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DEVELOPMENT OF METHODOLOGIES FOR THE CHARACTERISATION OF BIOCHARS PRODUCED FROM HUMAN AND ANIMAL WASTES

A thesis presented in partial fulfilment of the requirements for the
degree of
Doctor of Philosophy in Soil Science



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ABSTRACT

Biochar is charcoal made from waste biomass and intended to be added to soil to improve soil function and reduce emissions from the biomass caused by natural degradation to CO₂. Biochar technology has many environmental benefits, such as carbon (C) sequestration, waste management, soil improvement and energy production. High quality biosolids (e.g., low in heavy metals) and animal wastes represent an adequate feedstock for production of biochars. Wide variation in biochar properties, dependent on feedstocks, process conditions and post-treatments, lead to large uncertainties in predicting the effects of biochar application on the surrounding ecology, and the productivity of particular crops under specific pedoclimatic conditions. It is essential to well-characterise biochars prior to its incorporation into soils. Therefore, the aims of this thesis were (i) to investigate the C stability and nitrogen (N) and phosphorus (P) availability in biochars produced from municipal and animal organic wastes at different pyrolysis temperatures; and (ii) to develop simple and robust methods for characterisation of C stability and nutrient availability in biochars.

Two types of feedstock, (i) a mixture (1:1 dry wt. basis ratio) of alum-treated biosolids (from anaerobic digestion of sewage, ~5% dry wt. of Al) and eucalyptus wood chips (BSe), and (ii) a mixture (1:1 dry wt. basis ratio) of cattle manure (from a dairy farm) and eucalyptus wood chips (MAe), were used to produce biochars at four different pyrolysis temperatures (highest heating temperature: 250, 350, 450, and 550°C).

The stability of C in charred materials increased as pyrolysis temperature increased, as proved by the increase of aromaticity and the decrease of atomic H to organic C (H/C_{org}) ratio, volatiles to (volatiles + fixed C) ratio, C mineralisation rate and % K₂Cr₂O₇ oxidisable C. According to the IBI Guidelines (IBI 2012), an upper H/C_{org}

ratio limit of 0.7 is used to distinguish biochar samples from other carbonaceous biomass based on the consideration of C stability. According to this classification system, MAe-450 and MAe-550 biochars complied with this specific C stability requirement; this was also the case of BSe-450 and BSe-550 when their H values were corrected to eliminate the contribution of inorganic H from Al oxy-hydroxides. Both organic H (H_{org}) and C_{org} forms were used in the calculation of this index instead of their total amounts, as the latter would also include their inorganic C or H forms – which can represent a considerable amount of C or H in ash-rich biochars – and these do not form part of the aromatic structure. Therefore, various methods, including titration, thermogravimetric analysis (TGA), acid fumigation and acid treatment with separation by filtration, were compared to quantify the carbonate-C in biochars. Overall, the titration approach gave the most reliable results as tested by using a CaCO_3 standard (average recovery >96% with a relative experimental error <10% of carbonate-C). To assist in the prediction of the mean residence time (MRT) of biochar C in soils, simple models, based on their elemental composition and fixed C content, were established to calculate C aromaticity of biochars. This was able to replace methods using more costly solid state ^{13}C NMR spectroscopy.

Biochar samples produced from MAe and BSe feedstocks were hydrolysed with a 6 M HCl to extract labile N (hydrolysable), which was considered the fraction of N that would be available in short term; and with 0.167 M $\text{K}_2\text{Cr}_2\text{O}_7$ acid solution (dichromate) to determine potentially available N in the long term. An incubation study of biochars mixed with acid washed sand was also conducted at 32 °C for 81 d to study short-term N turnover pattern. Results showed that fractionation of biochar N into ammonia N (AN), amino acid N (AAN), amino sugar N (ASN), and uncharacterisable hydrolysable N (UHN) revealed the progressive structural rearrangement of N with

pyrolysis temperature. Hydrolysable- and dichromate oxidisable-N decreased as pyrolysis temperature increased from 250 to 550 °C, suggesting N in biochar becomes more stable as pyrolysis temperature increased. Organic N was an integral part of the biochar structure, and the availability of this N also depended on the stability of biochar C. The ratio of volatile C (representing labile C) to total hydrolysable N (THN) was proposed as a useful indicator of whether net N mineralisation or immobilisation of N in biochar occurred.

Phosphorus in feedstock was fully recovered and enriched in the biochars under study. Various methodologies were employed to investigate the bioavailability of P in biochars, including (i) a bioassay test using rye-grass grown in a sandy soil fertilised with biochars; (ii) soluble P extractions (resin extraction and Olsen extraction) from biochar amended soils; and (iii) successive resin P extractions of soils treated with biochars. The results obtained with the different methods confirmed that P bioavailability diminished following the order of dihydrogen phosphate (CaP) > MAe biochars > BSe biochars > Sechura phosphate rocks (SPR). Plant availability of P in biochars could be predicted from the amount of P extracted in 2% formic acid extractable P (FA-P). In addition, resin-P was considered as a useful test for characterising P bioavailability in soils fertilised with P-rich biochars. However, more investigations with a wider range of soils and biochars are needed to confirm this. Pyrolysis temperature played a minor role on P availability in biochars produced below 450°C compared to the influence of the type of feedstock. This was supported by the results on (i) plant P uptake, (ii) 2% formic acid extraction, and (iii) successive resin P extractions. The availability of P in biochars produced at 550°C decreased noticeably compared with that in lower temperature biochars. The Hedley P fractionation procedure was also carried out to examine the forms and transformation of P in biochar

after its application into soils under the influence of plant growth. Generally, biochar P contributed to the readily available resin-P and moderately available NaOH-Pi fractions, and some equilibrium likely existed between these two fractions, both of which provided P for plant uptake. In a plant-sandy soil system, depletion of P in resin-P and NaOH-Pi fractions was attributed to plant uptake rather than conversion into less available P forms (e.g. from NaOH-Pi to $\text{H}_2\text{SO}_4\text{-P}$). High-ash biochars with high P concentrations could be potential slow-release P sources with high-agronomic values. To determine appropriate agronomically effective rates of application and avoid the risk of eutrophication associated with biochar application, it is recommended to determine available P using 2% formic acid extraction in biochars, so that dose, frequency and timing of application are correctly established.

All the information obtained in this thesis will support the future use of the biochar technology to recycle nutrients and stabilise carbon from agricultural and municipal organic wastes of good quality.

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TABLE OF CONTENTS

ABSTRACT	I
ACKNOWLEDGEMENTS	V
TABLE OF CONTENTS	VII
LIST OF TABLES	XI
LIST OF FIGURES	XII
ACRONYMS	XV
CHAPTER 1. GENERAL INTRODUCTION	1
1.1 General background	2
1.2 Research objectives	5
1.3 Thesis outline	6
References	7
CHAPTER 2. LITERATURE REVIEW	13
2.1 Organic wastes	14
2.1.1 <i>Organic wastes and their treatment</i>	14
2.1.2 <i>Greenhouse gas (GHG) emissions from organic waste streams</i>	17
2.2 Pyrolysis of organic waste to biochars	21
2.2.1 <i>A sustainable biochar concept</i>	22
2.2.2 <i>Indices for stability of C in biochar</i>	24
2.3 Nutrients in biochars and their bioavailability	26
2.3.1 <i>Influencing factors of nutrient properties of biochar</i>	27
2.3.2 <i>Nitrogen</i>	27
2.3.3 <i>Phosphorus</i>	29
2.3.4 <i>Methodologies used for characterisation of available N and P in biochars</i>	30
2.3.5 <i>Other nutrient elements</i>	31
2.4 Pollutants in biochars and their bioavailability	32
2.5 Current research demand for the characterisation of biochars produced from organic waste streams in New Zealand	35
References	36
CHAPTER 3. PREDICTING C AROMATICITY OF BIOCHARS BASED ON THEIR ELEMENTAL COMPOSITION	43
Abstract	44
Keywords	44
3.1 Introduction	45
3.2 Materials and methods	46
3.2.1 <i>Biochar preparation and characterisation</i>	46
3.2.2 <i>Data collection and modelling</i>	48
3.3 Results and discussion	52
3.3.1 <i>General description of biochars</i>	52
3.3.2 <i>Calibration of the models</i>	55
3.3.3 <i>Comparison and validation of models</i>	58
3.3.4 <i>Notes for future users of Models 1 and 2 and suggestions to future research</i>	59
3.4 Conclusion	60
Acknowledgements	61
References	61
CHAPTER 4. DETERMINATION OF CARBONATE-C IN BIOCHARS	65
Abstract	66
Keywords	66

4.1 Introduction	67
4.2 Materials and methods.....	69
4.2.1 Biochars.....	69
4.2.2 Determination of carbonate-C via a coulometric titration	69
4.2.3 Thermogravimetric and derivative thermogravimetric (TG/DTG) analysis .	70
4.2.4 Carbonate-C removal with acid fumigation.....	71
4.2.5 A bubble test for the selection of carbonate-rich biochars	71
4.2.6 Data analysis	72
4.3 Results and discussion.....	73
4.3.1 Selected properties of biochars	73
4.3.2 Comparison of methods to determine carbonate-C in biochars	74
4.3.3 Simple tests for screening samples for accurate carbonate-C analysis	80
4.4 Conclusion.....	83
Acknowledgements	84
References	84
CHAPTER 5. CHEMICAL AND BIOASSAY CHARACTERISATION OF NITROGEN AVAILABILITY IN BIOCHARS PRODUCED FROM DAIRY MANURE AND BIOSOLIDS	87
Abstract.....	88
Keywords.....	89
5.1 Introduction	89
5.2 Material and methods	91
5.2.1 Feedstock and biochar preparation	91
5.2.2 Acid hydrolysis and N determination	92
5.2.3 Thermogravimetric and derivative thermogravimetric (TG/DTG) analysis .	93
5.2.4 Chemical oxidation.....	94
5.2.5 Incubation study for C and N turnover.....	94
5.2.6 Data analysis	96
5.3 Results	97
5.3.1 Biochar characterisation.....	97
5.3.2 N forms in biochar solubilised by acid hydrolysis	97
5.3.3 DTG curve	102
5.3.4 Chemical oxidation by K ₂ Cr ₂ O ₇ acid solution	102
5.3.5 C and N turnover in feedstock and biochar.....	106
5.4 Discussion.....	107
5.4.1 C and N change during pyrolysis, acid hydrolysis and chemical oxidation	107
5.4.2 C turnover.....	111
5.4.3 N lability in biochar.....	113
5.5 Conclusion.....	116
Acknowledgements	117
References	117
CHAPTER 6. PREDICTING PHOSPHORUS BIOAVAILABILITY FROM HIGH- ASH BIOCHARS	123
Abstract.....	124
Keywords.....	124
6.1 Introduction	125
6.2 Materials and methods.....	127
6.2.1 Feedstocks and biochar preparation.....	127
6.2.2 Biochar characterisation.....	128
6.2.3 Phosphorus extraction and analysis.....	129

6.2.4 <i>Metal analysis and X-ray diffraction (XRD) analysis</i>	130
6.2.5 <i>Bioassay test</i>	130
6.2.6 <i>Model and data analysis</i>	132
6.3 Results	133
6.3.1 <i>Biochar characterisation</i>	133
6.3.2 <i>Phosphorus and cation extractability in feedstocks and biochars</i>	134
6.3.3 <i>Ryegrass yield and P uptake</i>	141
6.4 Discussion	144
6.5 Conclusion	148
Acknowledgements	149
References	149
CHAPTER 7. THE FATE OF PHOSPHORUS OF ASH-RICH BIOCHARS IN A SOIL-PLANT SYSTEM	153
Abstract	154
Keywords	154
7.1 Introduction	155
7.2 Materials and methods	157
7.2.1 <i>Feedstocks and biochar preparation and characterisation</i>	157
7.2.2 <i>Greenhouse experiment</i>	157
7.2.3 <i>Olsen and acid ammonium oxalate extraction</i>	159
7.2.4 <i>Soil P fractionation</i>	159
7.2.5 <i>Release of P via successive resin extractions</i>	160
7.2.6 <i>Data analysis</i>	160
7.3 Results	161
7.3.1 <i>Biochar characterisation and soil available P test</i>	161
7.3.2 <i>Plant yields and P uptake</i>	162
7.3.3 <i>P fractionation</i>	167
7.3.4 <i>P release kinetics via successive resin extractions</i>	167
7.4 Discussion	170
7.4.1 <i>Soil P tests for soils amended with biochars</i>	170
7.4.2 <i>P forms and availability</i>	171
7.4.3 <i>Transformation of P forms</i>	173
7.5 Conclusion	176
Acknowledgements	177
References	177
CHAPTER 8. OVERALL SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH	181
8.1 Overall summary	182
8.1.1 <i>Carbon in biochars</i>	182
8.1.2 <i>Availability of N in biochars</i>	184
8.1.3 <i>Availability of P in biochars</i>	185
8.1.4 <i>Highlights of this thesis</i>	187
8.2 Recommendations for future research	188
References	190
APPENDIX	191
Appendix I. Supporting information for Chapter 3 (S3)	A1
<i>Materials and methods</i>	A1
<i>References</i>	A6
Appendix II. Supporting information for Chapter 4 (S4)	A8
<i>References</i>	A12

Appendix III. Supporting information for Chapter 5 (S5).....	A13
<i>Modelling ammonia volatilization from the biochar-sand mixtures in a sealed jar</i>	A15
<i>References</i>	A16
Appendix IV. Supporting information for Chapter 7 (S7)	A17

LIST OF TABLES

Table 2-1. Nitrogen release during pyrolysis by model compounds and biomass. Source: Becidan et al (2007)	28
Table 3-1. Elemental composition (dry-ash free basis, <i>daf</i>) and predicted aromaticity (f_{a-pre}) of biochars treated and untreated (original) with 10% HF solution. f_{a-exp} is the measured f_a by DP/NMR techniques. Data were presented as mean±standard deviation (n=2). 100% of aromaticity was set as 1 f_a -unit. RMSE was calculated after excluding BSe-250 and MAe-250. M denotes model and n/a not applicable.	49
Table 4-1. Selected properties of biochars used in this study	76
Table 4-2. Carbonate-C determined by different methods	77
Table 4-3. Correlation matrix of carbonate-C in biochars determined by various methods.	78
Table 5-1. Selected properties of biochar samples	100
Table 5-2. C, N and organic N forms in whole samples of feedstock (F) and biochar (pyrolysed at different temperatures) and in fractions produced from 6 M HCl hydrolysis (n.d., not detected), ±standard deviation (n=3).	101
Table 5-3. TG analysis of biochars and their non-hydrolysable residues	104
Table 5-4. Changes in C and N in biochars after $K_2Cr_2O_7$ oxidation.....	105
Table 5-5. Estimation of C turnover dynamics of the decomposable fraction of C in biochars (the recalcitrant fraction is thus not included) fitted to a two-component decay model.	107
Table 6-1. Selected properties of Waitarere sandy soil.....	136
Table 6-2. Selected properties of biochars used in this study	136
Table 6-3. Phosphorus extractability of biochars in 2% formic acid (FA-P), 2% citric acid (CA-P) and 1M neutral ammonium citrate (NAC-P). Fraction is the % of TP extracted. Standard deviation (n = 3) in parentheses. For FA-P, data from official method (FA-P, 30 min shaking only) and modified method (FAs-P, official method+10min sonication) are presented.	137
Table 6-4. Selected parameters of dry matter yields and P uptake by ryegrass fitted by the Mitscherlich equation.....	141
Table 7-1. Selected characteristics of feedstocks and biochars	161
Table 7-2. Estimated maximum release capacity (Q_{max}) of soil fertilised with different P sources (at T_0) and estimated fast and slowly releasable P pools via a 2-component model. For Q_{fast} , k_1 , Q_{slow} and k_2 , left column are mean values and right standard errors.	169

LIST OF FIGURES

Figure 2-1. New Zealand’s greenhouse gas emissions by sector: 2007. Source: Ministry for the Environment New Zealand (2009).....	19
Figure 2-2. Overview of the sustainable biochar concept. Source: Woolf et al (2010) .	22
Figure 2-3. Schematics for biomass or biochar remaining after charring and decomposition in soil. Source: Lehmann et al (2006).	23
Figure 2-4. Possible reaction paths and release mechanisms of S during devolatilization and combustion with special emphasis on combustion of annual. Source: Johansen et al (2011).....	32
Figure 3-1. Solid state ¹³ C DP-MAS-NMR spectra of biochars produced from biosolids-eucalyptus wood mixture (BSe) and cattle manure-eucalyptus wood mixture (MAe). (***) refers to spinning side bands.	54
Figure 3-2. Plot of f_a -measured (f_{a-exp}) against atomic H/C ratios. Data were from literature (Table S3-1) and this study. 100% of aromaticity was set as 1 f_a -unit.....	55
Figure 3-3. Comparison between f_a -measured (f_{a-exp}) and f_a -predicted (f_{a-pre}) obtained from different models.....	55
Figure 4-1. The calibration curve used for correcting concentration of carbonate-C in biochars determined by a titration method. Oven-dried CaCO ₃ was used as a standard.....	75
Figure 4-2. Examples of deconvolution of the derivative thermogravimetric (DTG) curves of biochars. The dark-filled peak of Sample EuW400 around 500°C represents the decomposition of whewellite (hydrated calcium oxalate).	81
Figure 4-3. An overview of carbonate-C contents in biochars from literature and this study. The curve is the Normal curve representing the Normal distribution the data.	82
Figure 4-4. Effervescence tests for carbonate-C in biochars. Numbers are the samples numbers in Table 4-1. Sample “N ^o 7x” is sample N ^o . 7 after acid treatment; “N ^o 7x+” is “N ^o 7x” plus 5mg of dry CaCO ₃	82
Figure 4-5. Relationship between atomic H/total C ratio and fixed C/total C ratio.	84
Figure 5-1. Correlation between hydrolysable N determined by difference between original biochar N content and residual N content and by alkaline potassium peroxodisulfate digestion.	97
Figure 5-2. Concentrations of different hydrolysable N forms by 6 M HCl hydrolysis. AN, ammonia-N; ASN, amino sugar-N; AAN, α-Amino acid N and; UHN, unknown hydrolysable N.	99
Figure 5-3. DTG curves of feedstocks and biochars and their residues after acid hydrolysis.....	102
Figure 5-4. Cumulative C mineralized on the basis of per unit of initial C.	103
Figure 5-5. Extractable mineral N [$\Sigma(\text{NH}_4^+ + \text{NO}_3^-)$] change in a biochar-sand mixture system. All data were obtained by subtracting the values from the blank control. .	106
Figure 5-6. A modified C:N ratio for assessing net N mineralization or immobilization. VC, C fraction in volatile matter fraction; THN, total hydrolysable N by 6 M HCl hydrolysis.....	116
Figure 6-1. XRD spectra of biochars and biosolid feedstock (BSe-F). Possible struvite peaks in MAe were lined out by dotted lines; the region in the ellipse in BSe was attributed to“organic hump”.	135
Figure 6-2. Shoot dry matter yield (a) and P uptake (b) from 6 harvests of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and P fertilisers. In the same treatment, deeper colour indicated higher dose amendment.	

Doses for biosolid biochars (BSe) are 2.5t ha ⁻¹ and 5t t ha ⁻¹ ; for manure biochars (MAe), 5 t ha ⁻¹ and 7.5 t ha ⁻¹ ; for phosphate rocks (SPR), 0.25, 0.5, 1 and 2 t ha ⁻¹ ; for calcium dihydrogen phosphate (CaP) , 100, 200, 800 kg ha ⁻¹ . Error bars indicate standard deviations of experimental replicates (n=3). Different letters indicate statistically significant according to the S-N-K test at the 0.05 level.	138
Figure 6-3. Shoot dry matter yield of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and P fertilisers at first 3 harvests (a) and first 6 harvests (b). Data were fitted by a Mitscherlich equation. Error bars indicate standard deviations of experimental replicates (n=3).....	139
Figure 6-4. P uptake by ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and P fertilisers at first 3 harvests (a) and first 6 harvests (b). Data were fitted by a Mitscherlich equation. Error bars indicate standard deviations of experimental replicates (n=3).	140
Figure 6-5. Relationship between dry matter yields and formic acid extractable P after sonication (FAs-P) (a), plant P uptake and extractable P concentration (b). Data were fitted by a Mitscherlich equation. Error bars indicate standard deviations of three experimental replicates (n=3).	142
Figure 6-6. Relationship between P uptake predicted by the CaP model and measured P uptake using either FA-P (official method; shake for 30 min only) or FAs-P (modified method; 30 min shaking plus 10 min sonication) as the available P content.	144
Figure 7-1. Soil available P as tested by resin-P, Olsen P, oxalate P and total plant P uptake in soil amended with different P sources at T ₀ (after 21 days of equilibration with moist soil).	163
Figure 7-2. Shoot dry matter yields and root dry weight of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and conventional P fertilisers (mean ± std., n=3). Shoots (5 cm above soil surface) were harvested for 9 times successively. Means of shoot yields from 1-3 harvests, 4-6 harvests and 7-9 harvests, root weights and total biomass (shoot + root) were compared using one way ANOVA method. Values not sharing the same letter indicate a significant difference (Turkey HSD at a level of 0.05). Lower case was used for shoot yields of every 3 harvests and root weights; capital letters for total biomass.	164
Figure 7-3. P uptake of ryegrass grown in pots of Waitarere sandy soil fertilised with feedstocks, biochars, and conventional P fertilisers (mean ± std., n=3). Shoots (5 cm above soil surface) were harvested for 9 times successively. Means of shoot P contents from 1-3 harvests, 4-6 harvests and 7-9 harvests, root P content and total P uptake (shoot + root) were compared using one way ANOVA method. Values not sharing the same letter indicate a significant difference (Turkey HSD at a level of 0.05). Lower case was used for shoot P content of every 3 harvests and root P content; capital letters for total P uptake.	165
Figure 7-4. Extractable soil P in soils A) at T ₀ (after pre-equilibrating for 3 weeks but before sowing the seeds); B) at T _h (after the separation of the root and soil) and; C) plant P uptake and difference in extractable P before and after plant growth. Values not sharing the same letter indicate a significant difference (Turkey HSD at a level of 0.05) (Figure 2A and 2B); (0.1), (*) and (**)) denote a statistically significant difference with 0 at the P<0.1, P< 0.05 and P<0.01 according to Student's t test (one-tailed).	166
Figure 7-5. Release pattern of P in soils fertilised with different P sources (at T ₀): A) Control and CaP; B) MAe; C): BSe and; D) SPR. For Control, CaP, MAe and BSe treatments, data were fitted via a 2-component model (Equations (7-3) and (7-4))	

after exploring the maximum release capacity according to Equation (7-2); data of SPR treatments were fitted by a linear model. Parameters are shown in Table 7-2. 168

Figure 7-6. Relationship between estimated $Q_{\max}-T_0$ and ($Q_{\max}-T_h$ + total plant P uptake). 170

Figure 7-7. Total plant P uptake as a function of extractable P of three successive resin extractions (at T_0). Three successive resin extractions were chosen according to the amount of total plant P uptake. Data are mean of three replicates for P uptake and of two replicates for extractable P. The curve is the fit line of CaP data via a Mitscherlich-type modelling. 174

ACRONYMS

AN	NH ₃ N
AAN	α -amino acid N
ASN	Amino sugar-N
BD	Bloch-decay
BSe	A mixture of biosolids and eucalyptus wood chips
C	Carbon
CaP	Ca(H ₂ PO ₄) ₂
C/N	C to N ratio (mass)
C _{org}	Organic C
DP/MAS	Direct polarization/magic angle spinning
F_a	C aromaticity
FC	Fixed C
DTG	Derivative thermogravimetric analysis
FC	Fixed carbon
H/C	An atomic H to C ratio
H _{org}	Organic H
H ₂ SO ₄ -P	0.5 M H ₂ SO ₄ extractable P
MAe	A mixture of dairy manure and eucalyptus wood chips
NaOH-Pi	0.1 M NaOH extractable inorganic P fraction
NaOH-Po	0.1 M NaOH extractable organic P fraction
NaOH-Pt	total 0.1 M NaOH extractable P fraction
N	Nitrogen
NMR	Nuclear magnetic resonance
P	Phosphorus
P _{ox}	Acid ammonium oxalate extractable P
PSO	Pseudo-second-order kinetic model
PR or SPR	Sechura phosphate rock
SD	Standard deviation
TGA	Thermogravimetric analysis
THN	Total hydrolysable nitrogen
UHN	uncharacterisable hydrolysable N
VC	Carbon in volatile matter
VM	Volatile matter