Producing biochars for New Zealand soils

Marta Camps-Arbestain[A], Peter Bishop[A], Kiran Hina[A], Fenxia Yao[B], William Aitkenhead[A], Jason Hindmarsh[C], Roberto Calvelo-Pereira[D], Juan Antonio Maciá-Agulló[E], Mike Hedley[A]

[A]Institute of Natural Resources, Private Bag 11222, Massey University, Palmerston North 4442, New Zealand
[B]NEIKER, Berreaga kalea 1, 48160-Derio, Bizkaia, Spain
[C]Institute of Food, Nutrition and Human Health, Massey University, Palmerston North, New Zealand
[D]Departamento de Edafoloxia e Quimica Agricola, Facultad de Bioloxia, Universidade de Santiago de Compostela, Spain
[E]Instituto Nacional del Carbón (CSIC), Apartado 73, 33080-Oviedo, Spain.

Abstract
To understand the potential impacts of biochar on New Zealand soils, it is crucial to assess its capability to achieve a desired soil outcome. The present research is focused on (i) the characterization of biochars obtained from different types of feedstocks and pyrolysis conditions, (ii) the use of pre-treatments to enhance surface activity of biochars, and (iii) the simulation of long-term geochemical weathering of a mineral-rich ash biochar so that its fertilizing value can be assessed. The results obtained indicate that the different properties of the biochars produced are controlled to a large extent by process conditions (e.g., high or low temperature) and feedstock (e.g., low and high mineral ash content). Surface charge of biochars from eucalyptus and pine bark increased after treating the feedstocks with alkaline tannery waste. This effect was more evident with the biochar made from hard-wood bark. Up to 18 and 14% of K and P originally present in biochar made from biosolids were lost through intense weathering, whereas less than 1% of N was leached from the system. The knowledge acquired in this study is valuable to recognize, not only the different characteristics of the fresh biochars produced, but also their potential changes over time.

Key Words
Biochar characteristics, activation, surface charge, weathering

Introduction
Biochar-production technologies that convert biomass (short-term biodegradable carbon) into a more durable form (e.g., charcoal) and, at the same time, produce bioenergy, may provide the ideal greenhouse gas (GHG) mitigation solution for New Zealand's unique mix of pastoral and forestry land-uses. However, research needs to be conducted to ensure the sustainability of biochar-amended soils across New Zealand before this technology can be adopted by end users. Specifically, within the biochar and soil science stream, it is crucial to develop a predictive capability for the beneficial application of biochar in the diverse land-use systems of New Zealand. To attain such an objective, the physical, chemical and biological mechanisms behind its impact in soil functions must be fully understood. This study is focused on the physical and chemical properties of different biochars – obtained from very diverse types of feedstocks, different pyrolysis conditions, and with and without chemical activation – with the objective of understanding their potential impacts on New Zealand soils.

Methods
Pretreatment and pyrolysis conditions were varied with different feedstocks. Biochars from different forest (pine, eucalyptus, willow, poplar, Chinese silver grass), agricultural (corn stover) and urban (sewage sludge) waste streams were produced using a rotating drum kiln at 550 °C. Pine, poplar and willow were pyrolysed at 400 °C, corn stover at 350 and 400 °C; and pine and eucalyptus barks were treated with alkaline tannery waste before pyrolysis at 550 °C to promote surface activity. The biochar produced from biosolids was weathered using a modified Soxhlet reactor during a 300-h period to evaluate its long-term geochemical evolution. Carbonaceous materials were characterized by: SEM imaging, and solid-state ^{13}C NMR and FT-IR spectroscopy. Elemental composition, pH, effective cation exchange capacity, and yield were determined. For specific biochars, a characterisation using XPS spectroscopy was carried out, and acid group contents and BET were determined. For the weathering study, the leaching kinetics and the transformations within the solid phase were examined.

Results and Discussion
Influence of process conditions and type of feedstock on biochar properties
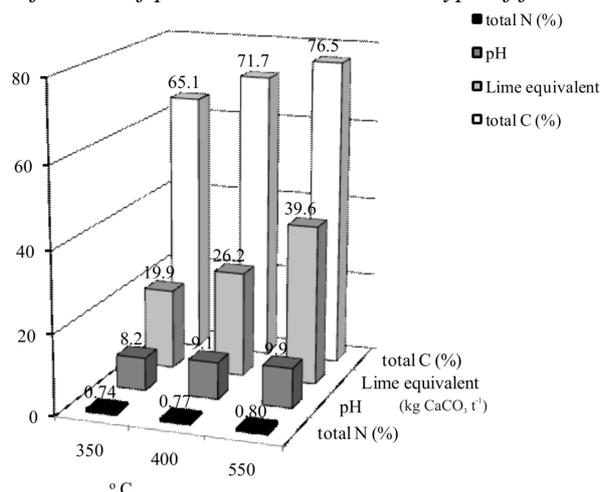
Figure 1 Changes in several chemical properties of biochars produced from corn stover at increasing temperatures.
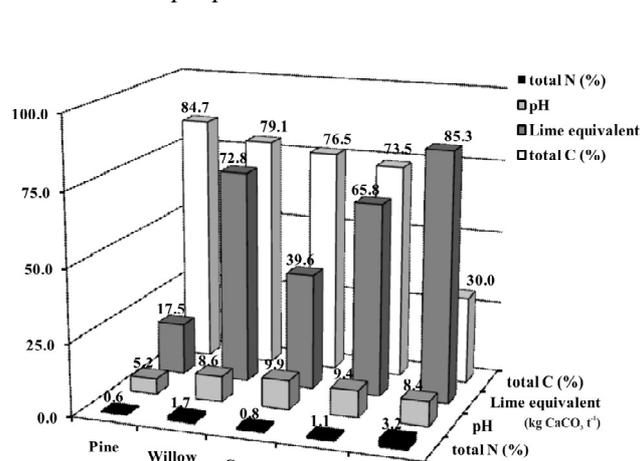
Figure 2. Chemical properties of bichars produced from different feedstocks at 550°C

Pyrolysis at increasing temperatures produced an increase in pH, lime equivalence, and C and N concentrations, as expected (Figure 1). On the other hand, product yield, the amount of carbon fixed, and H and O concentrations decreased with increasing temperatures (data not shown). This resulted in lower O/C and H/C ratios in the high temperature biochars than in the low temperature ones, indicating a greater degree of condensation of the former. Solid-state ^{13}C NMR spectra, acquired using both cross and direct polarization techniques, showed the increasing aromaticity of the chars with increasing temperature (data not shown). Different types of feedstocks had varied effects (Figure 2). The composition of the starting material had a large effect on the biochars produced at lower temperatures (350°C), but as heat increased (up to 550°C) this effect was less pronounced (data not shown).

Influence of alkaline pre-treatments on the surface activity of biochars
Biochars were produced by pyrolysis of fibrous debarking waste from eucalyptus and pine that either had, or had not, been pretreated with diluted (L) or undiluted (S) alkaline float tannery waste. Biochars made from treated eucalyptus feedstocks (L-EU and S-EU) contained less fixed carbon (39 and 37%, respectively) than the respective control (Ctr-EU; 40 %). However, they showed greater change in chemical characteristics than those from pine (L-PI and S-PI, respectively), which showed minimal decrease in C content compared to their control (Ctr-PI; 43%). The differences were mainly attributed to different types of lignin (S-type/G-type) in pine and eucalyptus. Biochars made from treated eucalyptus feedstocks had higher surface charge than the corresponding control, the highest value being in the L-EU biochar (Figure 3). L-PI and S-PI biochars also showed a higher surface charge than the corresponding control biochar (Ctr-PI), although values were always smaller than in the EU samples (Figure 3). The specific surface area of the biochars decreased with the alkaline treatments (from > 135 m^2 g^{-1} to < 9 m^2 g^{-1}) (data not shown).

In subsequent filtration experiments, in which NH$_4^+$ sorption and desorption properties were studied, treated biochars sorbed greater NH$_4^+$ from a 40 mg N L^{-1} stream than untreated biochars, with higher retention in the eucalyptus samples (Figure 3). The amount of NH$_4^+$ retained was not directly related to the new surface charge generated. Desorption of the sorbed NH$_4^+$ was low, especially in treated biochars (0.1-2 % out of total retained) compared to untreated biochars (14-27%) (data not shown). The results obtained indicate the contribution of other mechanisms of NH$_4^+$ retention, in addition to electrostatic interactions. They also suggest that a decrease in surface area does not necessarily imply a decrease in surface charge.
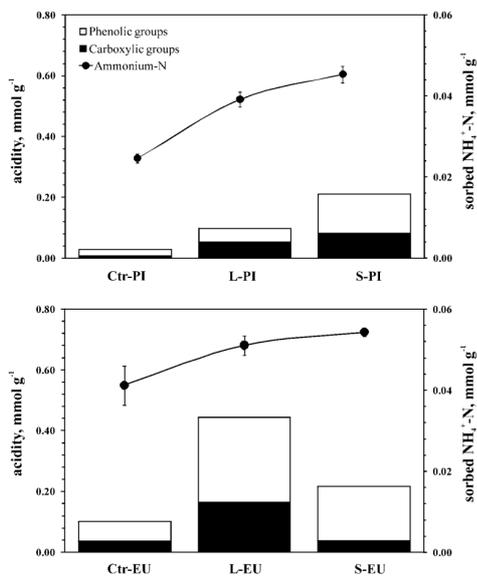
Figure 3. Surface functional groups of the different biochars and NH$_4^+$-N sorption after filteration with 1 40 mg N L^{-1} waste stream.
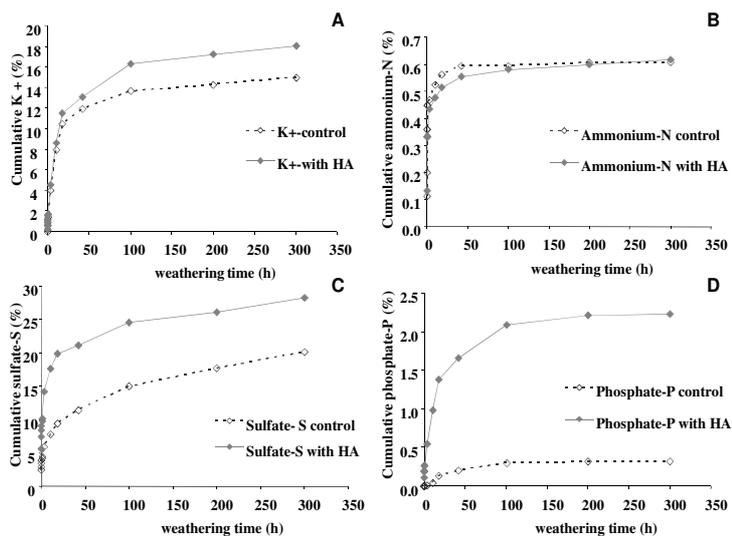
Figure 4. Cumulative amounts of (A) K, (B) NH$_4^+$-N, (C) SO$_4^{2-}$-S, and (D) PO$_4$-P in the weathering solutions.

Simulated long-term geochemical weathering of a high mineral ash biochar

The weathering process of a biochar produced from sewage sludge was studied with and without the presence of humic acids (BC-B and BC-HA, respectively). The pH values of the BC-B leachates rapidly decreased from ~ 9 to neutrality in the first hours, and the pH at the end of the experiment was 7.8. The BC-HA leachates had an initial pH of 7.5 and fluctuated between 7.0 and 7.4 during the rest of the experiment. The overall amount of dissolved organic C (DOC) in the weathering solutions was as low as 0.3 and 0.8% of the initial total C, for the BC-B and BC-HA, respectively. Substantial K (15 and 18 % for the BC-B and BC-HA treatments, respectively) and S (20.2 and 28.3 %) were released within 300 h of geochemical weathering (Figure 5A-B). The solubilisation of less readily soluble salts (e.g., P salts) was particularly promoted by the presence of HA. Once leached and their ionic activity in solution reached saturation, new precipitates were formed at the inner surface of the flask, probably as a Ca-phosphate salt. This would explain why the amounts of P and Ca recovered in the leachates (e.g., 2.2 % of P in the BC-HA) (Figure 5C-D) were far below the decrease in P and Ca detected in the solid fraction (e.g., 14 % of P decrease in the BC-HA). Less than 1% of the total N was leached out of the system at the end of the experiment, with a predominance of NH$_4^+$ over NO$_3^-$. As the C/N ratio of this biochar was < 11, the results reveal the presence of very recalcitrant forms of N.

According to XRD analysis (data not shown), there were a few crystalline minerals present in the biochar: quartz, trace amounts of albite, Ti-magnetite and olivine. In addition, trace amounts of calcite were detected in the fresh biochar and the BC-B sample, but disappeared in the BC-HA after weathering. The oxygen containing functional groups present at the outer surface of the biochar particles were analysed by XPS. The C 1s core level spectra (curve fitted data) obtained for fresh and weathered biochar samples are shown in Figure 5. For these materials, the C1s spectra contains four signals attributed to, to aliphatic/aromatic carbon group (CHx, C-C/C=C) (284.6 eV), hydroxyl and ether groups (-C-OR) (285.8 eV), carbonyl groups (>C=O) (287.2 eV) and carboxylic groups, esters and lactones (-COOR) (288.8-288.9 eV). Generally, the XPS results showed that the BC-HA biochar had a higher proportion of hydroxyl-ether groups than the other two biochars. The two weathered biochars displayed higher concentrations of carbonyl and carboxylic groups than fresh biochar. This could be originated through biochar oxidation and, in the BC-HA, also from the added HA.
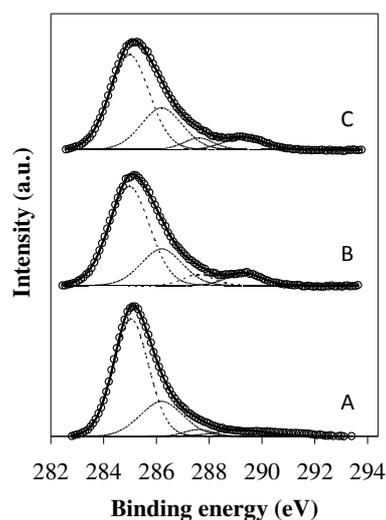
Figure 5. C 1S core level spectra of (A) fresh biochar, (B) BC-B,and (C) BC-HA.

Conclusions

This research represents a first step in the identification of the factors with the greatest influence on the final properties of biochars. This knowledge is crucial for fine-tuning the biochar production systems and the conditions under which the biochars will be beneficial to soils and to plant growth. Provision of an additional value to biochars, other than the sequestration of a stable C form in soils, may be critical for the economic feasibility of biochar production systems. Biochars with greater surface activity, and thus, suitable as filtering material, could be obtained through chemical activation, by use of an alkaline waste from the tannery industry. This could be attained with negligible impairment to the final fixed carbon. Mineral-rich ash biochars, such as those produced from biosolids, have been shown to represent an important source of P and K nutrients, but not of N. This may have key implications for the use of such biochars as fertilisers. The knowledge acquired in this study is valuable for recognising the different characteristics of the fresh biochars produced, and also any potential changes in them over time.