catena. European Journal of Soil Science 58, 1330-1347.

Buurman, P., Roscoe, R., 2011. Different chemical composition of free light, occluded light and extractable SOM fractions in soils of Cerrado and tilled and untilled fields, Minas Gerais, Brazil: a pyrolysis-GC/MS study. European Journal of Soil Science 62, 253-266.

Camps Arbestain, M., Barreal, M.E., Mourenza, C., Álvarez, E., Kidd, P., Macías, F., 2003. Rhizosphere chemistry in acid forest soils that differ in their degree of Al-saturation of organic mattter. Soil science 168, 267-279.

Candan, F., Broquen, P., 2009. Aggregate stability and related properties in NW Patagonian Andisols. Geoderma 154, 42-47.

Chefetz, B., Tarchitzky, J., Deshmukh, A.P., Hatcher, P.G., Chen, Y., 2002. Structural characterization of soil organic matter and humic acids in particle-size fractions of an agricultural soil. Soil Science Society of America Journal 66, 129-141.

Chesworth, W., 2008. Encyclopedia of soil science. Springer.

Chevallier, T., Woignier, T., Toucet, J., Blanchart, E., 2010. Organic carbon stabilization in the fractal pore structure of Andosols. Geoderma 159, 182-188.

Chinu, K., Marjo, C.E., Joseph, S., Singh, B., 2016. Chapter 6: Dissolved carbon and LC-OCD of biochar. In: Balwant Singh, Marta Camps Arbestain, Lehmann, J. (Eds.), Methods of Biochar Analysis for Environmental Applications. CSIRO Publishing, Melbourne (In press).

Chung, J.-B., Zasoski, R.J., 1994. Ammonium-Potassium and Ammonium-Calcium Exchange Equilibria in Bulk and Rhizosphere Soil. Soil Science Society of America Journal 58, 1368-1375.

Churchman, G., 2000. The alteration and formation of soil minerals by weathering. Handbook of soil science, 3-76.

Claassen, N., Jungk, A., 1982. Kaliumdynamik im wurzelnahen Boden in Beziehung zur Kaliumaufnahme von Maispflanzen. Z. Pflanzenernaehr. Bodenkd 145, 513-525.

Conant, R.T., Paustian, K., Elliott, E.T., 2001. Grassland management and conversion into grassland: effects on soil carbon. Ecological Applications 11, 343-355.

Crush, J., Nichols, S., 2010. Progress towards forage plant root systems for sustainable dairying. Proceedings of the 4th Australasian Dairy Science Symposium, pp. 50-52.

Dahlgren, R.A., Saigusa, M., Ugolini, F.C., 2004. The Nature, Properties and Management of Volcanic Soils. Advances in Agronomy. Academic Press, pp. 113-182.

Dahlgren, R.A., Shoji, S., Nanzyo, M., 1993. Mineralogical characteristics of volcanic ash soils. Developments in Soil Science 21, 101-143.

Das, S.K., Varma, A., 2010. Role of enzymes in maintaining soil health. Soil enzymology. Springer, pp. 25-42.

Davis, M., 2001. Soil properties under pine forest and pasture at two hill country sites in Canterbury. New Zealand Journal of Forestry Science 31, 3-17.

de Neergaard, A., Gorissen, A., 2004. Carbon allocation to roots, rhizodeposits and soil after pulse labelling: a comparison of white clover (Trifolium repens L.) and perennial ryegrass (Lolium perenne L.). Biology and Fertility of Soils 39, 228-234.

DeLaune, R., Reddy, K., 2005. Redox potential. Encyclopedia of Soils in the Environment 3, 366-371.

Dinkelaker, B., Römheld, V., Marschner, H., 1989. Citric acid excretion and precipitation of calcium citrate in the rhizosphere of white lupin (Lupinus albus L.). Plant, Cell & Environment 12, 285-292.

Dodd, M., Crush, J., Mackay, A., Barker, D., 2011. The “root” to more soil carbon under pastures. Proceedings of the New Zealand Grassland Association, pp. 43-50.

Duchaufour, P., 1977. Pedology. 1. Pedogenesis and classification. Masson SA.

Eglinton, G., Hamilton, R.J., 1967. Leaf epicuticular waxes. Science 156, 1322-1335.

Eswaran, H., Van Den Berg, E., Reich, P., 1993. Organic Carbon in Soils of the World. Soil Science Society of America Journal 57, 192-194.

FAO, ISRIC, IUSS, 1998. World reference base for soil resources. World soil resources reports 84, 21-22.

FAO, ISRIC, IUSS, 2014. World reference base for soil resources 2014 international soil classification system for naming soils and creating legends for soil maps. FAO, Rome.

Fenton, T., Brown, J., Mausbach, M., 1999. Effects of long-term cropping on organic matter content of soils: implications for soil quality. Soil and Water Con. J 95, 124.

Fernandes, E.C., Motavalli, P.P., Castilla, C., Mukurumbira, L., 1997. Management control of soil organic matter dynamics in tropical land-use systems. Geoderma 79, 49-67.

Filimonova, S., Kaufhold, S., Wagner, F.E., Häusler, W., Kögel-Knabner, I., 2016. The role of allophane nano-structure and Fe oxide speciation for hosting soil organic matter in an allophanic Andosol. Geochimica et Cosmochimica Acta 180, 284-302.

Fontaine, S., Barot, S., Barre, P., Bdioui, N., Mary, B., Rumpel, C., 2007. Stability of organic carbon in deep soil layers controlled by fresh carbon supply. Nature 450, 277-280.

Fontaine, S., Mariotti, A., Abbadie, L., 2003. The priming effect of organic matter: a question of microbial competition? Soil Biology and Biochemistry 35, 837-843.

Garcia-Rodeja, E., Silva, B., Macías, F., 1987. Andosols developed from non-volcanic materials in Galicia, NW Spain. Journal of Soil Science 38, 573-591.

Ghani, A., Dexter, M., Perrot, K., O'Connor, M.B., Hawke, M.F., 1994. Role of pine needles in declining soil pH and nutrient cycling under agroforestry systems of cultivation. Proceedings of the New Zealand Society of Soil Science Conference, Lincoln University, November, p. 58.

Giddens, K.M., Parfitt, R.L., Percival, H.J., 1997. Comparison of some soil properties under Pinus radiata and improved pasture. New Zealand Journal of Agricultural Research 40, 409-416.

Goh, K.M., 2004. Carbon sequestration and stabilization in soils: Implications for soil productivity and climate change. Soil Science and Plant Nutrition 50, 467-476.

Gregorich, E.G., Janzen, H.H., 2000. Decomposition. Handbook of soil science. CRC Press Boca Raton London, NY, Washington, DC C-107–C-120.

Gregory, P.J., 2006. Roots, rhizosphere and soil: the route to a better understanding of soil science? European Journal of Soil Science 57, 2-12.

Gregory, P.J., 2007. The Rhizosphere. Plant Roots: Growth, Activity and Interactions with Soils. Blackwell Publishing Ltd, pp. 216-252.

Gregory, P.J., Hinsinger, P., 1999. New approaches to studying chemical and physical changes in the rhizosphere: an overview. Plant Soil 211, 1-9.

Grimalt, J.O., Sáiz-Jiménez, C., 1989. Lipids of soil humic acids. I. The hymatomelanic acid fraction. Science of the total environment 81, 409-420.

Guo, L.B., Gifford, R., 2002. Soil carbon stocks and land use change: a meta analysis. Global change biology 8, 345-360.

Gutiérrez, A., Martínez, M.J., Almendros, G., González-Vila, F.J., Martínez, A.T., 1995. Hyphal-sheath polysaccharides in fungal deterioration. Science of The Total Environment 167, 315-328.

Haider, K., Schäffer, A., 2009. Turnover of Nitrogen, Phosphorus and Sulfur in Soils and Sediments. Soil Biochemistry. Science Publishers, pp. 49-75.

Harsh, J., Chorover, J., Nizeyimana, E., 2002. Allophane and imogolite. Soil Mineralogy with environmental applications, 291-322.

Hashizume, H., Theng, B.K., 2007. Adenine, adenosine, ribose and 5′-AMP adsorption to allophane. Clays and Clay Minerals 55, 599-605.

Hassink, J., 1997. The capacity of soils to preserve organic C and N by their association with clay and silt particles. Plant Soil 191, 77-87.

Hedley, C.B., Kusumo, B.H., Hedley, M.J., Tuohy, M.P., Hawke, M., 2009. Soil C and N sequestration and fertility development under land recently converted from plantation forest to pastoral farming. New Zealand Journal of Agricultural Research 52, 443-453.

Henmi, T., Wada, K., 1976. Morphology and composition of allophane. American Mineralogist 61, 379-390.

Hewitt, A., 1989. New Zealand soil classification (version 2.0). DSIR Division of Land and Soil Sciences Technical Record DN 2. DSIR, New Zealand.

Hewitt, A., 2010. New Zealand soil classification. Landcare research science series.

Hewitt, A., Dymond, J., 2013. Survey of new zealand soil orders. Ecosystem services in New Zealand: conditions and trends, 121-131.

Higashi, T., 1983. Characterization of Al/Fe—humus complexes in dystrandepts through comparison with synthetic forms. Geoderma 31, 277-288.

Hiltner, L., 1904. Über neuere Erfahrungen und Probleme auf dem Gebiete der Bodenbakteriologie unter besonderer Berücksichtigung der Gründüngung und Brache. Arbeiten der Deutschen Landwirtschaftlichen Gesellschaft 98, 59-78.

Hinsinger, P., Gilkes, R., 1997. Dissolution of phosphate rock in the rhizosphere of five plant species grown in an acid, P-fixing mineral substrate. Geoderma 75, 231-249.

Hinsinger, P., Plassard, C., Tang, C., Jaillard, B., 2003. Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: a review. Plant Soil 248, 43-59.

Högberg, P., Nordgren, A., Buchmann, N., Taylor, A.F., Ekblad, A., Högberg, M.N., Nyberg, G., Ottosson-Löfvenius, M., Read, D.J., 2001. Large-scale forest girdling shows that current photosynthesis drives soil respiration. Nature 411, 789-792.

Huang, Y.-T., Lowe, D.J., Churchman, G.J., Schipper, L.A., Cursons, R., Zhang, H., Chen, T.-Y., Cooper, A., 2016. DNA adsorption by nanocrystalline allophane spherules and nanoaggregates, and implications for carbon sequestration in Andisols. Applied Clay Science 120, 40-50.

Huygens, D., Boeckx, P., Van Cleemput, O., Oyarzun, C., Godoy, R., 2005. Aggregate and soil organic carbon dynamics in South Chilean Andisols. Biogeosciences 2, 159-174.

Inoue, K., Higashi, T., Kinloch, D., Shoji, S., Beinroth, F., Eswaran, H., 1988. Al and Fe-humus complexes in Andisols. Proceedings of the Ninth International Soil Classification Workshop, Japan.

Johnson-Maynard, J., McDaniel, P., Falen, A., Ferguson, D., 1997. Chemical and mineralogical conversion of Andisols following invasion by bracken fern. Soil Science Society of America Journal 61, 549-555.

Jones, L., Darrah, R., 1994. Amino-Acid Influx at the Soil-Root Interface of Zea-Mays L and Its Implications in the Rhizosphere. Plant Soil 163, 1-12.

Keiluweit, M., Bougoure, J.J., Nico, P.S., Pett-Ridge, J., Weber, P.K., Kleber, M., 2015. Mineral protection of soil carbon counteracted by root exudates. Nature Climate Change 5, 588-595.

Keith, H., Oades, J., Martin, J., 1986. Input of carbon to soil from wheat plants. Soil Biology and Biochemistry 18, 445-449.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., Nico, P.S., 2015. Mineral–Organic Associations: Formation, Properties, and Relevance in Soil Environments. Advances in Agronomy 130, 1-140.

Kuzyakov, Y., 2010. Priming effects: interactions between living and dead organic matter. Soil Biology and Biochemistry 42, 1363-1371.

Kuzyakov, Y., Blagodatskaya, E., 2015. Microbial hotspots and hot moments in soil: Concept & review. Soil Biology and Biochemistry 83, 184-199.

Kuzyakov, Y., Cheng, W., 2001. Photosynthesis controls of rhizosphere respiration and organic matter decomposition. Soil Biology and Biochemistry 33, 1915-1925.

Lal, R., 2006. Encyclopedia of soil science. CRC Press.

Lawrence-Smith, E., Curtin, D., Beare, M., Kelliher, F., 2015. Potential applications of full inversion tillage to increase soil carbon storage during pasture renewal in New Zealand.

Leamy, 1984. International Committee on the Classification of Andisols (ICOMAND) Circular letter No. 6. New Zealand Soil Bureau, DSIR, Lower Hutt.

Lehmann, J., Joseph, S., 2015. Biochar for environmental management: science, technology and implementation. Routledge.

Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. Nature 528, 60-68.

Lennon, J.T., Jones, S.E., 2011. Microbial seed banks: the ecological and evolutionary implications of dormancy. Nature Reviews Microbiology 9, 119-130.

Lewis, N.G., Yamamoto, E., 1990. Lignin: occurrence, biogenesis and biodegradation. Annual review of plant biology 41, 455-496.

Longhurst, B., Rajendram, G., Miller, B., Dexter, M., 2017. Nutrient content of liquid and solid effluents on NZ dairy cow farms. 2017 FLRC Conference, Palmerston North. Poster.

Lorenz, S., Hamon, R., McGrath, S., 1994. Differences between soil solutions obtained from rhizosphere and non-rhizosphere soils by water displacement and soil centrifugation. European Journal of Soil Science 45, 431-438.

Lowe, D.J., 1986. Controls on the rates of weathering and clay mineral genesis in airfall tephras: a review and New Zealand case study. Rates of chemical weathering of rocks and minerals, 265-330.

Lowe, D.J., Palmer, D.J., 2005. Andisols of New Zealand and Australia. Journal of Integrated Field Science 2, 39-65.

Lynch, J., Whipps, J., 1991. Substrate flow in the rhizosphere. The rhizosphere and plant growth. Springer, pp. 15-24.

Matus, F., Amigo, X., Kristiansen, S.M., 2006. Aluminium stabilization controls organic carbon levels in Chilean volcanic soils. Geoderma 132, 158-168.

Matus, F., Garrido, E., Sepúlveda, N., Cárcamo, I., Panichini, M., Zagal, E., 2008. Relationship between extractable Al and organic C in volcanic soils of Chile. Geoderma 148, 180-188.

Matus, F., Panichini, M., Godoy, R., Borie, F., 2009. Soil carbon storage in allophanic soils: study of a temperate pristine rainforest Nothofagus pumilio in the altitudinal limit.

Proceedings in Ecological Advances on Chilean Temperate Rainforests. Academic Press, Belgium, pp. 147-169.

Matus, F., Rumpel, C., Neculman, R., Panichini, M., Mora, M.L., 2014. Soil carbon storage and stabilisation in andic soils: a review. Catena 120, 102-110.

McLay, C., Barton, L., Tang, C., 1997. Acidification potential of ten grain legume species grown in nutrient solution. Australian Journal of Agricultural Research.

McNear Jr, D.H., 2013. The rhizosphere-roots, soil and everything in between. Nature Education Knowledge.

Merckx, R., Den Hartog, A., Van Veen, J., 1985. Turnover of root-derived material and related microbial biomass formation in soils of different texture. Soil Biology and Biochemistry 17, 565-569.

Mimmo, T., Del Buono, D., Terzano, R., Tomasi, N., Vigani, G., Crecchio, C., Pinton, R., Zocchi, G., Cesco, S., 2014. Rhizospheric organic compounds in the soil-microorganism-plant system: their role in iron availability. European Journal of Soil Science 65, 629-642.

Minchin, F.R., Summerfield, R.J., Hadley, P., Roberts, E.H., Rawsthorne, S., 1981. Carbon and nitrogen nutrition of nodulated roots of grain legumes. Plant, Cell & Environment 4, 5-26.

Miyazawa, M., Takahashi, T., Sato, T., Kanno, H., Nanzyo, M., 2013. Factors controlling accumulation and decomposition of organic carbon in humus horizons of Andosols. Biology and fertility of soils 49, 929-938.

Mizota, C., Van Reeuwijk, L., 1989. Clay mineralogy and chemistry of soils formed in volcanic material in diverse climatic regions. ISM Monograph.

Mohammad, M., Shibli, R., Ajlouni, M., Nimri, L., 1998. Tomato root and shoot responses to salt stress under different levels of phosphorus nutrition. Journal of plant nutrition 21, 1667-1680.

Nanzyo, M., 2002. Unique properties of volcanic ash soils. Global environmental research 6, 99-112.

Neall, V.E., Beinroth, F.H., Luzio, W.L., Maldonado, F.P., Eswaran, H., 1985. Parent materials of Andisols. Proc. Sixth Int. Soil Classif. Workshop, Chile and Ecaudor. Part, pp. 9-19.

Nguyen, C., Todorovic, C., Robin, C., Christophe, A., Guckert, A., 1999. Continuous monitoring of rhizosphere respiration after labelling of plant shoots with 14CO2. Plant Soil 212, 189-199.

Nielsen, K.L., Lynch, J.P., Jablokow, A.G., Curtis, P.S., 1994. Carbon cost of root systems: an architectural approach. Belowground Responses to Rising Atmospheric CO2: Implications for Plants, Soil Biota, and Ecosystem Processes. Springer, pp. 161-169.

Nierop, K., 1998. Origin of aliphatic compounds in a forest soil. Organic geochemistry 29, 1009-1016.

Nierop, K.G., Jansen, B., 2009. Extensive transformation of organic matter and excellent lipid preservation at the upper, superhumid Guandera páramo. Geoderma 151, 357-369.

Nierop, K.G.J., van Bergen, P.F., Buurman, P., van Lagen, B., 2005. NaOH and Na4P2O7 extractable organic matter in two allophanic volcanic ash soils of the Azores Islands—a pyrolysis GC/MS study. Geoderma 127, 36-51.

Norstadt, F.A., Porter, L.K., 1984. Soil gases and temperatures: a beef cattle feedlot compared to alfalfa. Soil Science Society of America Journal 48, 783-789.

Oades, J., Waters, A., 1991. Aggregate hierarchy in soils. Soil Research 29, 815-828.

Oh, N.H., Richter, D.D., 2004. Soil acidification induced by elevated atmospheric CO2. Global Change Biology 10, 1936-1946.

Olsen, S.R., Cole, C.V., Watanabe, F.S., Dean, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular 939, pp19.

Parfitt, R., 1990. Allophane in New Zealand-a review. Soil Research 28, 343-360.

Parfitt, R., 2009. Allophane and imogolite: role in soil biogeochemical processes. Clay Minerals 44, 135-155.

Parfitt, R., Percival, H., Dahlgren, R., Hill, L., 1997a. Soil and solution chemistry under pasture and radiata pine in New Zealand. Plant Soil 191, 279-290.

Parfitt, R., Saigusa, M., 1985. Allophane and humus-aluminum in Spodosols and Andepts formed from the same volcanic ash beds in New Zealand. Soil Science 139, 149-155.

Parfitt, R., Theng, B.K.G., Whitton, J.S., Shepherd, T.G., 1997b. Effects of clay minerals and land use on organic matter pools. Geoderma 75, 1-12.

Parfitt, R.L., Wilson, A., 1985. Estimation of allophane and halloysite in three sequences of volcanic soils, New Zealand. Volcanic Soils. Catena Suppl 7, 1-8.

Paterson, E., 2003. Importance of rhizodeposition in the coupling of plant and microbial productivity. European journal of soil science 54, 741-750.

Paul, S., Martinson, G.O., Veldkamp, E., Flessa, H., 2008. Sample pretreatment affects the distribution of organic carbon in aggregates of tropical grassland soils. Soil Science Society of America Journal 72, 500-506.

Percival, H.J., Parfitt, R.L., Scott, N.A., 2000. Factors Controlling Soil Carbon Levels in New Zealand Grasslands Is Clay Content Important? Soil Science Society of America Journal 64, 1623-1630.

Philippot, L., Raaijmakers, J.M., Lemanceau, P., van der Putten, W.H., 2013. Going back to the roots: the microbial ecology of the rhizosphere. Nature Reviews Microbiology 11, 789-799.

Pigna, M., Violante, A., 2003. Adsorption of sulfate and phosphate on Andisols. Communications in soil science and plant analysis 34, 2099-2113.

Poirier, N., Sohi, S.P., Gaunt, J.L., Mahieu, N., Randall, E.W., Powlson, D.S., Evershed, R.P., 2005. The chemical composition of measurable soil organic matter pools. Organic Geochemistry 36, 1174-1189.

Powlson, D., Whitmore, A., Goulding, K., 2011. Soil carbon sequestration to mitigate climate change: a critical re-examination to identify the true and the false. European Journal of Soil Science 62, 42-55.

Rasse, D.P., Rumpel, C., Dignac, M.-F., 2005. Is soil carbon mostly root carbon? Mechanisms for a specific stabilisation. Plant Soil 269, 341-356.

Reid, C., Kidd, F., Ekwebelam, S., 1983. Nitrogen nutrition, photosynthesis and carbon allocation in ectomycorrhizal pine. Plant Soil 71, 415-431.

Saggar, S., Tate, K.R., Feltham, C.W., Childs, C.W., Parshotam, A., 1994. Carbon turnover in a range of allophanic soils amended with 14C-labelled glucose. Soil biology and biochemistry 26, 1263-1271.

Sáiz-Jiménez, C., 1994. Production of alkylbenzenes and alkylnaphthalenes upon pyrolysis of unsaturated fatty acids. Naturwissenschaften 81, 451-453.

Sáiz-Jiménez, C., De Leeuw, J., 1986. Chemical characterization of soil organic matter fractions by analytical pyrolysis-gas chromatography-mass spectrometry. Journal of Analytical and Applied Pyrolysis 9, 99-119.

Sarathchandra, S., Burch, G., Cox, N., 1997. Growth patterns of bacterial communities in the rhizoplane and rhizosphere of white clover (Trifolium repens L.) and perennial ryegrass (Lolium perenne L.) in long-term pasture. Applied Soil Ecology 6, 293-299.

Schellekens, J., Buurman, P., 2011. n-Alkane distributions as palaeoclimatic proxies in ombrotrophic peat: the role of decomposition and dominant vegetation. Geoderma 164, 112-121.

Schellekens, J., Buurman, P., Pontevedra-Pombal, X., 2009. Selecting parameters for the environmental interpretation of peat molecular chemistry–a pyrolysis-GC/MS study. Organic Geochemistry 40, 678-691.

Scherer, H., Ahrens, G., 1996. Depletion of non-exchangeable NH 4-N in the soil—root interface in relation to clay mineral composition and plant species. European journal of agronomy 5, 1-7.

Schipper, L.A., Baisden, W.T., Parfitt, R.L., Ross, C., Claydon, J.J., Arnold, G., 2007. Large losses of soil C and N from soil profiles under pasture in New Zealand during the past 20 years. Global Change Biology 13, 1138-1144.

Schipper, L.A., Parfitt, R.L., Fraser, S., Littler, R.A., Baisden, W.T., Ross, C., 2014. Soil order and grazing management effects on changes in soil C and N in New Zealand pastures. Agriculture, Ecosystems & Environment 184, 67-75.

Schipper, L.A., Parfitt, R.L., Ross, C., Baisden, W.T., Claydon, J.J., Fraser, S., 2010. Gains and losses in C and N stocks of New Zealand pasture soils depend on land use. Agriculture, Ecosystems & Environment 139, 611-617.

Scott, N.A., Tate, K.R., Ford-Robertson, J., Giltrap, D.J., Smith, C.T., 1999. Soil carbon storage in plantation forests and pastures: land-use change implications. Tellus B 51, 326-335.

Shindo, H., Honna, T., Yamemoto, S., Homna, H., 2002. Distribution of charred plant fragments in Japanese volcanic ash soils with reference to origins of black humic acids. Proceedings of the International Humic Substances Society, 20 th Anniversary Conference, pp. 466-468.

Shoji, S., Nanzyo, M., Dahlgren, R.A., 1994. Volcanic ash soils: genesis, properties and utilization. Elsevier.

Six, J., Conant, R., Paul, E.A., Paustian, K., 2002. Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. Plant Soil 241, 155-176.

Six, J., Elliott, E., Paustian, K., 2000. Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. Soil Biology and Biochemistry 32, 2099-2103.

Smith, G.D., 1978. A preliminary proposal for reclassification of Andepts and some andic subgroups. Reprinted as: The Andisol proposal.

Soil Survey Staff, 1960. Soil Classification: A Comprehensive System. 7th Approximation. Soil Survey Staff, Soil Conservation Service, United States. Department of Agriculture.

Soil Survey Staff, 1999. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. Natural Resources Conservation Service. U.S. Department of Agriculture Handbook 436.

Soil Survey Staff, 2006. Keys to Soil Taxonomy. Natural Resources Conservation Service, U.S. Department of Agriculture.

Sollins, P., Homann, P., Caldwell, B.A., 1996. Stabilization and destabilization of soil organic matter: mechanisms and controls. Geoderma 74, 65-105.

Southard, S., Southard, R., 1989. Mineralogy and classification of andic soils in northeastern California. Soil Science Society of America Journal 53, 1784-1791.

Stankiewicz, B.A., van Bergen, P.F., Duncan, I.J., Carter, J.F., Briggs, D.E.G., Evershed, R.P., 1996. Recognition of Chitin and Proteins in Invertebrate Cuticles Using Analytical Pyrolysis/Gas Chromatography and Pyrolysis/Gas Chromatography/Mass Spectrometry. Rapid Communications in Mass Spectrometry 10, 1747-1757.

Stuczynski, T., McCarty, G., Reeves, J., Wright, R., 1997. Use of Pyrolysis GC/MS for Assessing Changes in Soil Organic Matter Quality. Soil Science 162, 97-105.

Suárez-Abelenda, M., Ahmad, R., Camps-Arbestain, M., Herath, S.H.M.S.K., 2015. Changes in the chemical composition of soil organic matter over time in the presence and absence of living roots: a pyrolysis GC/MS study. Plant Soil 391, 161-177.

Suárez-Abelenda, M., Buurman, P., Camps Arbestain, M., Kaal, J., Martinez-Cortizas, A., Gartzia-Bengoetxea, N., Macías, F., 2011. Comparing NaOH-extractable organic matter of acid forest soils that differ in their pedogenic trends: a pyrolysis-GC/MS study. European Journal of Soil Science 62, 834-848.

Suárez-Abelenda, M., Kaal, J., Camps-Arbestain, M., Knicker, H., Macías, F., 2014. Molecular characteristics of permanganate-and dichromate-oxidation-resistant soil organic matter from a black-C-rich colluvial soil. Soil Research 52, 164-179.

Sweeney, C., Fraser, B., Hunt, M., Fyfe, J., Gulliver, S., Petrie, S., Godber, D., Tsui, K., Dahya, A., Pickering, A., Austin, D., 2011. New Zealand's Greenhouse Gas Inventory 1990-2009., Report No. ME 1045, New Zealand Ministry for the Environment.

Takahashi, J., Higashi, T., 2015. Sulphate retention: a simplified method for categorizing soils into allophanic and non-allophanic Andosols. European Journal of Soil Science 66, 65-73.

Takahashi, T., Dahlgren, R.A., 2016. Nature, properties and function of aluminum–humus complexes in volcanic soils. Geoderma 263, 110-121.

Takahashi, T., Ikeda, Y., Fujita, K., Nanzyo, M., 2006. Effect of liming on organically complexed aluminum of nonallophanic Andosols from northeastern Japan. Geoderma 130, 26-34.

Takahashi, T., Mitamura, A., Ito, T., Ito, K., Nanzyo, M., Saigusa, M., 2008. Aluminum solubility of strongly acidified allophanic Andosols from Kagoshima Prefecture, southern Japan. Soil science and plant nutrition 54, 362-368.

Takahashi, T., Shoji, S., 2002. Distribution and classification of volcanic ash soils. GLOBAL ENVIRONMENTAL RESEARCH-ENGLISH EDITION- 6, 83-98.

Tang, C., Hinsinger, P., Drevon, J., Jaillard, B., 2001. Phosphorus deficiency impairs early nodule functioning and enhances proton release in roots of Medicago truncatula L. Annals of Botany 88, 131-138.

Tate, R.L., 1987. Organic matter transformations: ecosystem examples. Soil Organic Matter, Biological and Ecological Effects. Wiley, New York, 26-53.

Taylor, M.D., Lowe, D.J., Hardi, P., Smidt, G.A., Schnug, E., 2016. Comparing volcanic glass shards in unfertilised and fertilised Andisols derived from rhyolitic tephras, New Zealand: Evidence for accelerated weathering and implications for land management. Geoderma 271, 91-98.

Tegelaar, E., De Leeuw, J., Derenne, S., Largeau, C., 1989. A reappraisal of kerogen formation. Geochimica et Cosmochimica Acta 53, 3103-3106.

Tisdall, J., Oades, J., 1979. Stabilization of soil aggregates by the root systems of ryegrass. Soil Research 17, 429-441.

Tokashiki, Y., Wada, K., 1975. Weathering implications of the mineralogy of clay fractions of two Ando soils, Kyushu. Geoderma 14, 47-62.

Torn, M.S., Trumbore, S.E., Chadwick, O.A., Vitousek, P.M., Hendricks, D.M., 1997. Mineral control of soil organic carbon storage and turnover. Nature 389, 170-173.

Trolldenier, G., 1992. Techniques for observing phosphorus mobilization in the rhizosphere. Biology and fertility of soils 14, 121-125.

Tsuge, S., Matsubara, H., 1985. High-resolution pyrolysis-gas chromatography of proteins and related materials. Journal of Analytical and Applied Pyrolysis 8, 49-64.

Ugolini, F.C., Dahlgren, R.A., 2002. Soil development in volcanic ash. Global environmental research 6, 69-82.

Uren, N.C., 2007. Types, amounts, and possible functions of compounds released into the rhizosphere by soil-grown plants. The rhizosphere. Biochemistry and organic substances at the soil-plant interface. Marcel Dekker, New York, 1-21.

Van Veen, J., Liljeroth, E., Lekkerkerk, L., Van de Geijn, S., 1991. Carbon fluxes in plant-soil systems at elevated atmospheric CO2 levels. Ecological applications 1, 175-181.

Verde, J.R., Camps Arbestain, M., Macias, F., 2010. Influence of Agricultural Practices on the Stability of Organo-Al Complexes in an Alu-Andic Andosol: A Laboratory Study. Soil Science 175, 390-397.

Verde, J.R., Camps Arbestain, M., Macías, F., 2005. Expression of andic properties in soils from Galicia (NW Spain) under forest and agricultural use. European Journal of Soil Science 56, 53-64.

Verde Vilanova, J.R., 2009. Influencia de los factores de formación y uso del suelo en las propiedades ándicas, formas y mecanismos de estabilización de carbono en suelos del noroeste de la Península Ibérica. Univ Santiago de Compostela.

Wada, K., 1980. Mineralogical characteristics of Andisols. In: Theng, B.K.G. (Ed.), Soils with variable charge. Soil Bureau, Lower Hutt, New Zealand.

Wada, K., 1989. Allophane and imogolite. In: Dixon, J.B., Weed, S. (Eds.), Minerals in Soil Environments. Soil Science Society of America, Madison, Wisconsin, pp. 1051-1087.

Wang, T., Camps-Arbestain, M., Hedley, C., 2016. Factors influencing the molecular composition of soil organic matter in New Zealand grasslands. Agriculture, Ecosystems & Environment 232, 290-301.

Warembourg, F., Estelrich, H., 2001. Plant phenology and soil fertility effects on below-ground carbon allocation for an annual (Bromus madritensis) and a perennial (Bromus erectus) grass species. Soil Biology and Biochemistry 33, 1291-1303.

Warembourg, F., Roumet, C., Lafont, F., 2003. Differences in rhizosphere carbon-partitioning among plant species of different families. Plant Soil 256, 347-357.

Wild, B., Schnecker, J., Alves, R.J.E., Barsukov, P., Bárta, J., Čapek, P., Gentsch, N., Gittel, A., Guggenberger, G., Lashchinskiy, N., Mikutta, R., Rusalimova, O., Šantrůčková, H., Shibistova, O., Urich, T., Watzka, M., Zrazhevskaya, G., Richter, A., 2014. Input of easily available organic C and N stimulates microbial decomposition of soil organic matter in arctic permafrost soil. Soil Biology and Biochemistry 75, 143-151.

Yuan, G., Theng, B., Parfitt, R., Percival, H., 2000. Interactions of allophane with humic acid and cations. European Journal of Soil Science 51, 35-41.

Supplementary Information

1. Detailed Information of pH

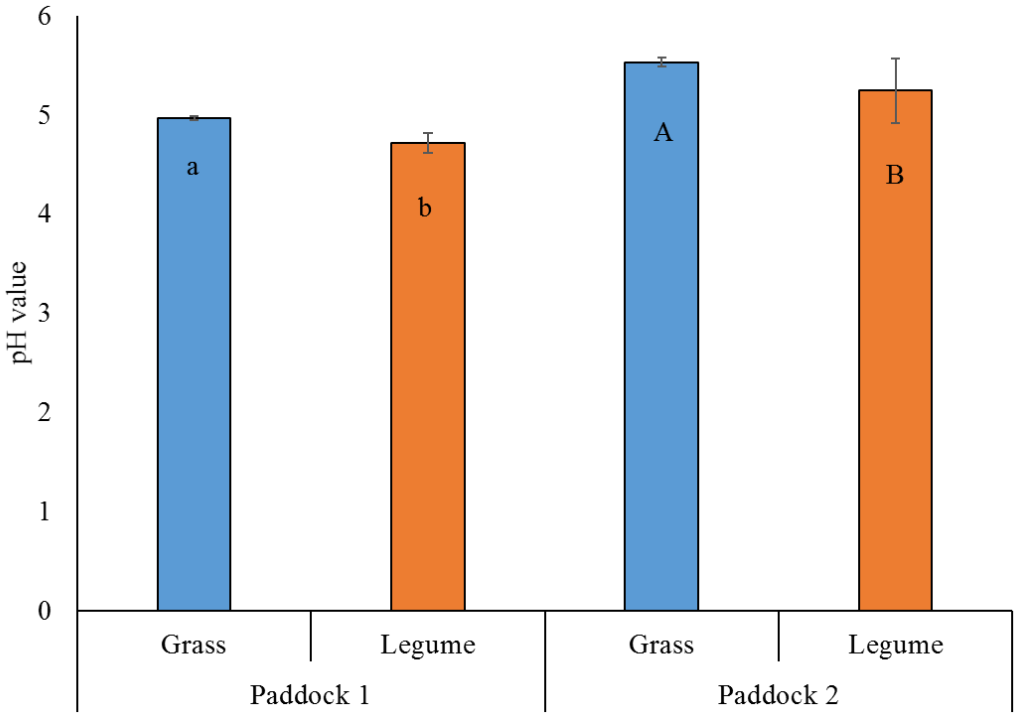

Figure S 1: Values of pH-KCl of bulk soil in Paddock 1 (grass and legume) and in Paddock 2 (grass and legume). Bars represent standard deviation of means. Different letters of the same style (small letters for Paddock 1 and capital letters for Paddock 2) show significant differences of pH-KCl of soils under grass and legume at the same paddock.

2. Detailed Information of Al_p

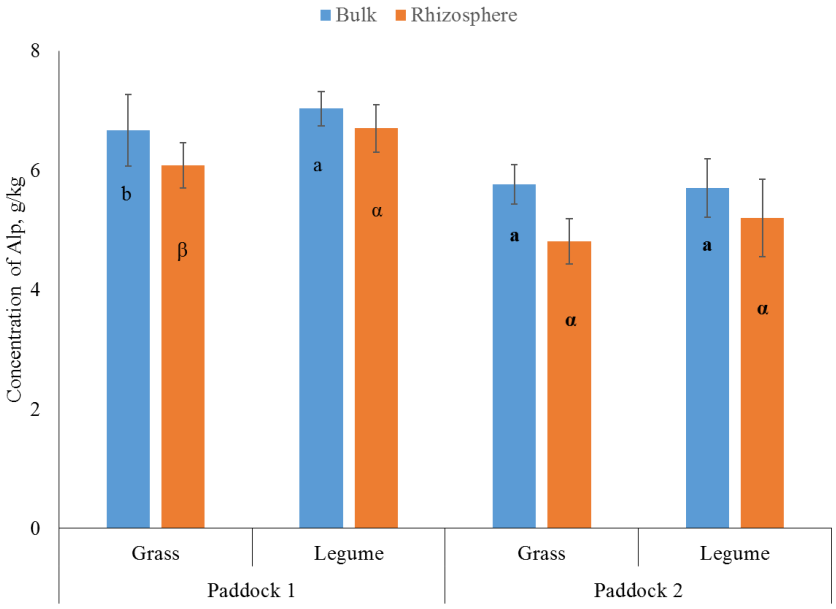

Figure S 2: Values of Al_p of bulk and rhizosphere from Paddock 1 (grass and legume) and Paddock 2 (grass and legume). Bars represent standards deviation of means. Significant differences between species of the same paddock are marked by different letters in the same style (regular-faced letters for Paddock1 and bold-faced letters for Paddock 2).

3. List of pyrolysis products

Table S 1: Pyrolysis product list, molecular mass (M+), fragment ion used (m/z) and average retention time (RT). - indicates unknown molecular mass. MAHs, monocyclic aromatic hydrocarbons; PAHs, polycyclic aromatic hydrocarbons*

Group	Code	Compound	M^+	*m/z*	RT
Polysaccharides	Ps1	Furan, 3-methyl-	82	53+82	1.948
Polysaccharides	Ps2	Acetic acid	60	45+60	2.073
MAHs	Ar1	Benzene	78	52+78	2.365
Polysaccharides	Ps3	Furan, 2,5-dimethyl-	96	95+96	2.798
N-compounds	N1	Pyridine	79	52+79	3.290
Polysaccharides	Ps4	Furan, 2-methyl-	82	53+82	3.373
N-compounds	N2	Pyrrole	67	67	3.448
MAHs	Ar2	Toluene	92	91+92	3.632
Chitin	N3	Acetamide	59	59	3.932
Polysaccharides	Ps5	(2H)-Furan-2-one	84	54+84	4.123
Fatty acids	FA4	C4 Fatty acid	88	60+73	4.307
Polysaccharides	Ps6	3-furaldehyde	96	95+96	4.423
N-compounds	N4	Pyridine, 2-methyl-	93	66+93	4.515
Polysaccharides	Ps7	2,5 furandione	98	54+98	4.757
Polysaccharides	Ps8	2-Furaldehyde	96	95+96	4.832
N-compounds	N5	1H-Pyrrole, 1-methyl-	81	80+81	5.015
N-compounds	N6	1H-Pyrrole, 3-methyl-	81	80+81	5.215
N-compounds	N7	Pyridine, 3-methyl-	93	66+93	5.473
MAHs	Ar3	Ethylbenzene	106	91+106	5.490
MAHs	Ar4	Ethylbenzene	106	91+106	5.682
Polysaccharides	Ps9	4-cyclopentene-1,3-dione	96	68+96	6.015
MAHs	Ar5	Styrene	104	78+104	6.190
MAHs	Ar6	1,3 dimethylbenzene	106	91+106	6.257
Fatty acids	FA5	C5 Fatty acid	102	60+73	6.440
Polysaccharides	Ps10	2-ethyl-5-methylfuran	110	95+110	6.465
Polysaccharides	Ps11	2-acetylfuran	110	95+110	6.690
Polysaccharides	Ps12	5H-furan-2-one	84	55+84	6.773
Polysaccharides	Ps13	2-Furaldehyde, 3-methyl-	110	109+110	6.782
Polysaccharides	Ps14	dihydro-3-methylene-2(3H)-furanone	98	68+98	7.015
Polysaccharides	Ps15	2,3-dihydro-5-methylfuran-2-one	98	55+98	7.098
N-compounds	N8	1H-pyrrole, 3-ethyl	95	80+95	7.123
N-compounds	N9	Pyridine, 2,5-dimethyl-	107	107+106	7.240
N-compounds	N10	1H-Pyrrole, 2,4-dimethyl-	95	94+95	7.432
N-compounds	N11	Pyridine, x,x-dimethyl-	107	107+106	7.598
N-compounds	N12	1H-Pyrrole, 1-ethyl-	95	80+95	7.648
N-compounds	N13	3-methyl-pyridine	93	66+93	7.948
MAHs	Ar7	Benzaldehyde	106	77+106	8.015
Polysaccharides	Ps16	2-Furaldehyde, 5-methyl-	110	109+110	8.098
Phenols	Ph1	Resorcinol (benzenediol)	110	82+110	8.515
Phenols	Ph2	Phenol	94	66+94	8.773
Other aliphatics	ee1	intermediate alkene	116	55+69	8.898
Alkenes	10.1	C10:1	140	55+69	8.998
N-compounds	N14	1H-pyrrole-2,5-dione	97	69+97	8.998
Polysaccharides	Ps17	Benzofuran	118	89+118	9.032
Fatty acids	FA6	C6 Fatty acid	116	60+73	9.048
Polysaccharides	Ps18	4-Hydroxy-5,6-dihydro-2H-pyran-2-one	114	114+58	9.098
Alkanes	10.0	C10:0	142	57+71	9.148
N-compounds	N15	1H-Pyrrole-2-carboxaldehyde	95	66+95	9.548
Polysaccharides	Ps19	3,4-dihydropyran-2,5-dione	112	55+112	9.565
Polysaccharides	Ps20	3-hydroxy-2-methyl-2-cyclopenten-1-one	112	55+112	9.982
Polysaccharides	Ps21	2,3-dimethylcyclopent-2-en-1-one	110	67+110	10.265
Polysaccharides	Ps22	dianhydrorhamnose	128	113+128	10.332
MAHs	Ar8	Indene	116	115+116	10.423
Phenols	Ph3	Phenol, 3-methyl-	108	107+108	10.840

N-compounds	N16	2-acetylpyrrole (or Ethanone, 1-(1H-pyrrol-2-YL)-)	109	94+109	11.007
Phenols	Ph4	acetophenone	120	105+77	11.065
Phenols	Ph5	Phenol, 4-methyl-	108	107+108	11.448
N-compounds	N17	oxazole, 2,4-dimethyl	97	68+97	11.515
Polysaccharides	Ps23	2,5-dimethyl-4-hydroxy-3(2H)-furanone	128	57+128	11.640
Lignin	Lg1	Guaiacol	124	109+124	11.765
Alkenes	11.1	C11:1	154	55+69	11.815
Fatty acids	FA7	C7 Fatty acid	130	60+73	11.823
Polysaccharides	Ps24	Benzofuran, x-methyl-	132	131+132	12.007
Alkanes	11.0	C11:0	156	57+71	12.065
Polysaccharides	Ps25	Benzofuran, x-methyl-	132	131+132	12.165
Polysaccharides	Ps26	Benzofuran, x-methyl-	132	131+132	12.307
Polysaccharides	Ps27	4H-Pyran-4-one, 3-hydroxy-2-methyl- (maltol)	126	71+126	12.457
N-compounds	N18	2-hydroxypyridine	95	67+95	12.607
N-compounds	N19	1-H-pyrazole, 3-methyl	82	81+82	12.898
N-compounds	N20	Benzonitrile, 3-methyl-	117	90+117	13.190
Phenols	Ph6	Phenol, x,x-dimethyl-	122	107+122	13.273
Polysaccharides	Ps28	4H-pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl	144	101+144	13.407
MAHs	Ar9	1H-indene, x-methyl	130	115+130	13.490
Phenols	Ph7	Phenol, 2,6-dimethyl-	122	107+122	13.548
MAHs	Ar10	1H-indene, x-methyl	130	115+130	13.657
Polysaccharides	Ps29	sugar compound ? (beta.-l-Rhamnofuranoside, methyl-5-O-acetyl-??)	-*	71+87	13.790
PAHs	PA1	naphthalene, 1,2-dihydro	130	129+130	13.907
Phenols	Ph8	Phenol, 4-ethyl-	122	107+122	14.107
Phenols	Ph9	Phenol, 2-ethyl-	122	107+122	14.173
Polysaccharides	Ps30	1-Deoxy-2,4-methylene-3,5-anhydro-d-xylitol (most sure)	130	69+100	14.382
Phenols	Ph10	Phenol, x-ethyl-	122	107+122	14.407
PAHs	PA2	naphthalene	128	128	14.490
Fatty acids	FA8	C8 Fatty acid	144	60+73	14.573
Alkenes	12.1	C12:1	168	55+69	14.715
Lignin	Lg2	4-methyl guaiacol	138	123+138	14.782
Phenols	Ph11	Phenol, x-ethyl-	122	107+122	14.857
Alkanes	12.0	C12:0	170	57+71	14.957
Polysaccharides	Ps31	Benzofuran, 4,7-dimethyl-	146	145+146	15.190
Polysaccharides	Ps32	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	144	57+69	15.273
Phenols	Ph12	Catechol	110	64+110	15.373
Polysaccharides	Ps33	Benzofuran, 4,7-dimethyl-	146	145+146	15.398
Lignin	Lg3	4-vinylphenol	120	91+120	15.623
Chitin	N21	3-Acetamidofuran	125	83+125	16.065
Polysaccharides	Ps34	sugar compound	-*	57+73	16.407
N-compounds	N22	Picolinamide (Stankiezwicz #28)	122	79+122	16.640
Phenols	Ph13	1,2-Benzenediol, 3-methoxy- (= methoxy catechol)	140	125+140	16.782
Lignin	Lg4	4-Ethyl guaiacol	152	137+152	17.207
Fatty acids	FA9	C9 Fatty acid	158	60+73	17.215
Alkenes	13.1	C13:1	182	55+69	17.523
PAHs	PA3	Naphthalene, 1-methyl-	142	141+142	17.582
N-compounds	N23	Indole	117	90+117	17.623
Alkanes	13.0	C13:0	184	57+71	17.740
Polysaccharides	Ps35	1,4,-dideoxy-D-Glycero-Hex-1-enopyranos-3-ulose	144	87+144	17.982
PAHs	PA4	Naphthalene, 2/3-methyl-	142	141+142	18.040
Lignin	Lg5	4-Vinylguaiacol	150	135+150	18.165
Polysaccharides	Ps36	2(5H)-Furanone, -dimethyl-	112	69+97	18.323
Lignin	Lg6	Phenol, 4-(2-propenyl)	134	133+134	18.957
Lignin	Lg7	Syringol	154	139+154	19.157
Lignin	Lg8	4-(2-propenyl) guaiacol	164	77+164	19.323
Polysaccharides	Ps37	L-Glucose, 6-deoxy-3-O-methyl-?	-*	74+103	19.590
Fatty acids	FA10	C10 Fatty acid	172	60+73	19.765
N-compounds	N24	1H-Indole, x-methyl	131	130+131	20.090
Polysaccharides	Ps38	Levogalactosan	162	60+73	20.157
Alkenes	14.1	C14:1	196	55+69	20.182

Chitin	N25	Acetamide, N-(2-hydroxyphenyl)	151	80+109	20.265
Alkanes	14.0	C14:0	198	57+71	20.382
Lignin	Lg9	Vanillin	152	151+152	20.423
Lignin	Lg10	4-(prop-2-enyl) guaiacol, trans	164	149+164	20.648
Polysaccharides	Ps39	sugar? (methyl-4-O-methyl.alpha.d-glucopyranosideor 4-O-Methylmannose?)	-*	71+87	20.923
Polysaccharides	Ps40	sugar?	-*	74+101	21.082
Lignin	Lg11	4-methylsyringol	168	153+168	21.632
Lignin	Lg12	4(2-propenyl)guaiacol	164	149+164	21.698
Polysaccharides	Ps41	Levomannosan	162	60+73	22.198
Lignin	Lg13	4-Acetylguaiacol	166	151+166	22.640
Alkenes	15.1	C15:1	210	55+69	22.698
Alkanes	15.0	C15:0	212	57+71	22.890
Chitin	N26	Acetamide, N-(2,4-dihydroxyphenyl)	167	125+167	23.182
Polysaccharides	Ps42	Levoglucosan	162	60+73	23.582
Lignin	Lg14	propan-2-one guaiacol	180	137+180	23.723
N-compounds	N27	2-Pyrrolidone-5-carboxylic acid	143	56+84	24.048
Lignin	Lg15	4-vinylsyringol	180	165+180	24.523
Fatty acids	FA12	C12 Fatty acid	200	60+73	24.557
Lignin	Lg16	4-hydroxy-3methoxy benzoic acid (vanillic acid)	168	153+168	24.882
Alkenes	16.1	C16:1	224	55+69	25.090
Alkanes	16.0	C16:0	226	57+71	25.265
Lignin	Lg17	4-(prop-2-enyl)syringol, trans	194	91+194	25.407
Polysaccharides	Ps43	1,6-anhydro-beta-D-glucofuranose	162	69+73	25.890
Chitin	N28	3-acetamido-5-acetylfuran	167	110+125	26.490
Fatty acids	FA13	C13 Fatty acid	214	60+73	26.782
Alkenes	17.1	C17:1	238	55+69	27.357
Alkanes	17.0	C17:0	240	57+71	27.515
Lignin	Lg18	4-(prop-2-enyl)syringol, cis	194	91+194	27.623
N-compounds	N29	diketodipyrrole	186	93+186	27.740
Other aliphatics	ee2	branched alkene (1-undecene, 5-methyl)	168	55+69	28.190
Lignin	Lg19	4-Acetylsyringol	196	181+196	28.357
Lignin	Lg20	4-(3-hydroxy-1-propenyl)-guaiacol (coniferyl alcohol)	180	137+180	28.473
Fatty acids	FA14	C14 Fatty acid	228	60+73	28.940
Lignin	Lg21	4-(Propan-2-one) syringol	210	167+210	29.165
Alkenes	18.1	C18:1	252	55+69	29.515
Alkanes	18.0	C18:0	254	57+71	29.657
N-compounds	N30	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl) (Diketopiperazine derivative)	210	70+154	30.123
Fatty acids	FA15i	C15 Fatty acid iso	242	60+73	30.248
Fatty acids	FA15a	C15 Fatty acid anteiso	242	60+73	30.407
Other aliphatics	ee3	intermediate n-ene	-*	55+69	30.698
Fatty acids	FA15	C15 Fatty acid	242	60+73	30.990
Polysaccharides	Ps44	alpha-D-galactopyranoside, methyl 2-(acetylamino)-2-deoxy	235	59+60	31.515
Alkenes	19.1	C19:1	266	55+69	31.565
Alkanes	19.0	C19:0	268	57+71	31.698
N-compounds	N31	diketopiperazine derivative isomer	210	70+154	32.057
Fatty acids	FA16i	C16 Fatty acid iso/anteiso	256	60+73	32.248
N-compounds	N32	diketopiperazine derivative isomer	210	70+154	32.407
N-compounds	N33	diketopiperazine derivative	-*	70+194	32.657
Fatty acids	FA16	C16 Fatty acid	256	60+73	32.990
Alkenes	20.1	C20:1	280	55+69	33.523
Alkanes	20.0	C20:0	282	57+71	33.648
Fatty acids	FA17i	C17 Fatty acid iso/anteiso	270	60+73	34.165
Fatty acids	FA17	C17 Fatty acid	270	60+73	34.840
Alkenes	21.1	C21:1	294	55+69	35.390
Alkanes	21.0	C21:0	296	57+71	35.507
Methyl ketones	MK19	C19:0 MK	310	58+59	35.615
Fatty acids	FA18	C18 Fatty acid	284	60+73	36.673
Alkenes	22.1	C22:1	308	55+69	37.190
Alkanes	22.0	C22:0	310	57+71	37.290
Methyl ketones	MK20	C20:0 MK	324	58+59	37.423

Alkenes	23.1	C23:1	322	55+69	38.907
Alkanes	23.0	C23:0	324	57+71	38.998
Methyl ketones	MK21	C21:0 MK	338	58+59	39.148
Alkenes	24.1	C24:1	336	55+69	40.557
Alkanes	24.0	C24:0	338	57+71	40.640
Methyl ketones	MK22	C22:0 MK	352	58+59	40.815
Alkenes	25.1	C25:1	350	55+69	42.148
Alkanes	25.0	C25:0	352	57+71	42.223
Methyl ketones	MK23	C23:0 MK	366	58+59	42.415
Alkenes	26.1	C26:1	364	55+69	43.673
Alkanes	26.0	C26:0	366	57+71	43.748
Methyl ketones	MK24	C24:0 MK	380	58+59	43.957
Lignin	Lg22	alpha, beta-diguaiacylethene	272	272+273	44.632
Alkenes	27.1	C27:1	378	55+69	45.157
Alkanes	27.0	C27:0	380	57+71	45.215
Methyl ketones	MK25	C25:0 MK	394	58+59	45.440
Alkenes	28.1	C28:1	392	55+69	46.573
Alkanes	28.0	C28:0	394	57+71	46.632
Methyl ketones	MK26	C26:0 MK	408	58+59	46.865
Alkanes	29.0	C29:0	408	57+71	48.007
Alkenes	29.1	C29:1	406	55+69	48.015
Methyl ketones	MK27	C27:0 MK	422	58+59	48.257
Alkenes	30.1	C30:1	420	55+69	49.282
Alkanes	30.0	C30:0	422	57+71	49.323
Methyl ketones	MK28	C28:0 MK	436	58+59	49.598
Alkanes	31.0	C31:0	436	57+71	50.607
Alkenes	31.1	C31:1	434	55+69	50.673
Methyl ketones	MK29	C29:0 MK	450	58+59	50.890
Alkenes	32.1	C32:1	448	55+69	51.815
Alkanes	32.0	C32:0	450	57+71	51.840
Methyl ketones	MK30	C30:0 MK	464	58+59	52.140
Alkanes	33.0	C33:0	464	57+71	53.107
Methyl ketones	MK31	C31:0 MK	478	58+59	53.457
Alkanes	34.0	C34:0	478	57+71	54.523
Methyl ketones	MK32	C32:0 MK	492	58+59	54.973
Alkanes	35.0	C35:0	492	57+71	56.207
Methyl ketones	MK33	C33:0 MK	506	58+59	56.740
Methyl ketones	MK34	C33:0 MK	520	58+59	58.857
Methyl ketones	MK35	C33:0 MK	534	58+59	61.398