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 organomineral 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 unstabilise 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-H₂O, 5.3) was significantly lower (P<0.05) than that in Paddock 1 (pH-H₂O, 5.7), which was itself significantly lower (P<0.05) than pH in Paddock 2 (pH-H₂O, 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 ⁽²⁾), 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

Abstract	I
Acknowledgements	II
Table of Contents	IV
List of Figures	VI
Picture	VII
List of Tables	VIII
1. General introduction	1
1.1. Background	1
1.2. Research objective	2
2. Literature Review	3
2.1. Introduction	
2.2. Distribution and Development of Andisols	
2.2.1. Andisols and Distribution	
2.2.2. Development of Andisols	5
2.3. Classification of Andisols	6
2.3.1. International Classification Systems	6
2.3.2. Allophanic and Non-allophanic Andisols	
2.4. Properties of Andisols	
2.4.1. Phosphate Retention	
2.4.2. Low Bulk Density	14
2.4.3. SOM Accumulation	
2.4.3.1. Chemical Protection of SOM	
2.4.3.2. Physical Protection of SOM	
2.4.3.3. Other Mechanisms of SOM Protection	
2.4.4. Aggregate Stability	
2.5. Changes in Soil Properties due to Land Use Inte	ensification18
2.6. C Sequestration, C input belowground, and Prop	· · · · ·
2.6.1. C Sequestration from a New Zealand Perspect	
2.6.2. C Input Belowground and Rhizodeposition	
2.6.3. Biological and Chemical Changes in the Rhize	1
2.6.3.1. Biological Characteristics of the Rhizosph	
2.6.3.2. Chemical Characteristics of the Rhizosphe	
2.6.3.2.1. Ionic Concentration Changes in the R	-
2.6.3.2.2. pH Changes in the Rhizosphere	
2.7. Conclusion and Research Gap Identified	

3. Materi	als and Methods	29
3.1.	Soil Sampling	29
3.2.	Rhizosphere Separation	30
3.3.	Chemical Characterisation of Bulk and Rhizosphere Soils	30
3.4.	Additional Chemical Characterization of Bulk Soils	31
3.5.	Molecular Fingerprinting of Bulk SOM	32
3.6.	Statistical Analyses	33
4. Result	s	34
4.1.	Changes in Soil Chemical Properties across Land Uses	34
4.1.	1. Soil C and N	34
4.1.2	2. Soil pH	35
4.1.	3. Reactive Al and Fe	36
4.1.4	4. Olsen P concentration	38
4.1.	6. Specific Surface Area	38
4.2.	Soil Solution Composition	39
4.3.	Molecular Fingerprint of SOM	41
4.3.	1. General description of pyrolysis products	41
4.	3.1.1. Polysaccharides	41
4.	3.1.2. Lignin	45
4.	3.1.3. N compounds (including diagnostic chitin markers)	45
	3.1.4. Aliphatic structures: n-alkenes, n-alkanes, other aliphatics, n-fatty acids, n- hethyl ketones	
	3.1.5. Other groups: phenols, monocyclic aromatic hydrocarbons (MAHs) and olycyclic aromatic hydrocarbons (PAHs)	47
4.3.2	2. Distribution of soil samples and chemical compounds after factor analysis	47
	3.2.1. Factor analysis including pine (Forest) and pasture (Paddock 1 and Paddoc) soils	
4.3.	3. Factor analysis of only soils under pasture (Paddock 1 and Paddock 2)	49
5. Discus	sion	51
5.1.	Soil C, N Stocks and Fertility	51
5.3.	Reactive Al and Fe	53
6. Conclu	isions	56
Referenc	es	58

List of Figures

Figure 1: Diagram representing composition and structure of an allophane spherule, from	
Hashizume and Theng (2007)12	

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......36

Figure 7: Average and standard error of the mean (SEM) values of (a) $Al_o +\frac{1}{2} Fe_o$, (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.

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

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.

Picture

Photo 1: Map of the farm showing the three sampling sites (Google Earth)......29

List of Tables

Table 1: Suborders and Great Groups of Andisols in Soil Taxonomy 7
Table 2: Definition of andic properties 8
Table 3: Definitions of Andisols by profile of Soil Taxonomy
Table 4: Organic compounds exuded into rhizosphere
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;