Assessment of the fertilizer potential of biochars produced from slow pyrolysis of biosolid and animal manures

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Highlights:

- C and N contents in biochar increased by 32 and 69% compared to biomass.
- Highest N (5.78%) and K (2.12%) contents were in chicken manure biochar.
- Maximum P (5.06%) content was in biosolid biochar.
- SSA of animal manure/biosolid biochars ranged from 96 to 111 m^2 g^{-1}.

Abstract

Excessive amounts of animal manures and production of a large volume of biosolids pose serious environmental issues in terms of their safe disposal and management. Thermochemical treatment of bio-waste materials via pyrolysis can convert them into value-added products such as biochar-based fertilizers. In this study, fourteen biochars were produced from one biosolid and thirteen animal manures by slow pyrolysis at 300 °C. All feedstock and biochar samples were characterized by determining the yield, and physicochemical and surface properties, including the C-containing functional groups. Principal component and cluster analyses were used to classify the feedstock/biochar materials based on their mineral constituents. The biochar yield of various feedstocks ranged from 39 to 81%, with the highest yield for grain-fed cow manure. The highest N and K content was found in chicken manure biochar (57.8 and 29.2 g kg^{-1}, respectively), while the highest P was found in biosolid biochar (40.5 g kg^{-1}). The specific surface area of biochars ranged from 96.06 to 110.83 m^2 g^{-1}. Hierarchical analyses of the chemical compositions of feedstocks and biochars enabled grouping of the materials respectively into four and five distinguished clusters. Three principal components (PC) explained 86.8% and 83.3% of the variances in the feedstocks and biochars, respectively. The PC1 represented the content of the major nutrients (N, P and K), whereas PC2 and PC3 represented other nutrients (secondary and micronutrients) contents and physicochemical properties (pH and EC). The results of this study suggested that biochars produced from different manures and biosolids may potentially be a source of soil nutrients and trace elements. In addition, different biochars may be applied to different nutrient-deficient soils to avoid plausible nutrient and potentially toxic element contamination.

Keywords: Animal waste recycling; Biochar; Biosolids; Manures; Plant nutrients; Soil fertility

1. Introduction

In recent decades, the application of biochar to soil has generated a significant amount of interest in the scientific community. Research has focused on the cost-effectiveness and environmentally friendly features of biochar. Biochar can influence soil nutrients by acting both as a source [1] and sink [2] of plant nutrients. Upon application to soil, biochar in most cases improves soil fertility and crop productivity by increasing the nutrient contents and bioavailability of nutrients [3]. Biochar also enhances soil microbial activity, improves aeration and water retention, buffers soil reactions, reduces bulk density, and maintains soil aggregate structure [4,5]. Moreover, biochar reduces nutrient losses by altering the soil pH and enhancing the ion exchange capacity [6].

The characteristics of biochar are influenced by feedstock types and synthesis conditions including the pyrolysis temperature [7]. The physical and chemical properties of biochar also depend on factors such as heating rate, kiln pressure, gaseous atmosphere, and type of pre- or post-treatment of biochar: firstly, nutrient-enriched biochar by pre-treatment [8]; and secondly, biochar-based slow-release nutrients by post-treatment [9]. Biochar's physical characteristics, especially specific surface area (SSA) and pore size/volume/distribution, are controlled by the production process's temperature. Pyrolysis at high-temperature (>550 °C) can produce biochar with a large SSA (>400 $m^2\ g^{-1}$) and high aromaticity [10] but with less functional groups, for example –COOH, –OH [1].

Manures and sewage sludge can produce nutrient-rich biochar because these feedstocks have high nutrient content. For example, biochar produced from sewage sludge (at 350 °C) contained more N (31.7 $g\ kg^{-1}$) than that produced from sugarcane and eucalyptus wastes, the amounts being 14 and 4 $g\ kg^{-1}$, respectively [11]. Furthermore, N content of biochar declined when an increase in pyrolysis temperature occurred because of the loss of NH_4^+-N through NH_3

volatilization [5]. The P and K contents were found to be positively correlated with the pyrolysis temperature. For example, Xiao, et al. [12] produced biochar from chicken manure at 250, 350, and 550 °C, and they found that the corresponding P contents were 19.1, 21.5, and 29.6 g kg^{-1}, respectively. Moreover, the P content depends on the type of biomass. For instance, chicken manure (29.6 g kg^{-1}) [12], and poultry litter (25.7 g kg^{-1}) [13] contained more P than other biomasses such as rice husks (1.5 g kg^{-1}) [14] and apple stems (1.8 g kg^{-1}) [15]. Similarly, K content in chicken manure (59.3 g kg^{-1}) [12] was higher than rice husk (2 g kg^{-1}) [16]. Furthermore, the residence time and gaseous environment (N_2, CO_2 and Ar supply) during the pyrolysis of biomasses are important for enriching the nutrient composition of biochar [5].

Intensive mechanization of animal farming has resulted in an increase in the volume of animal wastes globally. Continuous application of animal manures created soil, air and water pollution due to accumulation and subsequent leaching of nutrients and metals, gaseous emissions of NH_3, CH_4 and N_2O, and the spread of pathogenic microorganisms [17]. Consequently, animal wastes and manures are contributing to various types of environmental and human health hazards. Similarly, the amount of biosolids or treated sewage sludge is rising due to the expansion of urban areas worldwide. Due to the limited number of stockpiling locations and exorbitant costs, biosolids can contribute to soil contamination, odor and pathogens around a given locality [18]. Moreover, direct land application of biosolids can introduce potential toxic elements (PTE) (Cu, Zn and Cd) and excessive nutrients, particularly P to the soil, and transfer new contaminants such as plastics, microbeads and chemicals to the environment [19].

From the agricultural perspective, biochar produced via thermal conversion of manures and biosolids has shown a promising alternative approach to the above-mentioned practices. After pyrolysis, biomass reduces in volume and converts into homogenous materials, suppresses residual antibiotics and pathogens, reduces PTE availability, and concentrates nutrients [17]. Furthermore, manure- and biosolid-derived biochars are rich in essential plant nutrients compared to other biomass-derived biochars [12], and thus have potential value as fertilizer. In recent years, a number of studies have concentrated on animal manure-derived biochars including chicken manure [12], poultry litter [13], cow manure [20], swine manure [21], and goat manure [22]. However, due to the extreme heterogeneity in the composition and physicochemical characteristics of various manures, and differences in preparation procedures, it is difficult to predict the corresponding biochar fertilizer values. The nutrient contents and other properties (e.g., pH) vary in different types of animal manures. For example, the N contents of chicken manure (4.52%) and cow manure (3.2%) are higher than camel manure (1.69%) and sheep manure (1.77%). The pH values of camel manure (8.31) and sheep manure (8.05) are greater than that of chicken manure (6.67) and rabbit manure (6.46). Only a few studies are currently available that have undertaken comprehensive analyses of fertilizer values of biochars produced from various manures and biosolids under uniform preparation conditions. Therefore, the aim of the current study is to: firstly, identify the biochars with high nutrient contents; and secondly, select the best biochar sample as a soil amendment. This was done by preparing and characterizing biochars from thirteen animal manure and one biosolid samples, followed by statistical analysis of the obtained data.

2. Materials and Methods

2.1 Feedstock collection and biochar production

Fourteen feedstock samples were used in biochar production in this study. Fresh manure samples of cow (grass-fed and grain-fed), chicken (chicken manure and chicken litter), horse, goat, camel, sheep, rabbit, wallaby, alpacas, Australian wood duck, and water buffalo were collected from local farms in the Newcastle region of New South Wales (NSW), Australia.

Biosolid feedstock was collected from a wastewater treatment plant at Winmalee in NSW. All the feedstocks were air-dried for two weeks, and then cleaned manually to remove foreign materials such as feathers and bedding materials. The feedstocks were then ground with a mortar and pestle, and sieved to a particle size <2 mm, and stored in airtight plastic bags. Biochar was produced by slow pyrolysis at 300 ºC temperature in a muffle furnace (Labec muffle furnace, CEMLS-SD, Australia). Since the synthesis of biochar at high temperature (>450 °C) would reduce biochar nutrient contents due to volatilization and/or mineral crystallization [17], a low temperature (300 °C) pyrolysis was employed in this study with the aim of maintaining high nutrient contents in the biochars. To maintain a limited oxygen state during pyrolysis, N_2 was supplied to the furnace at a flow rate of 20 $cm^3\ min^{-1}$. The heating rate was 7 °C min^{-1} in the muffle furnace. When the target temperature was reached, samples were retained in the furnace for a further 30 min. Following pyrolysis, the furnace was left over-night to cool down to room temperature (around 25 °C) for safety purpose. The biochar samples were transferred to a desiccator, weighed and stored in airtight plastic containers.

The yield of biochar was calculated using Eq. 1:

$$Yield\ (\%) = \frac{Mass\ of\ biochar(g)}{Mass\ of\ oven{-}dried\ (105\ °C)\ feedstock\ (g)} \times 100\% \quad \text{----------------------(Eq. 1)}$$

2.2 Chemical analysis of feedstock and biochar

The pH and electrical conductivity (EC) of feedstock and biochar samples were obtained by suspending 0.5 g of sample in 10 mL Milli-Q water (1:20 w/v) and shaken for 1.5 h on a rotary end-over-end shaker [23]. Once shaking was completed, samples were kept standing for 30 min before measuring the pH and EC using a LAQUA PC1100 multiprobe instrument (Kyoto, Japan). For measuring the elemental C, N and S contents in the feedstocks and biochars, 0.1 g sample was dried overnight in an oven at 105 °C to ensure that the samples were moisture-free. Samples were analyzed via the dry combustion method [24] using a CNS elemental analyzer (LECO Trumac, USA). The total P, K, Ca, Mg and other trace elements, including PTEs in the samples, were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7900, USA), and inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer, USA), following digestion of 0.2 g sample in 5 mL *aqua regia* ($HCl : HNO_3 = 3 : 1$) [25]. The digestion was conducted on a microwave digester (MARS 6250/50, Matthews, NC, USA), and heated at 180 °C for 30 min at 1 kW power. Accuracy of the elemental measurements using ICP-MS and ICP-OES was verified by analyzing Standard Reference Materials (SRMs): National Institute of Standard and Technology (NIST) 1640-trace elements in natural water and NIST 1643e-trace elements in water [19].

Relative enrichment (RE) of elements in biochar was calculated using Eq. 2:

$$RE = \frac{Elemental\ concentration\ in\ biochar\ (\%)}{Elemental\ concentration\ in\ feedstock\ (\%)} \times \frac{biochar\ yield\ (\%)}{100} \text{ --------- (Eq. 2)}$$

RE > 1 will indicate large enrichment of a particular element, whereas RE < 1 represents the volatilization loss of an element [26].

2.3 Surface area and porosity of biochar

SSA and porosity of biochar were measured using a 3H-2000PS2 surface area and porosity analyzer (Bei Shi De Instrument Technology, China). Prior to the measurements, biochar samples were outgassed at 110 °C under N_2 flow at a vapour pressure of 1.0389 bar for 4 h. The SSA, total pore volume (TPV) and average pore diameter (APD) were determined from the N_2 adsorption isotherms (273.15 K; $P/P_0 = 0.04$ to 0.32) using the Brunauer-Emmett-Teller (BET) multi-point equation.

2.4 Fourier transform infrared (FTIR) spectroscopy of biochar

The FTIR spectra were recorded using a Carry 660 FTIR (Agilent, USA) spectrometer to obtain the information on surface functional groups of biochar samples. This was done by applying the dehydrated potassium bromide (KBr) disc technique, where feedstock and biochar samples (150 µm) were mixed with spectroscopic grade KBr at a ratio of 1:100 to produce sufficient transmittance. Spectra over the 4000–400 cm^{-1} range were obtained by co-adding 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm s^{-1}.

2.5 Statistical analysis

Bulk chemical variables were chosen for the Cluster Analysis and Principal Components Analysis (PCA), as were chemical elements comprising more than 0.02%. The variables used in this analysis included pH, EC, C, N, S, P, K, Ca, Mg, Al, Fe, and Na. All variables were normalized against their means prior to analysis. This means that for each chemical variable, the transformation was done by subtracting the value of the variable from the mean of the group and divided by the standard deviation of the group. The classification of biochars into different groups was performed using the Hierarchical Cluster Analysis. The method of clustering was the unweighted pair-group average (UPGMA) method, while the similarity index behind the clustering was Euclidean Distance. How the variables interacted in the chemical analysis of biochars was examined by PCA. Data analysis was conducted using the platform PAleontological STatistics (PAST) [27].

3. Results and Discussion

3.1 Biochar yield

The biochar yields under slow pyrolysis at 300 ˚C ranged from 39.2% to 80.9% (Table 1). A similar range of biochar yields from swine manure (73.8%) [21], cow manure (58.1–84.1%) [20,28,29], and poultry manure (71%) [30] was previously obtained when biochars were produced at a similar temperature (300 °C). The highest yield (80.9%) was found in grain-fed cow manure biochar, and this could be attributed to the presence of some heterogeneous structure made of cellulose, lignin [31] as well as minerals such as Al_2O_3, Fe_2O_3, TiO_2, calcite, quartz and fine dust particles in the feedstocks [31,32]. The yield of water buffalo manure biochar (39.2%) was the lowest among all samples. Nevertheless, the availability of yield data for biochars produced (at low temperature) from animal manures is limited in the literature, and consequently, more studies are needed to expand that database.

3.2 Carbon content of feedstock and biochar

The Feedstock C content of all the samples ranged from 237.5 to 514.7 g kg^{-1} (Table 1). The highest C was found in rabbit manure feedstock (514.7 g kg^{-1}) followed by water buffalo (510 g kg^{-1}), sheep (504.5 g kg^{-1}) and goat (493.7 g kg^{-1}) manures. The lowest C was observed in the cow (grain-fed) manure feedstock (237.5 g kg^{-1}). In most cases, the C content rose by up to 32% in biochar, whereas in a few biochars the C content dropped by up to 21%, compared to their respective feedstocks. The largest amount C was observed in the horse manure biochar (604.5 g kg^{-1}), and the minimum was in the biosolid biochar (267.4 g kg^{-1}) (Table 1).

The C content in biochars increased due to the total mass reduction of biomasses. However, in a few biochars, the C content declined, which was in line with Cantrell, et al. [33] who reported 34% and 60% C reduction following biochar production from poultry litter at 350 and 700 °C, respectively. The reduction in C content in biochars compared to biomasses was likely explained by the loss by volatilization [34]. According to the European Biochar Certificate (EBC), a pyrolyzed material can be qualified as biochar product when it contains ≥ 50% of C (EBC, 2012) whereas and International Biochar Initiative (IBI) qualifies it as biochar when the C content is ≥ 10% ([35,36]). Therefore, the C contents of all pyrolyzed products in this study fulfilled the standard criteria of biochar, as suggested by IBI. According to EBC's definition, out of 14 biochar, seven biochar samples were qualified as biochars, and others can be termed as pyrogenic carbonaceous materials.

3.3 pH and EC of feedstock and biochar

The pH values of the feedstocks were slightly acidic to moderately alkaline (pH = 6.46 to 8.31) (Table 2). Most of the feedstock samples were alkaline, except for chicken, duck and rabbit manures. The pH of manures was likely to vary depending on their decomposition rates, and due to the presence of short-chain organic acids [37]. The biochar samples, however, were slight to strongly alkaline in reaction (pH = 7.09 to 9.49) (Table 2), which was consistent with previous studies [38,39] reporting a pH range from 8.1 to 10.0 for poultry manure, sewage sludge and miscanthus biochars. The increase of pH of biochars compared to feedstocks could be attributed to the degradation of acidic organic molecules during the pyrolysis [32], and accumulation of alkali metals (K, Ca and Na) in the products [39]. Since the feedstocks contained varying amounts of organic matter and alkali metals, the pH increase in biochars depended largely on the feedstock types [40].

The EC of the feedstock and biochar samples varied widely, ranging from 0.56–8.66 mS cm^{-1}, and 0.007–4.02 mS cm^{-1}, respectively. The highest EC was found in the chicken litter (8.66 mS cm^{-1}) and the corresponding biochar (4.02 mS cm^{-1}). In contrast, the lowest EC was observed in the wallaby manure feedstock (0.45 mS cm^{-1}) and water buffalo manure biochar (0.007 mS cm^{-1}). Most of the biochar EC values decreased after pyrolysis of the feedstocks, with the exceptions of goat, wallaby and duck manure biochars where the values increased in comparison to the feedstocks. These results were corroborated with the findings reported by [41], who noted that EC of biochar was more influenced by EC of the original feedstock than the pyrolysis temperature.

3.4 Primary nutrient contents of feedstock and biochar

3.4.1 Nitrogen content and C/N ratio

The nitrogen (N) content of all the feedstocks ranged from 9 g kg$^{–1}$ (wallaby manure) to 46.4 g kg$^{–1}$ (biosolid) (Table 1). The high N content of 46.4, 45.2, 39.8, and 32.1 g kg$^{–1}$ were found in biosolid, chicken manure, chicken litter and cow (grain-fed) manure, respectively. However, most of the feedstocks contained less than 20 g kg$^{–1}$ N. Compared to this, the N content of biochar samples ranged from >20 to 60 g kg$^{–1}$. After pyrolysis, the N contents increased (by 15–69%) in most biochar samples. These results were corroborated with those of other recent analyses [12,17,29]. However, the N content decreased by 5 and 25 g kg$^{–1}$ in alpacas manure biochar and biosolid biochar, respectively. This could be due to the volatilization of ammonium N from the solid structure of biomass during pyrolysis [42]. The chicken manure biochar resulted in the largest N content (57.8 g kg$^{–1}$), and wallaby manure biochar produced the smallest N (13.1 g kg$^{–1}$). The variation of N contents in the feedstocks could be due to seasonal variations and management practices for raising the animals [43], bedding materials, and residual feathers of poultry birds [44]. Chicken manure and chicken litter contained more N than animal manures, and this was most likely due to 50–60% N being excreted via urine in ruminants [45].

The C/N ratio of biochar could influence the microbial activity, and also the inorganic N content in soil [46]. The C/N ratio of the feedstocks ranged from 6.11 (biosolid) to 52.7 (wallaby manure) (Table 1). Most of the feedstocks contained a high C/N ratio (>20), and a few contained a low C/N ratio (<20). However, the majority of the biochar samples contained a low C/N ratio (<20), and the values ranged from 6.8 to 40.8. Thus, after producing biochar, the C/N ratios were decreased in comparison to the feedstocks, except in the biosolid biochar.

High C/N ratio amendments release inorganic N slowly in the soil due to immobilization, and vice versa [47]

3.4.2 Phosphorus

The P content was found to be dominant in biosolid (40.5 g kg^{-1}) and the corresponding biochar (50.6 g kg^{-1}), followed by cow (grass-fed) manure (16.9 g kg^{-1}) and the corresponding biochar (24.5 g kg^{-1}), and chicken manure and chicken litter biochar (Table 3). The lowest content of P was obtained in Australian wood duck manure (1.4 g kg^{-1}) and its biochar (1.8 g kg^{-1}) followed by rabbit and wallaby manures and the corresponding biochars. After pyrolyzing the feedstock materials, the P contents increased (by 2–290%) in all biochar samples, except in water buffalo manure biochar, where it dropped by 65% (Table 3). The P content in water buffalo manure-derived biochar decreased likely due to the formation of insoluble phosphate compounds such as $(CaMg)_3(PO_4)_2$ and $Fe_4(PO_4)_2O$ during the pyrolysis process[3]. The total P contents of the feedstocks varied greatly, probably because of the varying feed materials and animal diets [48]. The manure P contents in this study were similar to those of He, et al. [49] who found that the total P content ranged from 2.8–18.3 g kg^{-1} (cow manure), 5.4–12.4 g kg^{-1} (horse manure), and 8.6–30.4 g kg^{-1} (poultry manure). The P content in biosolid biochar was 2–32 times higher than other biochars derived from animal manures, which was due to higher P content (40.5 g kg^{-1}) in biosolid feedstock than manures (Table 3).

3.4.3 Potassium

The feedstock K contents generated widely ranging values: 0.74 g kg^{-1} (wallaby manure) to 21.24 g kg^{-1} (chicken manure), and that of biochars were 1.19 g kg^{-1} (wallaby manure biochar) to 29.23 g kg^{-1} (chicken manure biochar) (Table 3). In biochars, the K content increased (by 3–144%) in comparison to the feedstocks (Table 3). Biochars produced at 400

°C from cotton husks, swine manure, eucalyptus sawdust and sugarcane filter cake contained 17.3, 9.1, 0.7 and 0.6 g K kg^{-1}, respectively [50], outcomes of which were supported by this study. However, the K content of biochars here contradicted other studies [39,51], which found 43.9 and 81 g K kg^{-1} in biochars produced at 350–500 °C from chicken manure and rice straw, respectively.

3.5 Secondary nutrient content of feedstock and biochar

Among the secondary nutrients, Ca content was high in chicken manure (55.8 g kg^{-1}) and the corresponding biochar (116.7 g kg^{-1}) (Table 3). The lowest Ca content was found in rabbit manure (3.9 g kg^{-1}) and the corresponding biochar (6.2 g kg^{-1}). For feedstocks, the highest Mg content (5.8 g kg^{-1}) was found in the biosolid and the lowest in wallaby manure (0.7 g kg^{-1}). The Ca and Mg contents varied widely among the feedstocks, which might be due to feeding materials, animal diets [48] and industrial processes of biosolids [52]. The maximum Mg content (7.4 g kg^{-1}) was discovered in horse manure biochar, and the minimum in rabbit manure biochar (2.02 g kg^{-1}). The amount of S ranged from 0.99 to 10.70 g kg^{-1} in the feedstocks, and 0.63 to 8.91 g kg^{-1} in biochars (Table 3).

After pyrolyzing feedstocks, the Ca (4–215%) and Mg (1–188%) contents were mostly increased compared to their precursors, except in cow (grain-fed) manure, chicken manure and duck manure (Table 3). The Ca (1.00–322 g kg^{-1}) and Mg (1.13–19.32 g kg^{-1}) contents of biochar derived from various types of feedstock materials such as crop residue, manure, woody biomass, and biosolids at 190–850 °C [39,53-55] were similar to our results. However, the S contents decreased (by 2–83%) in most of the biochars, while in a few biochars it increased (by 2–331%) (Table 3). Generally, the S content was small in the feedstocks and their respective biochars. After producing biochar, the feedstock mass was reduced, and correspondingly the S contents also reduced, compared to their precursors except in biochar produced from the manure of cow (grain-fed), wallaby, duck and water buffalo. This statement was supported by [56] who found that S content was decreased in corn straw biochar (300 °C). The S contents in the selected biochars were decreased likely due to the loss of S-containing volatile organic compounds during heat treatment [3,56]. Contrarily, the S contents in other biochars were increased due to the presence of low S-containing volatile compounds in the concerned feedstocks, and/or organic S compounds being resistant to S-bond breakage by the heat treatment, and formation of mineral sulphates [56]. The amounts of S in the biochar samples of this study were similar to that of biochars produced at 350–850 °C from various types of biomass, as reported by Sanchez-Hernandez [57].

3.6 Micronutrient contents of feedstock and biochar

The Zn contents of feedstocks ranged from 37 (wallaby manure) to 427 mg kg^{-1} (biosolid), and that of biochars ranged from 59.5 (wallaby manure biochar) to 571.8 mg kg^{-1} (biosolid biochar) (Table 4). The Cu contents were also high in biosolid (201.1 mg kg^{-1}) and in its biochar (269.1 mg kg^{-1}). The lowest value of Cu was recorded in wallaby manure and its biochar (10.3 and 13.5 mg kg^{-1}, respectively). After synthesizing biochar, the amount of Zn and Cu increased by 4–121% and 7–115% compared to their feedstocks, respectively (Table 4). The Fe contents of feedstocks ranged from 529 (sheep manure) to 63,527 mg kg^{-1} (biosolid), and that of biochars were from 612 (sheep manure) to 89,575 mg kg^{-1}. The highest Mn content was found in chicken manure (382.7 mg kg^{-1}) and chicken litter biochar (438.4 mg kg^{-1}). The smallest amount of Mn was recorded in camel manure and its biochar (68.4 and 110 mg kg^{-1}, respectively). The range of Mo contents of the feedstocks were 1.03 (water buffalo manure) to 8.6 mg kg^{-1} (sheep manure), and that of biochars varied from 1.4 (rabbit manure biochar) to 8.7 mg kg^{-1} (chicken manure biochar). The Fe, Mn and Mo contents were increased by 4–276%, 2–201% and 1–182% in most of the biochars samples, respectively (Table 4).

Animal manure contained essential micronutrients (Cu, Zn, Fe, Mn and Mo) for plants which are mostly chelated or complexed by organic compounds, that can be soluble- or particle-bound [58]. However, the micronutrient contents were not high in both feedstock and biochar samples in our study. Most of them were below the maximum permissible limit (MPL) for soil application of the following: ‘sewage sludge in agriculture, UK’, [59], ‘Australian standard regulation 1997’ [60], ‘USEPA biosolid rules’ [61], ‘International Biochar Initiative biochar guidelines’ [35], ‘European Biochar Certificate basic & premium grade biochar’ [62], ‘German biowaste ordinance 1998’ [63] and ‘sewage sludge management in EU, Netherlands, France and Sweden’ [64]. Only, the Cu content in the biosolid feedstock sample was above the MPL of ‘German biowaste ordinance 1998’ [63], Zn content of cow (grain-fed) manure, chicken manure and biosolid crossed the MPL of ‘German biowaste ordinance 1998’ [63] and ‘sewage sludge management in EU, Netherlands, France and Sweden’[64]. In addition, the Mn content of cow (grass-fed) manure, chicken manure, chicken litter and biosolid crossed the MPL of ‘sewage sludge in agriculture, UK’, [59]. This was probably due to the use of micronutrients as growth promotors and as feed additives in intensive animal production farms to protect them from several health disorders [65,66]. Therefore, these feedstocks can be used as potential fertilizers. In the case of Mo, only five out of 14 biochars (cow manure, camel manure, chicken manure, chicken litter and biosolid biochar) were within the range of the ‘IBI biochar guidelines’ and others were below the MPL of other international and national MPL. Therefore, both the feedstock and biochar of these four manures and biosolid can potentially be used as fertilizer.

3.7 Potential toxic elements of feedstock and biochar

The potential toxic elements (PTE) such as As, Cd, Cr, Co, Pb, Ni, and Se contents of feedstocks and biochar are presented in Table 5. Differences in As, Cr and Pb contents between feedstocks and biochars were not consistent, whereas, the Cd, Co and Ni contents were increased in all biochars (Table 5). For the assessment of PTE levels in the feedstocks and biochars, various national (Australia, Germany, UK, France, Netherlands, Sweden & US) and international (IBI) guidelines, standards and regulations of biochar, compost, biosolid and fertilizer were considered (Table S6). The As and Cd contents of feedstocks and biochars were mostly below the threshold levels of 'sewage sludge in agriculture, UK' [59], 'Australian standard regulation 1997' [60], 'USEPA biosolid rules' [61], 'International Biochar Initiative biochar guidelines' [35], 'EBC basic & premium grade biochar' [62], 'German biowaste ordinance 1998' [63] and 'sewage sludge management in EU, Netherlands, France and Sweden' [64]. However, feedstock materials of cow (grain-fed) manure, Australian wood duck manure, water buffalo manure, chicken litter, biosolid and their respective biochars exceeded the level of Netherlands (1.25 mg kg^{-1}) and Sweden (2 mg kg^{-1}) [64] where chicken litter was below Sweden's level. Only the Cd content of biosolid biochar exceeded the level of EBC [62], which defined the basic and premium grade types of biochar. The amounts of Cr, Co, Pb, Ni and Se in all feedstocks and their respective biochars were also below the maximum allowed PTEs level. Only the Se level of biosolid was within the IBI [35] threshold level. Results of our study revealed that these manures and biosolid feedstocks and biochars could be used as potential fertilizers.

3.8 Specific surface area and porosity of biochars

The SSA, TPV and APD of all biochar samples are listed in Table 6. The SSA of all biochars were in a narrow range of 96.06–110.83 m^2 g^{-1} (Table 6). The highest SSA was obtained in the case of alpacas manure biochar (110.83 m^2 g^{-1}), and the lowest value was found for wallaby manure biochar (96.06 m^2 g^{-1}). The TPV of biochars ranged from 0.11 to 0.17 mL g^{-1}, and APD ranged from 4.36 to 6.94 nm (Table 6). The SSA of all biochars in our study was higher than that of cow manure (5.2 m^{-2} g) [20] and rice husk (2.57 m^{-2} g) [67] produced at a temperature range of 300–350 °C. The SSA differences could be due to the composition of feedstocks rather than biochar production procedure [32], and the presence of a larger amount of volatile organic compounds [68]. Therefore, biochars produced in our study could be used as potential soil amendments because high SSA would improve soil structure, increase water-holding capacity in the soil, and provide habitats for soil microorganisms [69]. The TPV values of biochars were relatively lower (0.11–0.17 mL g^{-1}) than in other studies such as by Yue et al. Yue, et al. [20] who reported the TPV of 0.82 mL g^{-1} in cow manure biochar. However, Batista et al. Batista, et al. [70] found much lower values (9.4×10^{-8} to 1.4×10^{-7} m^{-3} g) in various types of biochar (coconut shell, orange peel, palm oil bunch, sugarcane bagasse and water hyacinth) than our study.

3.9 FTIR of selected feedstocks and biochar

Figure 2 depicts the FTIR spectra of chicken manure and biosolid with their respective biochars. The feedstocks and their respective biochars showed bands between the wavelengths of 2500–3500 cm^{-1}, 1000–1800 and 500–1000 cm^{-1}. The results revealed that both the feedstocks and biochars had the following surface functional groups: hydroxylic –OH (3435 cm^{-1}), CH and amine (2927 cm^{-1}), amide –CO-NH (1650 cm^{-1}), carbonyl –CO (1550 cm^{-1}), methyl $–CH_3$ (1438 cm^{-1}), alcohol –C–OH (1029 cm^{-1}), Al-O-Si (560 cm^{-1}) [34,40,67]. Out of these feedstocks, chicken manure had strong bands at 1550 cm^{-1} and 1438 cm^{-1} that represented carbonyl –CO and methyl $–CH_3$ groups, respectively [71,72]. Conversely, biosolid had strong bands at 1029 cm^{-1} and 560 cm^{-1} that represented alcohol –C–OH and Al-O-Si groups, respectively. The presence of –OH groups corresponded to the moisture content [73], and represented phenols, and alcohols in feedstock and biochars [74]. After pyrolysis, chicken manure-biochar showed sharp bands at 2927 and 1650 cm^{-1}. This represented the shifting bond from the aliphatic to aromatic carbonyl groups [75]. This might be due to the degradation of straight C chains and synthesis of complex aromatic carbon structures [76]. On the other hand, biosolid biochar had medium bands at 2927 and 1029 cm^{-1}. The disappearance of these aliphatic groups has been corroborated in other studies [67].

3.10 Principal components analysis and classification of feedstock and biochar

Cluster analysis based on certain variables/parameters revealed the distance (similarity) of feedstocks and their respective biochars. Referring to the feedstocks, all 14 of them were classified into four clusters (Fig. 2 and Table S1). Cluster 1 comprised the only biosolid and cluster 2 included camel, sheep, alpacas, water buffalo, cow (grain-fed) and horse manure. Biomass of rabbit, wallaby, Australian wood duck and goat manure were classified into cluster 3 and cluster 4 including cow (grass-fed) manure, chicken manure and chicken litter. On the other hand, the respective 14 biochars were classified into 5 clusters (Fig. 3 and Table S4). Like the feedstocks, cluster 1 consisted of only biosolid biochar, and cluster 2 included only chicken manure and chicken litter-derived biochars. The majority of biochar samples were classified into cluster 3, constituting cow (grass-fed), horse, camel, sheep, rabbit and alpacas manure-derived biochars. Cluster 4 incorporated water buffalo and cow (grain-fed) manure biochar, and lastly, cluster 5 comprised of Australian wood duck, wallaby and goat manure derived biochars.

For feedstocks, three principal components (PC) were identified with eigenvalues larger than 1, explaining about 87% of the total variance (Table 7). PC1 explained 47.3% of the variance and exhibited strong correlations with C (–0.34); N (0.39); S (0.34); P (0.36); and Ca (0.34) (Table 7 and 9). This suggests that N, S, Ca and P varied in concert, as the magnitude of increase in one increased the magnitude in the other three. There was a strong inverse correlation with C (–0.34), suggesting that as N, Ca, or P increased, the amount of C decreased.

The above trends were reflected in the PC plot (Fig. 4). PC2 explained 29.5% of the variance and exhibited high positive correlations with K (0.36) and Na (0.35), and high negative correlations with Al (–0.44) and Fe (–0.46). These correlations are illustrated in Fig. 3. There were no shared chemical characteristics in PC1 and PC2, which means that the variance partitioned between them is maximized. PC3 explained 10.0% of the variance and exhibited high positive correlations with pH (0.84), Na (0.39) and C (0.22), and negative correlations with K (–0.15) and Ca (–0.15). High negative correlations of pH (0.52), Mg (0.42) and C (0.34) with EC (–0.40) were evident. This suggested that an increase in pH was accompanied by an increase in Na and C. It also indicated that as pH, Na, or C increased, K and Ca decreased. PC3 shared the chemical variables C and Ca with PC1, and K and Na with PC2, which suggested non-total orthogonality of the data set with respect to these PCs.

As with feedstocks, three PCs were identified for biochar samples with eigenvalues larger than 1, explaining about 83% of the total variance (Table 8). PC1 explained 41.5% of the variance and exhibited strong correlations with N (0.41), Ca (0.35), and P (0.33) (Tables 8 and 10). This infers that N, Ca and P co-varied in concentration, an increase in one increased the magnitude of the other two. There was a strong inverse correlation with C (–0.27), suggesting that as N, Ca, or P increased, the amount of C decreased. These trends were reflected in the PC plot (Fig. 5), in which the first PC was plotted versus the second PC. PC2 explained 30.1% of the variance and exhibited high positive correlations with K (0.33) and Na (0.32), and high negative correlations with Al (–0.47) and Fe (–0.46). These correlations were suggested in Fig. 4. There were no shared chemical characteristics in PC1 and PC2, which means that the variance partitioned between them is maximized. PC3 explained 11.7% of the variance and exhibited high positive correlations with pH (0.52), Mg (0.42), and C (0.34), and high negative correlations with EC (–0.40). This suggests that an increase in pH was accompanied by an increase in Mg and C. It also means that as pH, Mg or C increases, EC decreased. PC3 shared the chemical variable C with PC1, which suggested non-total orthogonality of the data set with respect to these two PCs. Since PC3 explained only 11.7% of the total variance, the individual correlations might not be conclusive, and this could be overcome by including more number of samples in the study.

4. Conclusions

A total of 14 feedstocks and their corresponding biochars were investigated comprehensively for their physical and chemical properties in this study to determine the materials' potential application in the soil as fertilizers. Initial characterization of the feedstocks revealed that these feedstocks were rich in nutrients and slightly alkaline. After producing biochars, the nutrient contents were mostly increased compared to their original feedstocks except for sulphur, which was decreased in some biochar samples. This could be due to volatilization loss. The high pH value can reduce soil acidity, and thus curtail the availability of PTEs in soil. The biochars contained higher SSA and porosity than plant-based biochars, which could represent an improvement in soil's water retention. Moreover, the PTE contents in all feedstocks and their corresponding biochars were below the maximum permissible limit as stipulated by international standards. The feedstocks and their respective biochars were classified into four and five clusters, respectively. Three PCs were extracted to explain the chemical composition of all feedstocks and their respective biochars. PCs showed a strong correlation with major nutrients (N, P and K) in feedstocks with their biochars. Therefore, biomasses and their respective biochars produced in this study were found rich in nutrients. Therefore, they can potentially be applied to the soil as fertilisers of organic origin. However, the biochar samples are better to use as fertilizer than the raw feedstocks. Based upon the physicochemical properties of the biochars (especially nutrient contents), all 14 biochar samples can be ranked them from best to worst fertilizer as follows biosolid>cow manure (grain-fed)>cow manure (grass-fed)>chicken manure>chicken litter> horse manure>goat manure>alpacas manure> camel manure>sheep manure>water buffalo manure>rabbit manure> wallaby manure> Australian wood duck manure. This work also encourages future research in effective resource recycling by converting animal wastes into value-added fertilizer products and its contribution to the circular economy.

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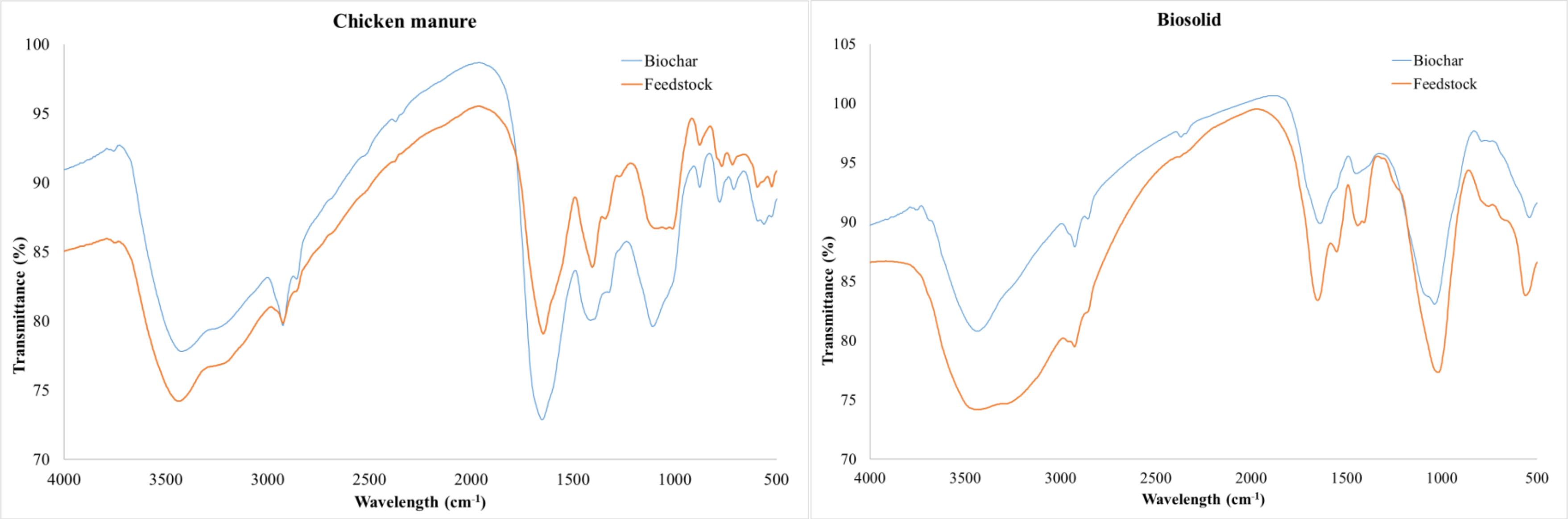

Figure 1: FTIR spectra: a) chicken manure and b) biosolid feedstock with their respective biochar

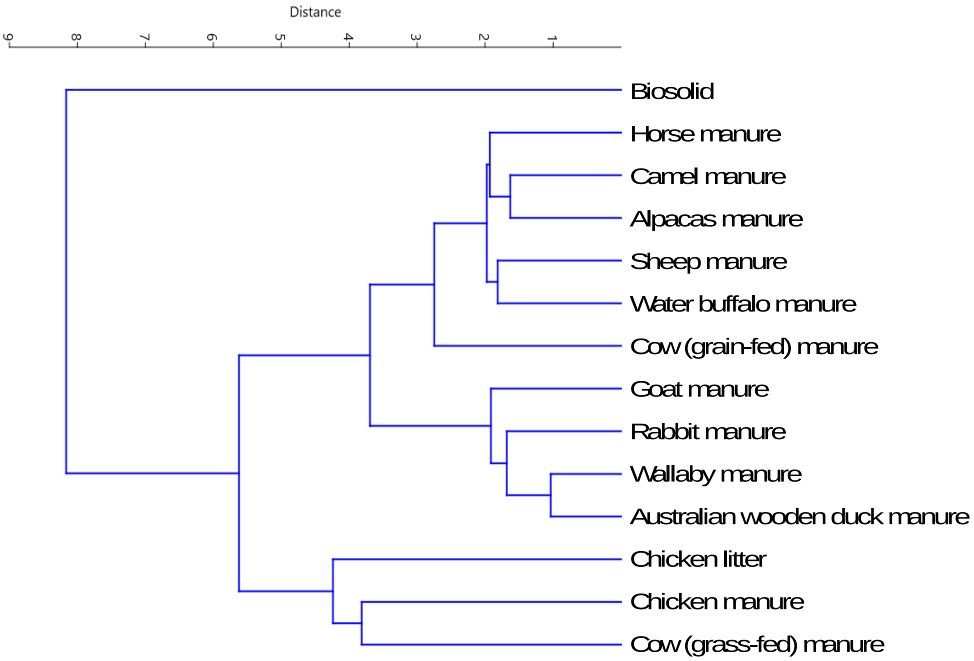

Figure 2: Hierarchical cluster analysis for the chemistry of feedstock

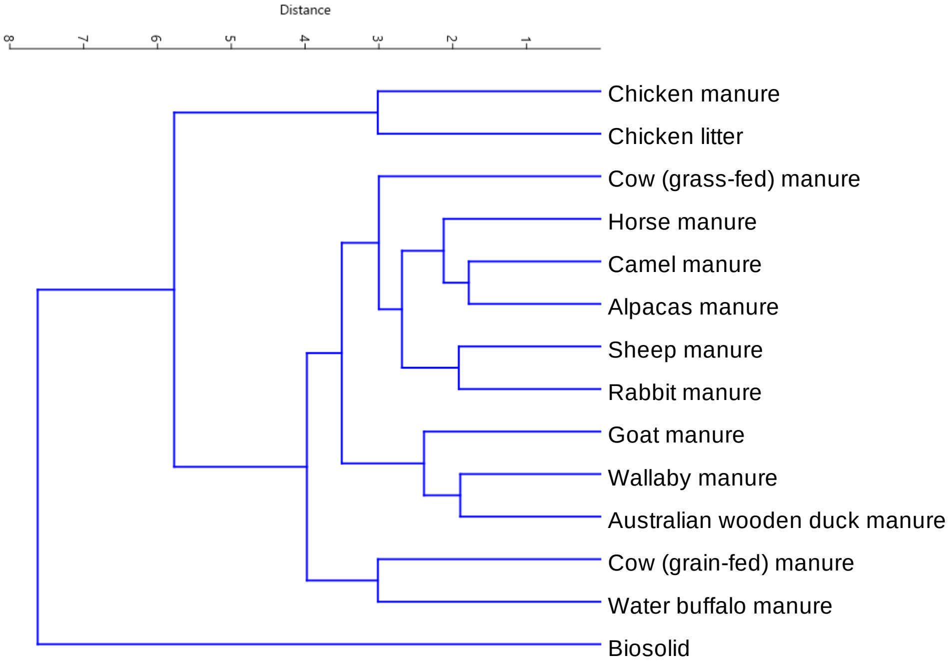

Figure 3: Hierarchical cluster analysis for the chemistry of biochar

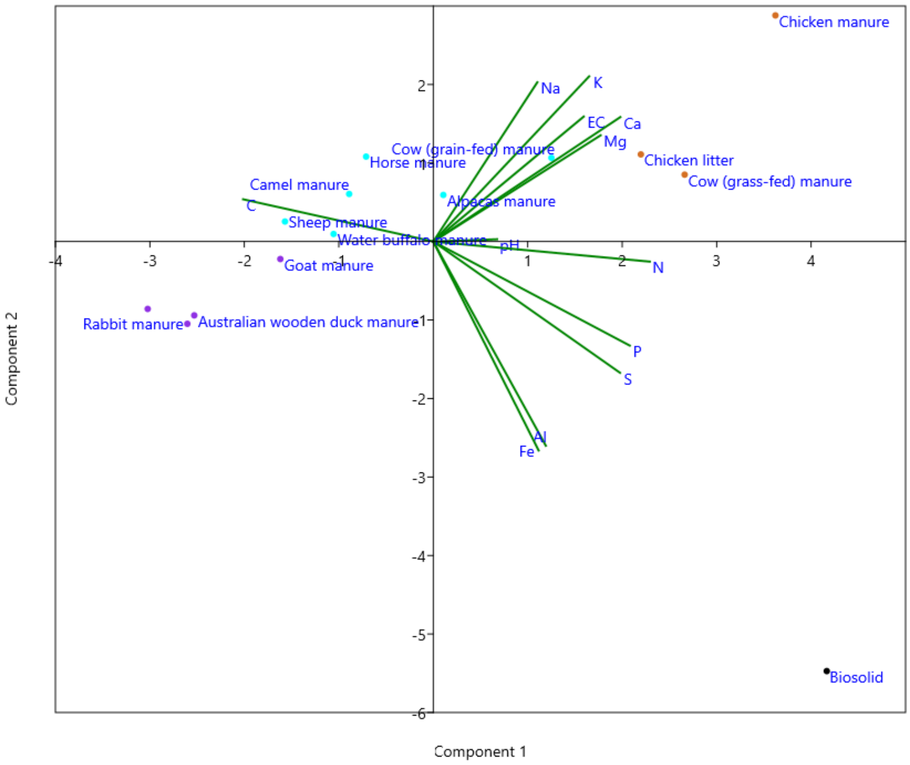

Figure 4: Principal components plot for the chemistry of feedstock

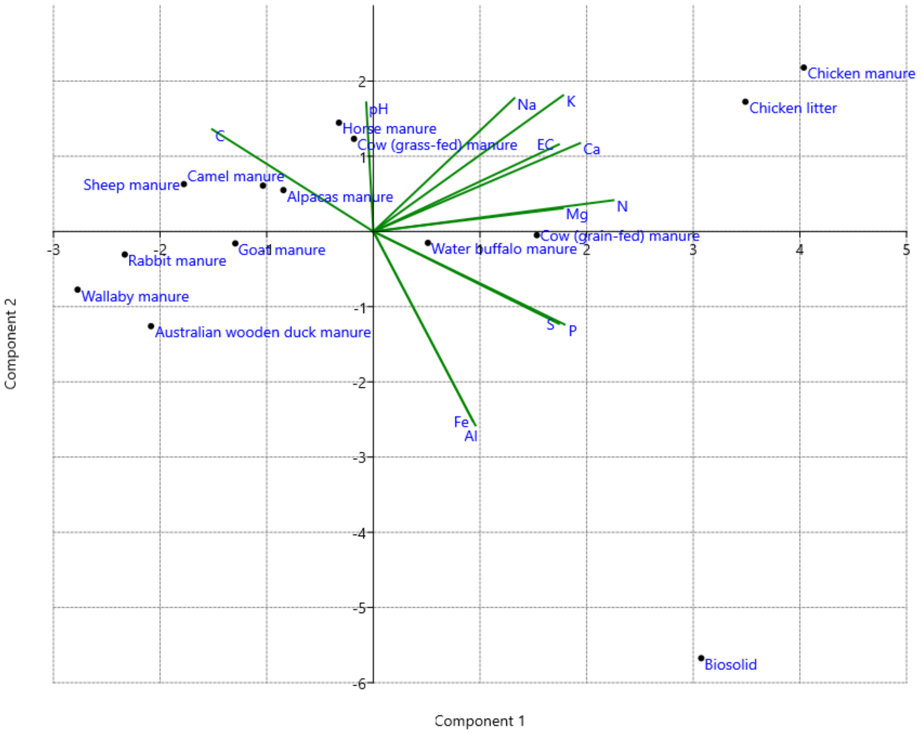

Figure 5: Principal components plot for the chemistry of biochar

Tables

Table 1: Biochar yield, Carbon, Nitrogen and C/N ratio including relative enrichment of feedstocks and their respective biochars

Sample	Yield (%)	Carbon			Nitrogen			C/N ratio	
		Feedstock (g kg^{-1})	Biochar (g kg^{-1})	RE	Feedstock (g kg^{-1})	Biochar (g kg^{-1})	RE	Feedstock (g kg^{-1})	Biochar (g kg^{-1})
Cow[ad]	80.96	237.5	291.6	0.99	32.1	36.4	0.99	7.39	8.01
Cow[ae]	58.67	432.9	563.4	0.76	24.1	32.7	0.80	17.96	17.23
Chicken[a]	66.22	360.1	392.3	0.72	45.2	57.8	0.85	7.97	6.79
Chicken[b]	48.89	397.8	402.2	0.49	39.8	41.1	0.65	9.99	9.79
Horse[a]	52.38	457.8	604.5	0.69	14.3	24.1	0.88	32.01	25.08
Biosolid	64. 72	283.9	267.4	0.59	46.4	39.1	0.48	6.11	6.84
Goat[a]	65.84	493.7	571.8	0.76	19.4	25.8	0.88	25.45	22.16
Camel[a]	68.20	492.7	543.3	0.75	16.9	19.4	0.78	29.15	28.01
Sheep[a]	62.21	504.5	575.5	0.71	17.7	22.7	0.80	28.50	25.35
Rabbit[a]	59.84	514.7	567.5	0.66	19.7	24.3	0.74	26.13	23.35
Wallaby[a]	62.49	474.1	534.6	0.70	9.0	13.1	0.91	52.68	40.81
Alpacas[a]	73.10	431.4	420.5	0.71	20.1	20.1	0.73	21.46	21.03
Duck[ac]	69.47	425.0	348.5	0.57	10.3	13.2	0.89	41.26	26.40
WB[af]	39.18	510.0	404.1	0.31	17.9	27.4	0.60	28.49	14.75

[a]= manure, [b]= litter, [c]=Australian wood, [d]=grain-fed, [e]=grass-fed, [f]=Water buffalo, RE=relative enrichment

Table 2: pH and electrical conductivity (EC) of feedstocks and their respective biochars

Sample	pH		EC (mS cm^{-1})	
	Feedstock	Biochar	Feedstock	Biochar
Cow[ad]	8.08	8.26	3.95	2.77
Cow[ae]	7.77	9.49	3.28	1.04
Chicken[a]	6.67	7.76	5.76	4.00
Chicken[b]	7.86	8.34	8.66	4.02
Horse[a]	7.41	8.71	2.22	0.31
Biosolid	7.82	7.09	1.50	0.46
Goat[a]	7.08	7.24	1.07	1.56
Camel[a]	8.31	8.51	1.52	0.32
Sheep[a]	8.05	8.73	1.24	0.19
Rabbit[a]	6.46	8.24	0.78	0.27
Wallaby[a]	7.16	7.11	0.45	0.52
Alpacas[a]	8.07	8.54	2.93	0.90
Duck[ac]	6.80	7.14	0.56	0.93
WB[af]	7.74	7.38	2.63	0.007

[a]= manure, [b]= litter, [c]=Australian wood, [d]=grain-fed, [e]=grass-fed, [f]=Water buffalo

Table 3: Major nutrient contents of feedstocks and their respective biochars

Sample	Total nutrient contents														
	Phosphorus			Potassium			Calcium			Magnesium			Sulphur		
	Feedstock (g kg^{-1})	Biochar (g kg^{-1})	RE	Feedstock (g kg^{-1})	Biochar (g kg^{-1})	RE	Feedstock (g kg^{-1})	Biochar (g kg^{-1})	RE	Feedstock (g kg^{-1})	Biochar (g kg^{-1})	RE	Feedstock (g kg^{-1})	Biochar (g kg^{-1})	RE
Cow[ad]	12.17	12.40	0.82	15.28	15.68	0.83	24.68	29.88	0.98	5.05	5.39	0.86	5.40	6.60	0.99
Cow[ae]	16.91	24.49	0.85	15.37	21.36	0.82	21.55	13.91	0.38	5.48	7.07	0.76	3.38	1.33	0.23
Chicken[a]	16.84	23.75	0.94	21.24	29.23	0.91	55.85	116.67	**1.38**	5.07	6.98	0.91	3.20	2.87	0.59
Chicken[b]	9.01	23.99	**1.30***	11.22	26.88	**1.17**	20.71	65.29	**1.54**	2.73	6.79	**1.22**	3.05	2.81	0.45
Horse[a]	8.59	16.65	**2.04**	7.95	14.51	0.96	11.00	17.89	0.85	4.08	7.39	0.95	1.66	1.24	0.39
Biosolid	40.52	50.62	0.81	1.65	2.20	0.86	14.69	20.38	0.90	5.85	7.23	0.80	10.70	8.91	0.54
Goat[a]	9.96	15.66	**1.06**	3.76	5.47	0.96	10.49	16.08	**1.01**	3.76	3.79	0.66	1.93	1.27	0.43
Camel[a]	5.69	8.18	0.98	3.20	5.04	**1.07**	16.13	22.96	0.97	5.53	7.53	0.93	2.33	1.53	0.45
Sheep[a]	4.93	7.71	0.97	2.43	3.37	0.86	7.55	10.43	0.86	2.35	3.21	0.85	2.37	1.90	0.50
Rabbit[a]	2.35	3.71	0.94	1.94	2.94	0.91	3.97	6.23	0.94	1.31	2.02	0.92	1.75	1.72	0.59
Wallaby[a]	2.98	4.66	0.98	0.74	1.19	**1.00**	4.47	7.06	0.99	0.74	2.13	**1.80**	0.99	0.63	0.40
Alpacas[a]	8.76	9.98	0.83	9.14	10.48	0.84	14.51	15.15	0.76	4.72	4.96	0.77	3.78	0.63	0.58
Duck[ac]	1.40	1.79	0.89	1.52	2.19	**1.00**	5.51	6.88	0.87	1.52	1.24	0.57	1.84	3.00	**1.13**
WB[af]	16.82	5.84	0.14	6.17	15.02	0.95	7.72	18.26	0.93	2.87	7.37	**1.01**	1.70	7.33	**1.69**

[a]= manure, [b]= litter, [c]=Australian wood, [d]=grain-fed, [e]=grass-fed, [f]=Water buffalo, RE=relative enrichment, * bold numbers refer to enrichment of element

Table 4: Micronutrient content of feedstocks and their respective biochars

Sample	Nutrient content														
	Copper			Zinc			Manganese			Molybdenum			Iron		
	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	RE	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	RE	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	RE	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	RE	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	RE
Cow[ad]	42.12	44.88	0.86	364.36	389.06	0.86	232.00	235.41	0.82	3.70	3.73	0.82	5901.50	6472.33	0.89
Cow[ae]	28.39	31.28	0.65	150.37	156.54	0.58	198.25	184.78	0.55	5.45	5.01	0.54	1044.50	933.00	0.52
Chicken[a]	39.89	52.47	0.87	321.60	365.18	0.83	382.73	351.04	0.61	7.88	8.66	0.73	1497.50	2058	0.91
Chicken[ab]	21.25	45.70	**1.05***	172.98	382.34	**1.08**	145.61	438.42	**1.47**	4.31	7.50	0.85	609.67	2289.50	**1.84**
Horse[a]	68.66	122.59	0.94	229.57	418.92	0.96	158.90	247.50	0.82	1.85	4.10	**1.16**	633.67	871.50	0.72
Biosolid	201.09	269.06	0.87	427.02	571.79	0.87	195.67	298.38	0.99	4.78	6.63	0.90	68195.50	89575.33	0.92
Goat[a]	15.79	24.75	**1.03**	87.99	132.99	**1.00**	173.01	208.67	0.79	1.30	2.93	**1.48**	554	683	0.81
Camel[a]	14.55	25.28	**1.18**	52.07	78.79	**1.03**	68.39	109.95	**1.10**	3.35	6.08	**1.24**	782	2281	**1.99**
Sheep[a]	14.76	24.06	**1.01**	81.50	114.67	0.88	151.11	165.87	0.68	8.61	1.89	0.14	529	612	0.72
Rabbit[a]	11.64	19.85	**1.02**	164.49	238.59	0.87	129.35	145.02	0.67	1.07	1.40	0.78	12986	470	0.02
Wallaby[a]	10.29	13.50	0.82	36.97	59.52	**1.01**	74.26	122.15	**1.03**	2.11	3.72	**1.10**	1390	2141	0.96
Alpacas[a]	22.35	23.43	0.77	84.24	98.79	0.86	168.36	147.11	0.64	3.77	2.26	0.44	2102	2403	0.84
Duck[ac]	14.12	21.23	**1.04**	58.58	76.68	0.91	88.45	125.91	0.99	3.10	1.59	0.36	2680	2738	0.71
WB[af]	14.37	28.66	0.78	130.51	218.28	0.66	134.74	221.150	0.64	1.03	2.90	**1.10**	1613	4458	**1.09**

[a]= manure, [b]= litter, [c]=Australian wood, [d]=grain-fed, [e]=grass-fed, [f]=Water buffalo, RE=relative enrichment, * bold numbers refer to enrichment of element

Table 5: Potential Toxic Elements (PTE) of feedstocks and their respective biochars

Biomass	Heavy Metal Content (mg kg^{-1})													
	Arsenic		Cadmium		Chromium		Cobalt		Lead		Nickel		Selenium	
	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})	Feedstock (mg kg^{-1})	Biochar (mg kg^{-1})
Cow[ad]	1.89	2.25	0.39	0.43	6.49	8.52	2.44	2.82	3.47	3.92	6.18	7.62	0.75	0.24
Cow[ae]	0.57	0.45	0.06	0.17	0.80	1.51	1.50	1.97	6.67	6.06	6.61	7.69	0.34	0.11
Chicken[a]	0.92	1.13	0.16	0.23	1.24	1.95	1.50	1.98	1.20	1.42	4.53	4.41	1.01	0.10
Chicken[b]	0.26	1.32	0.12	0.17	0.83	2.48	0.60	1.49	0.68	0.98	1.86	4.00	0.46	0.11
Horse[a]	0.30	0.54	0.12	0.17	1.13	2.02	2.14	4.39	0.67	1.09	4.08	6.41	0.27	0.09
Biosolid	2.18	0.51	1.55	2.03	26.98	40.29	2.28	3.11	8.75	11.67	16.90	23.51	2.18	0.51
Goat[a]	0.23	0.28	0.08	0.12	0.23	0.28	0.46	0.81	5.28	5.35	1.10	2.12	0.20	0.20
Camel[a]	0.35	1.30	0.05	0.15	0.35	1.30	0.30	0.81	10.06	7.16	2.55	4.42	0.20	0.20
Sheep[a]	0.31	0.30	0.09	0.13	0.31	0.30	0.34	0.51	6.61	5.87	1.11	1.83	0.20	0.20
Rabbit[a]	0.60	0.41	0.25	0.34	0.60	0.41	0.28	0.45	22.33	6.78	0.44	1.16	0.20	0.20
Wallaby[b]	0.42	0.62	0.06	0.10	0.42	0.62	0.61	0.94	5.90	7.20	0.20	3.71	0.20	0.20
Alpacas[a]	0.98	0.92	0.07	0.20	0.98	0.92	1.95	2.19	7.04	6.09	3.55	3.97	0.20	0.20
Duck[ac]	2.30	2.94	0.08	0.15	11.75	12.50	0.52	0.65	11.75	12.50	2.64	4.75	0.20	0.20
WB[af]	3.13	3.32	0.04	0.12	8.76	10.38	0.86	2.30	8.76	10.38	1.57	7.06	0.20	0.22

[a]= manure, [b]= litter, [c]=Australian wood, [d]=grain-fed, [e]=grass-fed, [f]=Water buffalo

Table 6: Specific surface area (SSA), total pore volume (TPV) and average pore diameter (APD) of biochars

Biochar	SSA (m^2 g^{-1})	TPV (ml g^{-1})	APD (nm)
Cow[ad]	97.03	0.11	4.53
Cow[ae]	97.50	0.11	4.55
Chicken[a]	102.73	0.15	5.71
Chicken[b]	97.87	0.14	5.89
Horse[a]	102.86	0.11	4.36
Biosolid	93.88	0.16	6.94
Goat[a]	98.80	0.11	4.52
Camel[a]	103.81	0.12	4.51
Sheep[a]	96.29	0.11	4.54
Rabbit[a]	105.61	0.12	4.36
Wallaby[b]	96.06	0.11	4.71
Alpacas[a]	110.83	0.12	4.40
Duck[ac]	100.71	0.12	4.65
WB[af]	101.61	0.17	6.67

[a]= manure, [b]= litter, [c]=Australian wood, [d]=grain-fed, [e]=grass-fed, [f]=Water buffalo

Table 7: Component matrixes for nutrients and other chemical properties of feedstocks

Chemical properties	Component matrix		
	PC1	PC2	PC3
pH	0.116	0.005	**0.836***
EC	0.272	**0.272**	0.068
C	-0.344	0.092	**0.216**
N	**0.392**	-0.044	-0.141
S	**0.338**	-0.286	0.112
P	**0.356**	-0.227	0.043
K	0.282	**0.360**	-0.152
Ca	**0.339**	0.271	-0.151
Mg	**0.303**	0.232	-0.101
Al	**0.204**	-0.445	0.066
Fe	**0.191**	-0.455	-0.011
Na	0.188	0.347	**0.394**

Principal component analysis, PC1: N, S, P, K, Ca, Mg, Al and Fe; PC2: EC and K; PC3: pH, C and Na
*Bold numbers refer to high loading

Table 8: Component matrixes for nutrients and other chemical properties of biochars

Chemical properties	Component matrix		
	PC1	PC2	PC3
pH	-0.012	0.312	**0.515***
EC	**0.317**	0.210	-0.401
C	-0.275	0.247	**0.335**
N	**0.409**	0.075	-0.052
S	**0.317**	-0.222	-0.069
P	**0.326**	-0.225	0.279
K	**0.324**	0.329	-0.009
Ca	**0.353**	0.213	-0.239
Mg	0.323	0.056	**0.419**
Al	0.174	-0.469	**0.172**
Fe	0.169	-0.459	**0.190**
Na	0.241	**0.322**	0.279

Principal component analysis, PC1: EC, N, S, P, K and Ca; PC2: Na; PC3: pH, C, Mg, Al and Fe
*Bold numbers refer to high loading

Supplementary materials for

Assessing the fertilizer value of biochars produced from slow pyrolysis of biosolid and diversified animal manures

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Supplementary Tables

Table S1: Cluster membership of feedstock types based on the chemical composition

Item	Hierarch Cluster
Biosolid	1
Camel manure	2
Sheep manure	2
Alpacas manure	2
Water buffalo manure	2
Cow (grain-fed) manure	2
Horse manure	2
Rabbit manure	3
Wallaby manure	3
Australian wood duck manure	3
Goat manure	3
Cow (grass-fed) manure	4
Chicken manure	4
Chicken litter	4

Table S2: Principal components of feedstock chemical composition

PC	Eigenvalue	% variance	Cum % variance
1	**5.67**	**47.29**	**47.29**
2	**3.54**	**29.53**	**76.82**
3	**1.20**	**9.97**	**86.80**
4	0.68	5.65	92.45
5	0.45	3.74	96.19
6	0.16	1.30	97.49
7	0.13	1.07	98.56
8	0.11	0.89	99.45
9	0.03	0.28	99.73
10	0.03	0.21	99.94
11	0.01	0.05	99.99
12	0.00	0.00	100.00

Table S3: Cluster membership of biochar types based on the chemical composition

Item	Cluster
Biosolid	1
Chicken manure	2
Chicken litter	2
Cow (grass-fed) manure	3
Horse manure	3
Camel manure	3
Sheep manure	3
Rabbit manure	3
Alpacas manure	3
Water buffalo manure	4
Cow (grain-fed) manure	4
Australian wood duck manure	5
Wallaby manure	5
Goat manure	5

Table S4: Principal components of biochar chemical composition

Principal Component (PC)	Eigenvalue	% variance	Cumulative % variance
1	**4.98**	**41.5**	**41.5**
2	**3.61**	**30.1**	**71.6**
3	**1.40**	**11.7**	**83.3**
4	0.84	7.0	90.3
5	0.52	4.3	94.6
6	0.22	1.8	96.4
7	0.16	1.3	97.7
8	0.14	1.2	98.9
9	0.10	0.8	99.7
10	0.02	0.2	99.9
11	0.01	0.1	100.0
12	0.00	0.0	100.0

Table S5: Variable loadings on principal components for biochar chemistry

Variable	PC 1	PC 2	PC 3
pH	-0.01	0.31	**0.52**
EC	0.32	0.21	**-0.40**
C	**-0.27**	0.25	**0.34**
N	**0.41**	0.08	-0.05
S	0.32	-0.22	-0.06
P	**0.33**	-0.22	0.28
K	0.32	**0.33**	-0.01
Ca	**0.35**	0.21	-0.24
Mg	0.32	0.06	**0.42**
Al	0.17	**-0.47**	0.17
Fe	0.17	**-0.46**	0.19
Na	0.24	**0.32**	0.28

Table S6: Guideline, standard and legislation threshold values for PTEs.

		As	Cd	Cr	Co	Cu
IBI biochar guidelines (2015)[a]	mg/kg	12 - 100	1.4 - 39	64 - 1200	40 - 150	63 - 1500
EBC basic grade biochar[b]	mg/kg		1.5	100		100
EBC premium grade biochar[b]	mg/kg		1	80		100
Sewage sludge in Agriculture (UK)[c]	mg/kg	50	3	400		80 - 200
USEPA-biosolid rules[d]	mg/kg	75	85	3000		4300
Australian standard regulation 1997[e]	mg/kg		10 - 300			
EU-sewage sludge[f]	mg/kg		20 - 40			1000 - 1750
Sweden[f]	mg/kg	2		100		600
Netherlands[f]	mg/kg	1.25		75		75
France[f]	mg/kg	20		1000		1000
Germany[g]	mg/kg		1	70		70
		Pb	**Ni**	**Se**	**Mo**	**Zn**
IBI biochar guidelines (2015)	mg/kg	70 - 500	47 - 600	2 - 36	5 - 20	200 - 7000
EBC basic grade biochar	mg/kg	150	50			400
EBC premium grade biochar	mg/kg	120	30			400
Sewage sludge in Agriculture (UK)	mg/kg	300	50 - 110	3	4	200 - 300
USEPA-biosolid rules	mg/kg	840	420	100	75	7500
Australian standard fertilizer	mg/kg	30 - 2000				
EU-sewage sludge	mg/kg	750 - 1200	300 - 400			2500 - 4000

Sweden	mg/kg	100	50			800
Netherlands	mg/kg	100	30			300
France	mg/kg	800	200			3000
Germany	mg/kg	100	35			300