

1 **Enhancing carbon sequestration in soil with coal combustion products: a**  
2 **technology for minimising carbon footprints in coal-power generation and**  
3 **agriculture**

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16 nitrogen

17

18 **Abstract**

19 Coal-fired power generation and agriculture account for more than half of global greenhouse gas  
20 emissions, but the coal fly ash (CFA) produced in the former can be a resource for reducing  
21 emissions from agriculture to minimise environmental footprints in both industries. Our aim in  
22 this study was to test how acidic and alkaline CFA addition could minimise loss of C and N from  
23 acidic soil, with or without added manure. We determined composition and structural  
24 characteristics of acidic and alkaline CFA for their capacity to adsorb organic carbon, but  
25 observed poor adsorption because of low concentrations of cenospheres and unburnt carbon as  
26 the primary absorbents in the ash. Addition of CFA had no impact on the loss of carbon or  
27 nitrogen from unmanured soil in which concentrations of these nutrients were low. Loss of  
28 carbon from manured soil was reduced by 36% with alkaline ashes and by 3-fold with acidic  
29 ashes; while loss of N was 30–50% lower with acidic ashes, but 28% higher with alkaline ashes,  
30 compared with no ash treatment. The increases in C sparing with CFA addition were achieved  
31 not by direct C absorption but by restraining microbial population and respiration, and  
32 potentially emissions. Alkaline CFA increased soil pH and if used to substitute just 10% of lime  
33 for ameliorating soil acidity would reduce CO<sub>2</sub> emission associated with the mining of the lime  
34 and its eventual dissolution in soil by ~ 2.66 Tg or 2.8% of Australia's annual agricultural  
35 emissions. High concentrations of oxides of phosphorus, silicon, titanium and clay particles in  
36 acidic ashes, and oxides of cations in alkaline ashes, were associated with potential for  
37 promoting C storage and acidity amelioration in soil.

38 *Keywords:* cenospheres, coal fly ash, liming, microbial respiration, manure, soil carbon, soil  
39 nitrogen

## 40 **1.0 Introduction**

41 Power generation and agriculture both generate substantial environmental footprints that pose  
42 significant risk to the long-term viability of these two industrial sectors. Greenhouse gas (GHG)  
43 emission is a major component of the environmental footprint for which the two industries  
44 account for ~80% and ~7%, respectively, of the total global GHG emissions in 2011 (UNFCCC  
45 2014). The majority of the emission in the energy sector arises from burning of fossil fuel. Coal  
46 contributes about 40% of total power generation (IAEA 2012) but accounts for 56% of the  
47 emission from the sector (ASN Bank/Ecofys 2013). A substantial part of the emissions from the  
48 agriculture sector emanate from soils which are responsible for up to 54% of agricultural  
49 emissions in the USA, 18% in Australia, 25% in China, and 34% in Brazil (UNFCCC 2014).  
50 Most of this is associated with the use of fertilisers and soil amendments (Garnuat 2011).

51 Between 5 and 15% of coal fed into boiler remains unburnt forming solid residues that are  
52 collectively termed Coal Combustion Products (CCPs). The majority of these residue (>85%)  
53 comprises of fine particles (<0.2 mm) referred to as coal fly ash (Heidrich et al. 2013) of which  
54 only about half of the 780 Mg global production is effectively used. The unused CFA stockpiles  
55 grow by 370 Mg annually, and along with gaseous emissions, has to be sustainably managed as  
56 part of the *Clean Coal Technology* (Seshadri et al. 2013). Potential use of coal fly ash (CFA) to  
57 ameliorate soil constraints on agricultural productivity, along with potential risks, has been  
58 extensively reviewed (Seshadri et al. 2013; Shaheen et al. 2014; Yunusa et al., 2012). Protocols  
59 for logistical, economic, monitoring and regulatory imperatives for routine agricultural  
60 application of CFA have been proposed (Yunusa et al. 2012). However, with the exception of a  
61 recent study (Masto et al. 2014), little attention has been given to potential application of CCPs

62 for mitigating GHG emissions from agriculture through promotion of C and N storage in soil  
63 proposed earlier (Amonette et al. 2004; Palumbo et al. 2004).

64 Furthermore, the C in limestone and dolomite used to ameliorate soil acidity on farms is  
65 inevitably released as CO<sub>2</sub> to the atmosphere (IPCC 2006). This emission accounts for about 9  
66 Tg CO<sub>2</sub> yearly in the United States of America (USEPA 2013). Liming contributes up to 7% of  
67 total greenhouse gas (GHG) emission from a typical wheat farm in Australia (Brock et al. 2012)  
68 and would account for about 30% of the total agricultural emissions by 2015 in Germany  
69 (Benndorf 2013). These farm emissions could be reduced by substituting liming products with  
70 CFA that contains non-oxidisable C and which reportedly increased pH of treated acidic soils by  
71 up to 2 units (Manoharan et al., 2010; Yunusa et al., 2013). Soil N is transformed into potentially  
72 volatile and/or soluble forms and easily lost from the soil during mineralisation of organic  
73 matter, and should be considered in strategies for abating farm emissions.

74 The CFA rich in lime CaO ( $\geq 3.0\%$ ) can directly adsorb CO<sub>2</sub> on to their particles through  
75 carbonation. Up to 7% w/w of CO<sub>2</sub> was absorbed through this process under natural conditions  
76 over a 20- year period, but the process is enhanced at high temperatures and pressure (60–90 °C;  
77 ~4.0 MPa) in the laboratory (Muriithi et al. 2013). Particulate organic C can also be absorbed  
78 onto ash particles, the unburnt C and/or cenospheres; the latter are ash particles that burst under  
79 high temperatures forming hollow spheres with large surface areas (Amonette et al. 2004;  
80 Palumbo et al. 2004). However, CFAs contain low amounts of cenospheres (<4% w/w) and  
81 unburnt C (Ngu et al. 2007) so that large amounts of ash would be required to achieve significant  
82 absorption of particulate C. Hence both carbonation and adsorption of organic C onto particles in  
83 CFA are therefore likely to have negligible short-term capacity for soil C sequestration.

84 Increased C storage in soil with CFA amendment is more likely to be indirect through alterations  
85 of processes and properties in the soil, such as aggregation, pH, salinity, and, where the ash  
86 contains significant amounts of unburnt C, the C/N (Palumbo et al., 2004; Amonette et al.,  
87 2004). Increases in pH due to ash addition reportedly enhanced humification in analytical  
88 organic monomers (Amonette et al. 2004), which along with reduced mineralisation stabilised  
89 peroxidase and tyrosinase activities and enhanced humification in ash-amended soil (Masto et  
90 al. 2014). Improved soil aggregation with ash amendment (Yunusa et al. 2011) should protect  
91 organic C from microbial decomposers (Beare et al 1994; Jastrow et al. 2007; Rabbi et al., 2013;  
92 Young and Ritz 2000).

93 In the current study, we determined the potential of acidic and alkaline CFA for enhancing  
94 storage of C and N in acidic soil with or without incorporation of sheep manure. Our objectives  
95 were to (1) quantify cenosphere and unburnt C contents of the CFA and their capacity to adsorb  
96 particulate organic C, (2) determine depletion of C and N from an acidic soil, (3) identify  
97 chemical properties that influence loss of C and N from ash-amended soil, and (4) identify  
98 knowledge-gaps in developing CFA technology for enhancing C and N storage in soils.

## 99 **2.0 Materials and methods**

100 Five CFAs were obtained from power stations in Western Australia, South Australia, Victoria,  
101 New South Wales and Queensland, in Australia. Three of the ashes were alkaline and the other  
102 two acidic; henceforth denoted as acidic1, acidic2, alkaline1, alkaline2 and alkaline3, and all five  
103 had low salinity except alkaline3 (Table 1) and used in the following experiments.

### 104 **2.1 Ash characterisation and adsorption of organic carbon**

105 Cenospheres were harvested by dispersing ash samples in distilled water in 1:20 (w/v) ash/water  
106 at room temperature, and then followed by a 24-hour sink-float separation. Chemical

107 composition of the cenosphere was determined in a two-step procedure of fusion and analysis  
108 prescribed in the Australian Standard AS 1038.14.1–2003 and reported by Yip et al. (2010). A  
109 scanning electron microscope (SEM) was used to determine morphological characteristics of  
110 cenospheres, while the unburnt C was quantified using thermogravimetric analysis (TGA)  
111 following a procedure reported (Ngu et al. 2007).

112 Adsorption of organic carbon by the CFA cenospheres was determined in a batch adsorption  
113 reactor system involving shaking 0.35 g of cenosphere in 200 ml of synthetic water containing  
114 methylene blue (10 ppm). The dye concentration in the solutions was determined before and  
115 after adsorption using a Spectrophotometer (Spectronic 20 Genesys<sup>TM</sup>, Thermo Scientific,  
116 Melbourne, Australia) to measure absorbance at  $\lambda_{\max}$  of 665 nm for methylene blue (Wang et al.  
117 2008).

## 118 **2.2 Soil incubation experiment**

119 An acidic sandy loam soil (Yellow Chromosol) equivalent to a Haplic Xerosol (FAO, 1974) was  
120 collected from the UNE research farm, Armidale (30° 29' 16" S, 151° 38' 29" E); it belongs to the  
121 order Alfisol in the USDA classification (Soil Survey Staff, 2012) and had been under lightly  
122 fertilized mixture of native pastures. It was amended with sheep manure and/or CFA for this  
123 study. The sheep manure was collected from a local shearing shed. The soil, manure and CFA  
124 were air dried, and the soil and manure were ground to pass a 2 mm sieve, and mixed in plastic  
125 containers to form the following factorial treatments:

- 126 i. Ash amendment: 85% soil (153 g) + 15% ash (27 g) + 0% manure
- 127 ii. Manure amendment: 85% soil (153 g) + 15% manure (27 g) + 0% ash
- 128 iii. Ash & manure amendment: 70% soil (126 g) + 15% ash (27 g) + 15% manure (27 g)
- 129 iv. Control: 100% soil (180 g) + 0% ash + 0% manure

130 The soil or mixtures were blended uniformly and then weighed at 180 g into 0.5 L clear plastic  
131 containers (80 mm x 110 mm x 90 mm) with each treatment prepared in 4 replicates. The  
132 containers were arranged randomly on benches in a glasshouse maintained at 22 °C and humidity  
133 at ~50%. The treatments were gradually wetted to bring their weights to predetermined field  
134 capacity and weight recorded. The treatments were covered with a black shade-cloth to minimise  
135 evaporation, and brought back to their prescribed weights with addition of water once a week for  
136 3 months.

### 137 **2.2.1 Measurements**

#### 138 *Carbon and nitrogen content and their stable isotopes*

139 After three months, half of the sample in each jar was taken by cutting cleanly vertically through  
140 the soil; the remaining half was stored in a fridge to be used for microbial analysis. The samples  
141 were air-dried and sieved to pass 2.0 mm screen, and used to determine salinity as electrical  
142 conductivity (EC) and pH using a portable bench-top pH-EC meter (LabCHEM Model 901-CP,  
143 TPS Pty Ltd, Australia) on filtrate of air dried sample mixed into deionised water (1:5). Both  
144 total C (TC) and total N (TN) were measured on 5 g samples in a high temperature furnace  
145 (LECO®, St Joseph, MI, USA), while  $\delta^{13}\text{C}$  was determined using a mass spectrometer (ANCA-  
146 GSL IRMS, Sercon Ltd., Cheshire, UK). The  $\delta^{13}\text{C}$  isotope composition of the samples was  
147 computed as (IAEA 2001):

$$148 \quad \delta^{13}\text{C} (\text{‰}) = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] 10^3 \quad (1)$$

149 in which  $R$  represents the mass ratio of  $^{13}\text{C}/^{12}\text{C}$  for the sample or 0.0112372 for the standard. The  
150  $\delta^{13}\text{C}$  for the mixtures at the start of incubation was calculated thus:

$$151 \quad \delta^{13}\text{C}_{\text{mixture at day 0}} = f_{\text{soil}} \times \delta^{13}\text{C}_{\text{soil}} + f_{\text{manure}} \times \delta^{13}\text{C}_{\text{manure}} + f_{\text{ash}} \times \delta^{13}\text{C}_{\text{ash}} \quad (2)$$

152 where  $f$  represents fractions of C for either the soil, manure or ash in the mixture. The TC and  
153 TN lost during the incubation period were estimated from their quantities (Q) at the start (day 0)  
154 and after the 3-month incubation ( $Q_3$ ):

$$155 \quad Q_{lost} = Q_0 - Q_3 \quad (3)$$

156 The quantities of TC and TN at the start of the incubation were estimated from the masses of  
157 soil, CFA and manure in the mixtures, and the respective concentrations of the two nutrients:

$$158 \quad Q_0 = \sum_{i=1}^{n=3} (m_i \times c_i) \quad (4)$$

159 where  $m_i$  are the masses of the component in the substrates,  $i$ , (soil, CFA and manure), and  $c_i$  are  
160 their respective TC or TN concentrations;  $n$  is the number of components (1–3) in the mixture.

161 The  $Q_3$  values were obtained from the product of the mass of the incubation substrate and its  
162 measured TC or TN values.

### 163 *Microbial biomass and respiration*

164 These were measured on the stored half of the samples using microplate-based respiration  
165 technique (MicroResp™, Craigiebukler, Aberdeen, UK) as per Campbell et al. (2003). Basal  
166 respiration rate (BSR) was monitored over three days after which 0.22 g of glucose was stirred  
167 into the soil and monitored for a further 24 hours to determined substrate-induced respiration and  
168 the dependent microbial biomass.

### 169 **2.3 Data analyses**

170 Data on cenosphere and unburnt carbon in the ashes were evaluated in a one-way analysis of  
171 variance. All data from the incubation experiment were subjected to two-way analysis of  
172 variance (ANOVA); statistical significance was determined when  $p \leq 0.05$ . Two sets of principal



173 component analyses (PCA) were undertaken to examine (i) interrelationships amongst TC and  
174 TN, EC, pH and microbial biomass and BSR at the completion of the incubation period, and (ii)  
175 whether TC and TN post-incubation could be associated with specific properties of the CFA.  
176 Both ANOVA and PCA were carried out using IBM SPSS Statistics, V22.0 (IBM Corp, Armonk,  
177 NY).

## 178 **3.0 Results**

### 179 ***3.1 Physico-chemical properties of the ashes and their cenosphere yields***

180 The five ashes consisted mostly of silt- and sand-size particles, whose mineral composition was  
181 dominated by SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (Table 1). The SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> accounted for >70% in four ashes,  
182 but <20% in alkaline3 in which Fe<sub>2</sub>O<sub>3</sub> dominated (30%) Other oxides, especially CaO, Na<sub>2</sub>O<sub>5</sub>,  
183 MgO, Mn<sub>3</sub>O<sub>4</sub>, SO<sub>3</sub>, were generally higher in alkaline3 than in the other ashes.

184 Only alkaline1 and alkaline2 yielded any cenospheres with an average of 0.5% w/w. The  
185 cenospheres had smooth round and spherical shapes (Fig. 1) with ~30 –150 µm diameter. Close-  
186 up views of individual cenospheres reveals macro-size (>10 µm) pores and finer spherical ash  
187 particles adhered onto the surface. The amount of unburnt C in the cenospheres was generally  
188 small, ~1.8% w/w in alkaline1 and ~0.2% in alkaline2.

### 189 ***3.2 Carbon adsorption onto cenospheres and unburnt carbon in ash***

190 The adsorption of methylene blue onto the cenospheres of alkaline1 and alkaline2 showed a two-  
191 phase trend (Fig. 2a): an initial exponential phase in the first 10 mins, followed by a slow linear  
192 phase in the following four hours. On the whole, the adsorption capacity of cenosphere after four  
193 hours was 0.7 mg methylene blue per gram of cenospheres. Over the same duration, the amounts

194 of methylene blue adsorbed by alkaline2 ash directly (2.0 mg/g) or by its unburnt carbon (~21  
195 mg/g) were larger than adsorption by its cenospheres alone (Fig. 2b).

### 196 **3.3 Soil incubation**

#### 197 **3.3.1 Total carbon and nitrogen concentrations in soil**

198 Concentrations of TC and TN at the start of the incubation were larger by factors of 4 and 9,  
199 respectively, in the manured soil compared with unmanured soil (Table 2). Addition of CFA to  
200 unmanured soil did not alter TC (Fig. 3a) or TN (Fig. 3b) after incubation; however, TC was  
201 higher in the manured soil supplied with ash compared with no ash. Post-incubation TN was  
202 higher with addition of the acidic CFAs than with the alkaline CFAs. The proportions of TC and  
203 TN lost during incubation from the manured soil were generally lower with CFA than without,  
204 and also differed with ash type (Table 2). The acidic ashes were more effective than the alkaline  
205 ashes in arresting losses of C (28% vs 43% or 2.65 g vs 4.37 g) and N (13% vs 39% or 0.11 g vs  
206 0.36 g). With exception of alkaline2 that reduced N loss only marginally, addition of alkaline1 or  
207 alkaline3 increased N loss by 28 and 36%, or 0.37 g and 0.45 g, respectively, compared with  
208 0.29 g when no ash was added. It was not possible to partition the losses in TC and TN amongst  
209 the three sources.

210 The amounts of TC measured in both manured and unmanured soils post-incubation as  
211 percentage of their pre-incubation concentrations averaged 57%; whereas proportionally more  
212 TN was lost from the manured (30%) compared with unmanured soil (2%). The losses of both  
213 nutrients from the soils during incubation were coupled:

$$214 N_{\text{loss}} = 1.57C_{\text{loss}} - 29.63; \quad r^2 = 0.94, n-2 = 18 \quad (4)$$

215

### 216 **3.3.2 Microbial respiration and biomass**

217 The BSR in unmanured soil was not affected by addition of acidic CFA, but increased with  
218 alkaline CFA (Fig. 3c). However, BSR was at least halved in manured soil with addition of any  
219 of the five ashes. Microbial biomass in unmanured soil was unaffected with acidic<sup>2</sup> and  
220 alkaline<sup>1</sup>, and significantly with alkaline<sup>3</sup> (Fig. 3d). Addition of any of the ashes significantly  
221 reduced microbial biomass in the manured soil; acidic<sup>1</sup> was the least detrimental to microbial  
222 biomass. Both BSR and microbial biomass were 4- and 5- times, respectively, larger in the  
223 manured soil compared with unmanured soil.

### 224 **3.3.3 Basic soil chemistry after incubation**

225 Changes in the soil chemical variables at the end of the incubation are presented in Table 3. With  
226 exception of acidic<sup>1</sup> and alkaline<sup>3</sup>, the pH was lower with ash additions in manured soil than in  
227 the unmanured soil. The electrical conductivity (EC) in unmanured soil was increased only with  
228 addition of alkaline<sup>1</sup> or alkaline<sup>3</sup>. Addition of any ash to the manured soil either had no impact  
229 on EC or reduced it, the exception being alkaline<sup>3</sup> that increased it significantly. The mean pH  
230 was similar for manured and unmanured soil, while the manured soil was more saline, had more  
231 depleted  $\delta^{13}\text{C}$ , but higher C/N, than the unmanured soil.

232 Addition of alkaline<sup>3</sup> enriched  $\delta^{13}\text{C}$  in unmanured soil, while addition of other ashes depleted  
233  $\delta^{13}\text{C}$  in unmanured and manured soil (Table 3). Relative to starting conditions, CFA additions  
234 depleted  $\delta^{13}\text{C}$  in unmanured soil during incubation, the exception was alkaline<sup>3</sup> that enriched  
235  $\delta^{13}\text{C}$ . There was general  $\delta^{13}\text{C}$  enrichment in the manured soil during incubation due to CFA  
236 addition, the exception being alkaline<sup>2</sup> that caused a slight depletion.

### 237 **3.3.4 Associations between CFA properties and post incubation total C and TN**

238 Principal component analysis (PCA) showed that most of the total variance (82%) was accounted  
239 by the first two principal axes of variations (Fig. 4a). The first axis (62.8%) had high negative  
240 loadings on TC, TN, microbial biomass and basal respiration, all of which were tightly coupled,  
241 and high positive loading on  $\delta^{13}\text{C}$ . There was also a clear separation between manured (suffix  
242 \_15) and unmanured (suffix \_0) soil along the first principal component (PC1) axis, showing  
243 manured soil as having high levels of TC, TN, microbial biomass and basal respiration, and  
244 depleted  $^{13}\text{C}$ . The PC2 (19.5% of variation) was dominated by pH and EC of the incubation  
245 substrate. It showed an inverse correlation between TC, TN and microbial biomass, and also,  
246 with BSR and with pH. Four major clusters could be discerned consisting of (i) alkaline1 and  
247 alkaline2 with 0% manure, (ii) acidic ashes with 0% manure, (iii) alkaline1 and alkaline2 with  
248 0% manure, and (iv) alkaline3 with either manure treatment.

### 249 **3.3.5 Associations between TC, TN, microbial dynamics and chemical attributes**

250 The PCA extracted 78% of the total variance in the CFA composition and their correlations with  
251 post-incubation TC and TN levels (Fig. 4b). The PC1 accounted for 53% of the total variance  
252 with high positive loadings on CaO,  $\text{Mn}_3\text{O}_4$ , MgO,  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_3$ ,  $\text{Na}_2\text{O}$  and associated EC, all of  
253 which had high negative correlations with  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$  and  $\text{SiO}_2$ . The PC2 extracted a further 25%  
254 of the total variance, with high positive loadings on pH and negative loadings on clay content,  
255 suggesting a strong inverse association between the two. Alkaline1 was the most benign of the  
256 ashes in terms of direct impact of its properties on TC and TN.

## 257 **4.0 Discussion**

### 258 **4.1 Cenosphere and unburnt carbon yields and their potential for carbon adsorption**

259 The ashes used here generally contained low amounts of cenospheres, and the average yield of  
260 0.5% w/w by the two alkaline ashes was within the range (0.2 –3.8%) for a number of CFA in  
261 Australia (Ngu et al. 2007). Ngu et al. (2007) reported cenosphere yields of 3.8% w/w for acidic2  
262 contrary to zero yields in the current study. This could be due to variability in the physico-  
263 chemical properties of different batches of CFA arising from the operating conditions of the  
264 boilers (Raask 1985), the source coal and other factors, including decomposition of carbonates,  
265 fusion of silicates and evaporation of pore water (Ngu et al. 2007). For instance, while the 69%  
266 w/w of silicates for acidic2 (Table 1) was comparable to the 65% reported earlier, the aluminate  
267 content of 24% in the current study was well below the 35% reported for this ash previously  
268 (Ngu et al. 2007). Alkaline3 had low concentrations of silicates and aluminates, suggesting an  
269 inherent low potential for cenosphere yield. Similarly low cenosphere production would be  
270 expected from acidic1 given its low silicate content. However, both the cenospheres and the  
271 unburnt C were poor adsorbents of methylene blue (Fig. 2). The unburnt C had superior C  
272 adsorption because its porous structure and associated surface area were preserved, while these  
273 were destroyed during melting of the cenospheres (Wang et al. 2005). Thus adsorption by  
274 unburnt carbon could be up to 9-fold greater than by CFA particles (Wang et al. 2008),  
275 consistent with the findings here (Fig 2b).

276 The bulk CFA as a whole therefore has low capacity for physical adsorption of organic carbon,  
277 with absorption being only 7–10 mg C/g for Australian CFAs (Wang et al. 2008). The current  
278 study, demonstrates that, even accounting for adsorption by the unburnt carbon, CFA is unlikely  
279 to have a major impact on soil carbon sequestration since the total C contents of these ashes are

280 generally low (<5.5% even in acidic<sup>1</sup>, Table 1). The capacity of unburnt carbon to absorb  
281 particulate organic carbon was  $\leq 1\%$  w/w for the ashes used in this study and demonstrated the  
282 poor capacity for direct adsorption of organic carbon by CFA. Therefore, any real benefit for soil  
283 C sequestration due to ash addition would accrue only from changes induced in the physico-  
284 chemical properties of ash/soil admixtures.

#### 285 **4.2 Changes in total carbon and total nitrogen during incubation**

286 Ash addition altered the properties of the media during incubation and explained the differences  
287 in the TC and TN observed afterwards. Addition of ash clearly reduced loss of TC, which along  
288 with TN and microbial variables, were strongly and inversely correlated with  $\delta^{13}\text{C}$  (Fig. 4a). This  
289 was because the manure was the dominant source of C in the mixture and its loss enriched  $\delta^{13}\text{C}$   
290 towards the soil value of -18.69. The general  $\delta^{13}\text{C}$  enrichment during incubation of manured soil  
291 was smaller with ash addition that also increased the C/N, compared with no ash addition (Table  
292 3). Maintenance of high C/N with ash addition would have restrained decomposition and  
293 subsequent loss of C (Drinkwater et al. 1998). Minimal loss of C (<40%) and N (<31%) were  
294 observed with addition of CFA that kept the incubate pH within 6.4–7.6 range (Table 2), well  
295 below pH of 9.4 for alkaline<sup>3</sup> that lost the most C and N. This was consistent with positive  
296 association found between acidic pH conditions and enhanced retention of C and N in soil (Bååth  
297 and Anderson 2003; Conyers et al. 2012).

298 The links between TN, TC and microbial variables, and also pH and the EC, are revealed along  
299 the PC-2 axis (Fig. 4a). Both TC and TN were coupled with treatment cluster consisting of acidic  
300 ashes and alkaline<sup>1</sup> and alkaline<sup>2</sup> in the third quadrant of PCA. These clusters could also be  
301 partly due to salinity of the ashes, in addition to the pH, that stressed the microbial populations  
302 and impaired mineralisation of the organic matter (Rietz and Haynes 2003). The clustering of

303 ashes reflected their chemical composition (Fig. 4b) such that alkaline1 and alkaline 2 were  
304 closely associated with  $K_2O$ , while alkaline3 was associated with a suite of alkali metals ( $Na_2O$ ,  
305  $MgO$ ,  $CaO$ ,  $Mn_3O_4$  and  $Fe_2O_3$ ). A third group consisting of the two acidic ashes was closely  
306 associated with  $P_2O_5$  and  $SiO_2$ ,  $TiO_2$  and clay particles. These two groups of oxides can then be  
307 used for identifying ashes with potential for C conservation in soil.

308 Losses of the two nutrients were tightly coupled (eq. 4), although on average about 30% TN was  
309 lost compared with 42% of TC (Table 2) possibly due to mineralisation of N lagging behind that  
310 of C, with the former reportedly commencing only after the microbes become C-starved  
311 (Weintraub and Schimel 2003). Differences in the labile fractions of the two nutrients in the  
312 manure, similarity in C/N notwithstanding, could affect their mineralisation (Blair et al., 2005),  
313 because mineralisation of C is dependent more on pH, while that of N is more on C/N (Tian et al.  
314 2013).

315 The reductions of 40 –70% in the loss of C with both ash types and N with acidic ashes  
316 demonstrated the capacity of CFA to mitigate GHG emission. Although we were unable to  
317 directly quantify the fluxes, negligible methane emissions from manure-rich arable soils, such as  
318 that used here, have been reported (Hütsch 1998). Despite the neutral impacts of CFA in  
319 unmanured soils, the capacity of alkaline ashes in raising soil pH (Table 3) as found in earlier  
320 studies (Manoharan et al. 2012; Yunusa et al. 2012) means these ashes can substitute lime for  
321 treating soil acidity and thereby avoid associated emissions. For example, applying just 2 Mg/ha  
322 of lime to the 1.7 M ha of agricultural land limed annually in Australia (ABS 2014), mining the  
323 required 3.4 Tg lime would generate ~ 2.66 Tg  $CO_2$  using the lime characteristics ( $CaO$ ,  $MgO$ ,  
324 water content) in Approach1 of the Greenhouse Gas Protocol (WRI 2008). This emission would  
325 be avoided as would the expected annual emission of 0.02 Tg  $CO_2$ , i.e. 0.059 Mg C/Mg lime

326 (West and McBride 2005), from eventual dissolution of the soil applied lime. This 2.66 Tg  
327 emission abatement is equivalent to 2.8% of the ~98 Tg annual emission from the Australian  
328 agricultural sector. Acidic ash additions would also significantly mitigate N emissions from the  
329 manure treated soil by as much as two-thirds (Table 2). Aerobic decomposition of soil applied  
330 manure disposes of at least half of the N as NH<sub>3</sub> or N<sub>2</sub>O within the first year (Dorahy et al.  
331 2010). Therefore, applying the manure with 3.39% N w/w (Table 1) at 10 Mg/ha over 100 ha  
332 would add 3.4 Mg N to the soil and generate 1.7 Mg of gaseous N emissions; this amount would,  
333 however, be cut by between 50 and 67% with the acidic ashes. This potential emission mitigation  
334 would be even larger in countries such as the United Kingdom where up to 42 Mg/ha of manures  
335 are prescribed routine farm applications (DEFRA 2009). Application of an acidic CFA should  
336 cut N emission from such practice in the first year to <10 Mg/ha compared with the expected 21  
337 Mg/ha.

338 In conclusion, use of CFA for promoting storage of carbon and nitrogen in cropping soils is a  
339 viable technology for reducing GHG emissions in agriculture and environmental foot prints in  
340 this and the coal-power generation by minimising the CFA disposed in landfill. In selecting  
341 ashes for mitigating the loss of these nutrients from soil, acidic ashes are preferred over alkaline  
342 ashes that were effective in minimising only C loss. High concentrations of P<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub>, TiO<sub>2</sub>  
343 and clay particles in acidic ashes, and alkali/alkaline-earth metals (Na<sub>2</sub>O, MgO, CaO, Mn<sub>3</sub>O<sub>4</sub> and  
344 Fe<sub>2</sub>O<sub>3</sub>) and sulphur in alkaline ashes, provided initial selection criteria for identifying CFAs for  
345 soil carbon sequestration. Knowledge-gaps to be addressed in developing this technology further  
346 include: (1) characterisation of the enzymatic processes in organic C mineralisation in ash  
347 amended soil, (2) major forms of N loss from the system, (3) whether similar C sparing is  
348 possible with plant residues, and (4) optimum rates and mode of ash additions.



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359

360 Table 1 Selected chemical properties and elemental composition of the five coal fly ashes, the soil  
 361 and manure used in this study

Properties	Acidic1	Acidic2	Alkaline1	Alkaline2	Alkaline3	Soil <sup>1</sup>	Manure
<i>Basic chemical properties and particle size distribution</i>							
pH	3.3	4.0	10.7	10.8	9.0	6.3	7.40
EC (dS/m)	1.10	0.14	0.70	0.54	19.0	0.08	10.03
Total C	0.11	0.68	0.04	2.10	0.45	1.03	34.04
Total N (%)	0.001	0.007	0.003	0.018	0.012	0.056	3.39
C/N	110	97	13	117	38	18	10
$\delta^{13}\text{C}$ (‰)	-22.84	-25.38	-24.77	-24.22	-24.32	-18.69	-23.02
Clay (%)	8.9	4.2	5.4	2.4	3.7	60.9	na
Silt (%)	78.2	68.0	66.3	51.9	45.5	23.2	na
Sand (%)	13.1	4.2	28.3	45.9	50.8	15.9	na
<i>Chemical composition (%)</i>							
SiO <sub>2</sub>	50.1	69	61.3	63.6	8.18	nd	nd
Al <sub>2</sub> O <sub>3</sub>	26.5	24	28.1	25.9	5.34	nd	nd
Fe <sub>2</sub> O <sub>3</sub>	13.5	1.7	2.42	2.83	33.1	nd	nd
K <sub>2</sub> O	0.64	0.44	3.01	3.58	0.24	nd	nd
Na <sub>2</sub> O	0.29	0.01	1.16	0.94	5.92	nd	nd
CaO	1.84	0.12	1.64	1.36	8.68	nd	nd
MgO	1.14	0.22	0.60	0.76	13.76	nd	nd
TiO <sub>2</sub>	1.15	1.7	0.87	0.79	0.26	nd	nd
Mn <sub>3</sub> O <sub>4</sub>	0.09	0.01	0.05	0.05	0.80	nd	nd
P <sub>2</sub> O <sub>5</sub>	1.43	0.1	0.24	0.09	0.08	nd	nd
SO <sub>3</sub>	0.37	0.2	0.52	nd	14	nd	nd
BaO	0.32	0.1	0.06	0.06	nd	nd	nd
SrO	nd	0.01	0.04	0.04	nd	nd	nd
<b>Total</b>	<b>97.37</b>	<b>97.61</b>	<b>100.00</b>	<b>100.00</b>	<b>90.36</b>	<b>na</b>	<b>na</b>

362 <sup>1</sup>determined on fresh soil soon after collection; na, not applicable; nd, not determined

363

364 Table 2 Calculated total C and total N at the start of incubation of soil amended with 0 or 15% sheep manure,  
 365 and proportions lost during the 3 month incubation

Fly ash treatment	Initial total C (%)		C loss (%)	Initial total N (%)		N loss (%)
	0%	15%		0%	15%	
Control	0.907	4.730	63.6	0.049	0.434	33.4
Acidic1	0.982	4.797	22.8	0.050	0.435	9.6
Acidic2	0.899	4.723	33.1	0.049	0.435	16.4
Alkaline1	1.167	4.960	43.7	0.051	0.436	42.6
Alkaline2	0.952	4.770	39.0	0.050	0.436	30.3
Alkaline3	1.027	5.333	47.4	0.056	0.491	45.3
<i>Mean</i>	<i>0.989</i>	<i>4.940</i>	<i>41.6</i>	<i>0.051</i>	<i>0.444</i>	<i>29.6</i>

366

367

368 Table 3 Impacts of ash additions on some chemical properties of soil amended with 0 or 15% sheep manure measured in October after 3-month incubation

Fly ash treatment	pH		C/N		Electrical conductivity (dS/m)		$\delta^{13}\text{C}$ (‰) initial <sup>1</sup>		$\delta^{13}\text{C}$ (‰) final	
	0%	15%	0%	15%	0%	15%	0%	15%	0%	15%
Control	6.96 <i>d</i>	7.41 <i>c</i>	9.08 <i>d</i>	5.97 <i>e</i>	0.11 <i>c</i>	1.88 <i>b</i>	-18.69	-22.30	-19.07 <i>b</i>	-20.91 <i>c</i>
Acidic1	6.91 <i>d</i>	7.41 <i>c</i>	10.47 <i>c</i>	9.30 <i>d</i>	0.11 <i>c</i>	1.75 <i>b</i>	-18.76	-22.30	-19.27 <i>b</i>	-21.38 <i>d</i>
Acidic2	6.88 <i>d</i>	6.74 <i>d</i>	10.45 <i>c</i>	8.86 <i>d</i>	0.10 <i>c</i>	1.95 <i>b</i>	-19.30	-22.35	-19.76 <i>b</i>	-21.20 <i>d</i>
Alkaline1	7.77 <i>c</i>	7.13 <i>c</i>	9.94 <i>b</i>	10.64 <i>c</i>	0.18 <i>b</i>	1.19 <i>c</i>	-18.73	-22.30	-19.28 <i>b</i>	-21.49 <i>d</i>
Alkaline2	8.23 <i>b</i>	7.65 <i>b</i>	13.37 <i>a</i>	10.17 <i>c</i>	0.11 <i>c</i>	0.98 <i>d</i>	-19.99	-22.39	-20.72 <i>c</i>	-22.42 <i>e</i>
Alkaline3	9.38 <i>a</i>	9.43 <i>a</i>	11.82 <i>b</i>	10.54 <i>c</i>	1.94 <i>a</i>	2.63 <i>a</i>	-19.04	-22.32	-18.65 <i>a</i>	-21.79 <i>e</i>
<i>Mean</i>	7.69 <i>A</i>	7.66 <i>A</i>	10.85 <i>A</i>	9.24 <i>B</i>	0.43 <i>B</i>	1.73 <i>B</i>	-19.08	-22.33	-19.46 <i>A</i>	-21.53 <i>B</i>

369 <sup>1</sup>calculated with eq. 2; means for the same variable followed by different letter(s) are statistically different at  $p \leq 0.05$  for the respective variables – the small letters compare  
 370 ash effects within the same response variables and capital letters compare the mean effects of manure amendment for the same response variables.

371 **Figures**

372

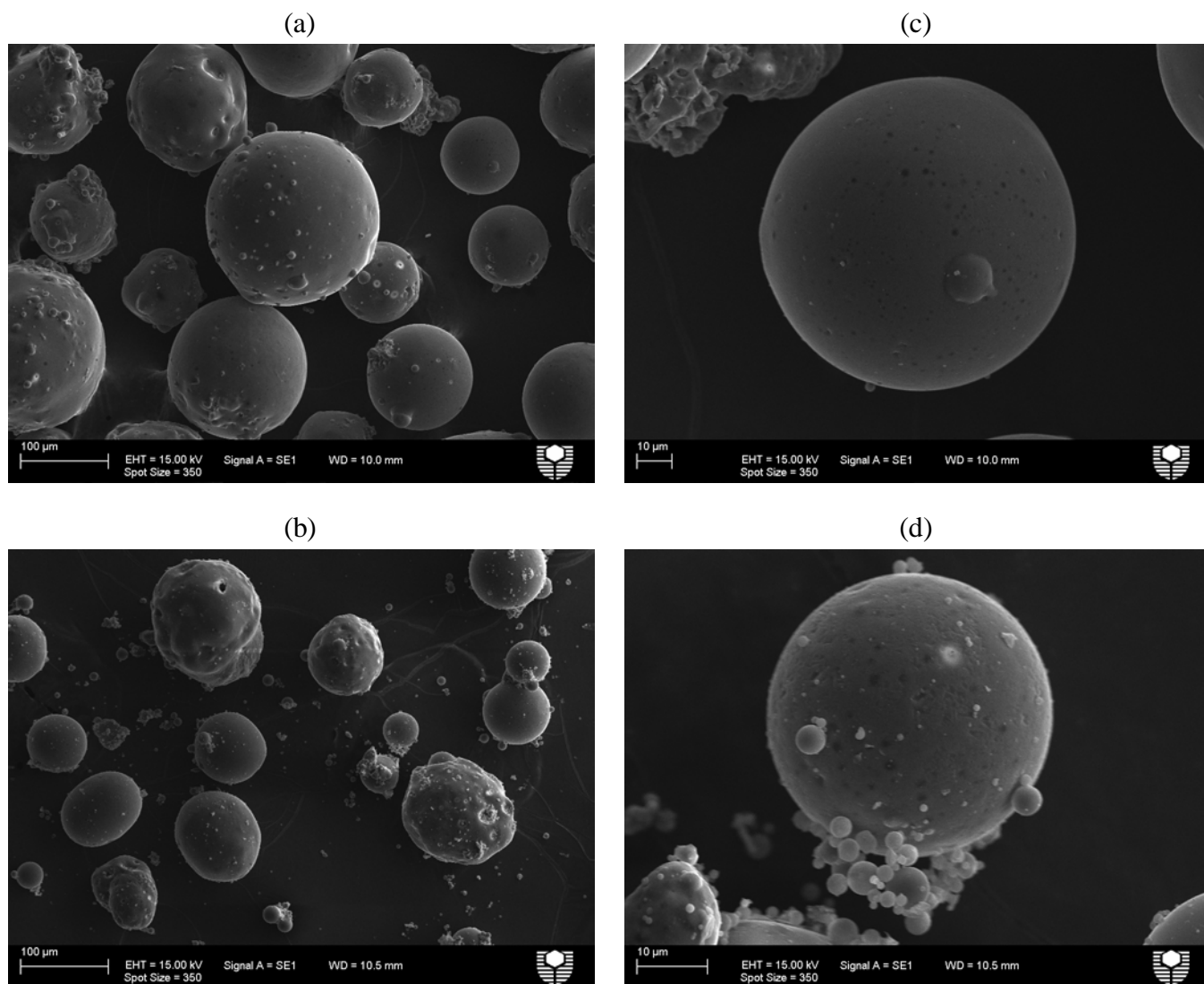
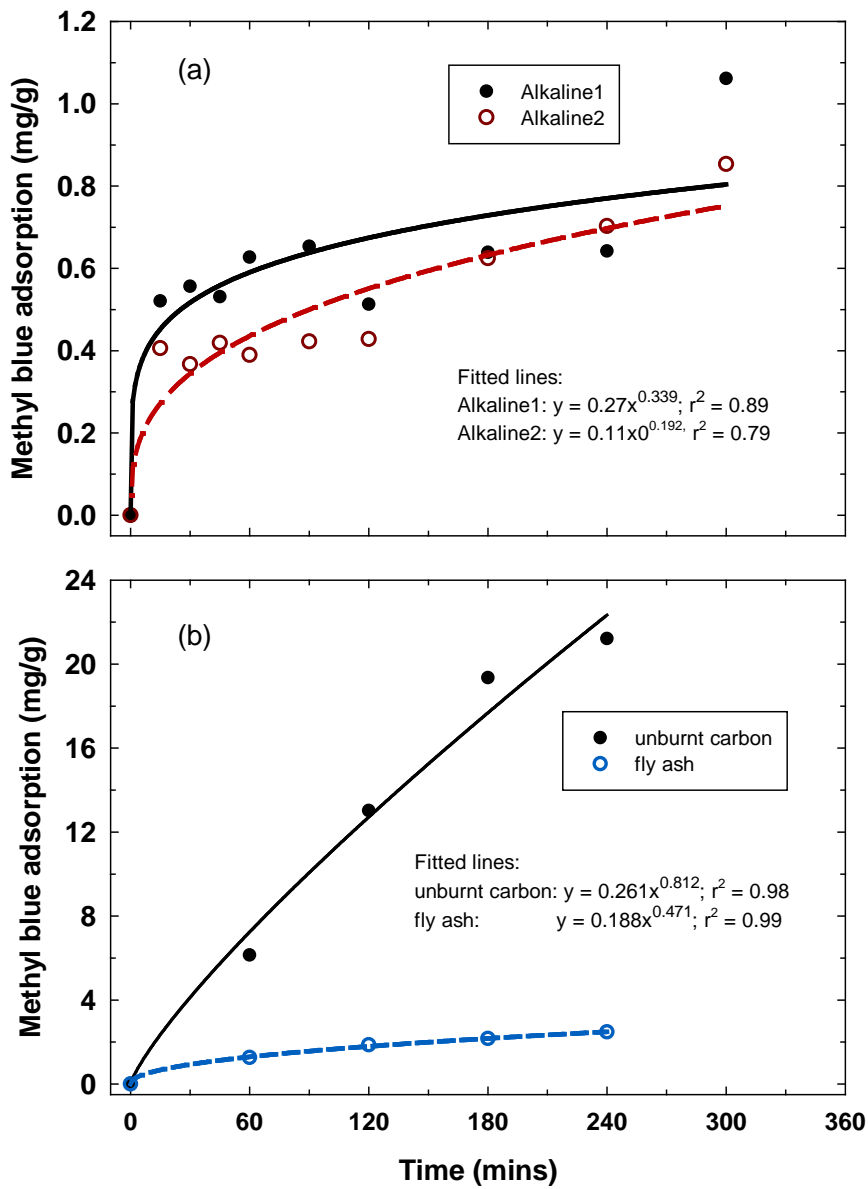


Fig 1 Scanning electron microscope images of collection of cenospheres for (a) alkaline1 and (b) alkaline 3, and of enlarged cenospheres for (c) alkaline1 and (d) alkaline3

373

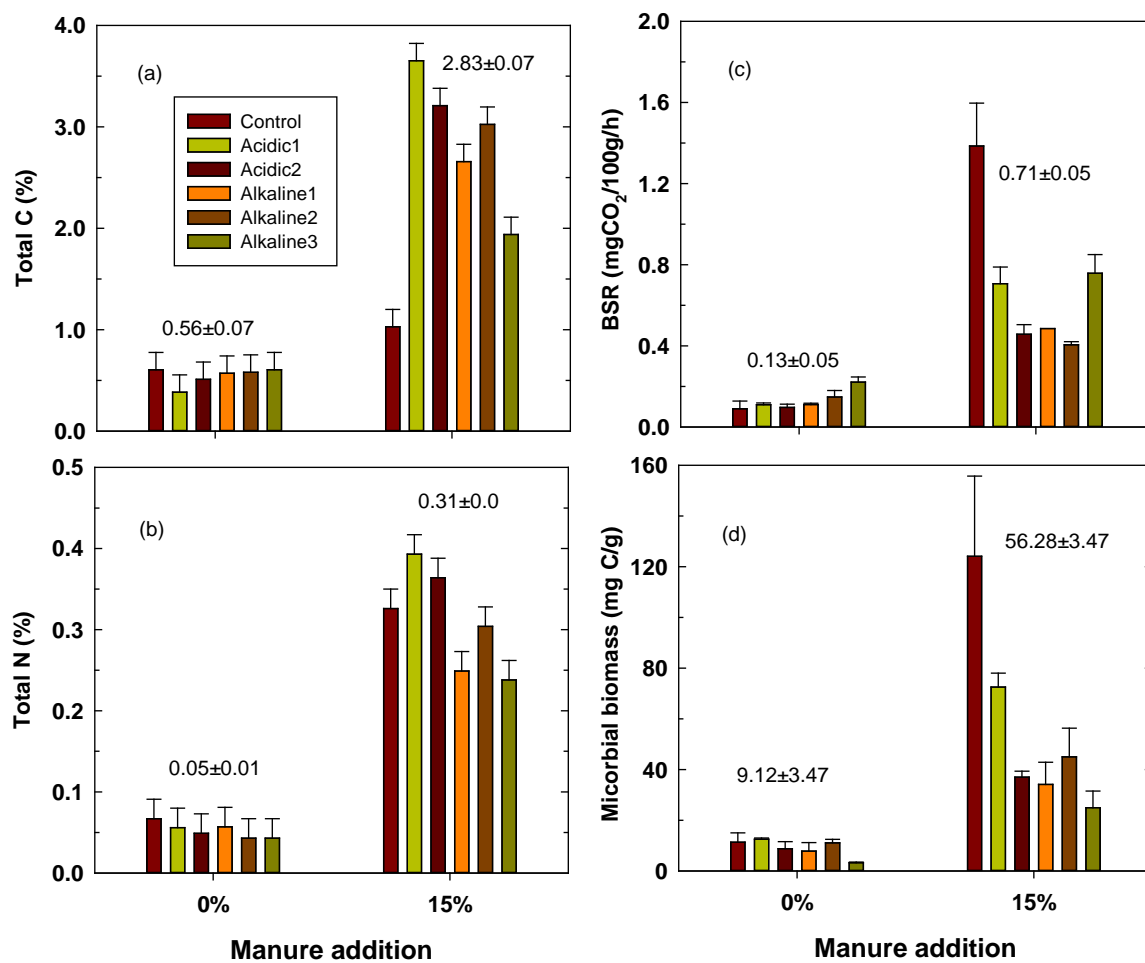


374

375 Fig 2 Adsorption of methyl blue by cenospheres of (a) alkaline1 and alkaline2 ashes, and by

376 (b) the alkaline2 or its unburnt carbon The equations for the fitted lines are given in each

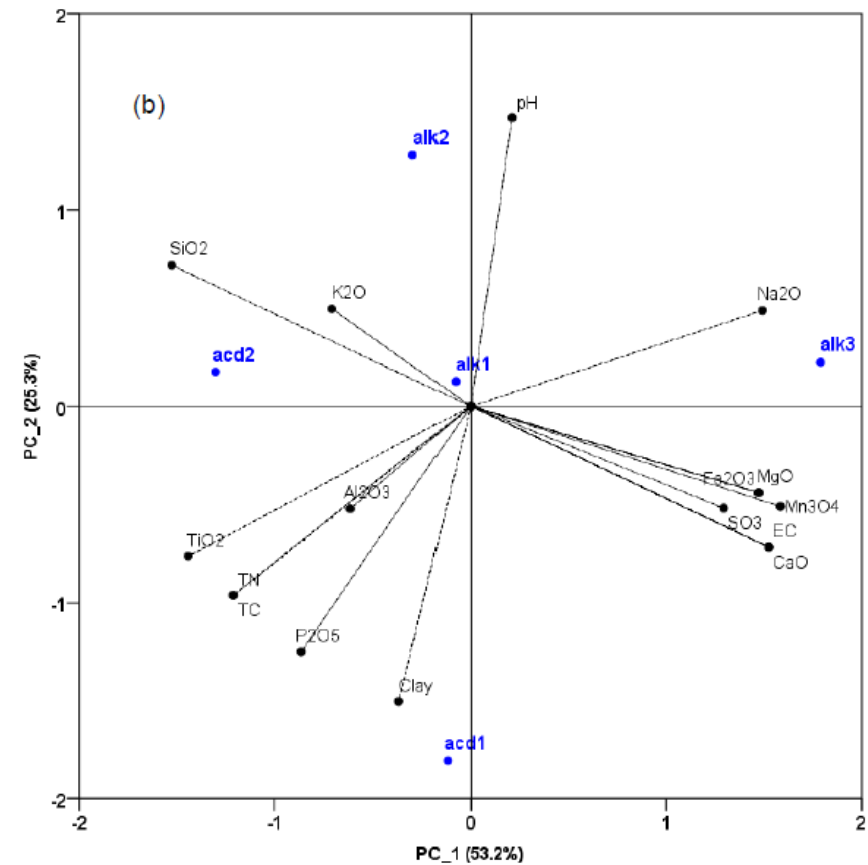
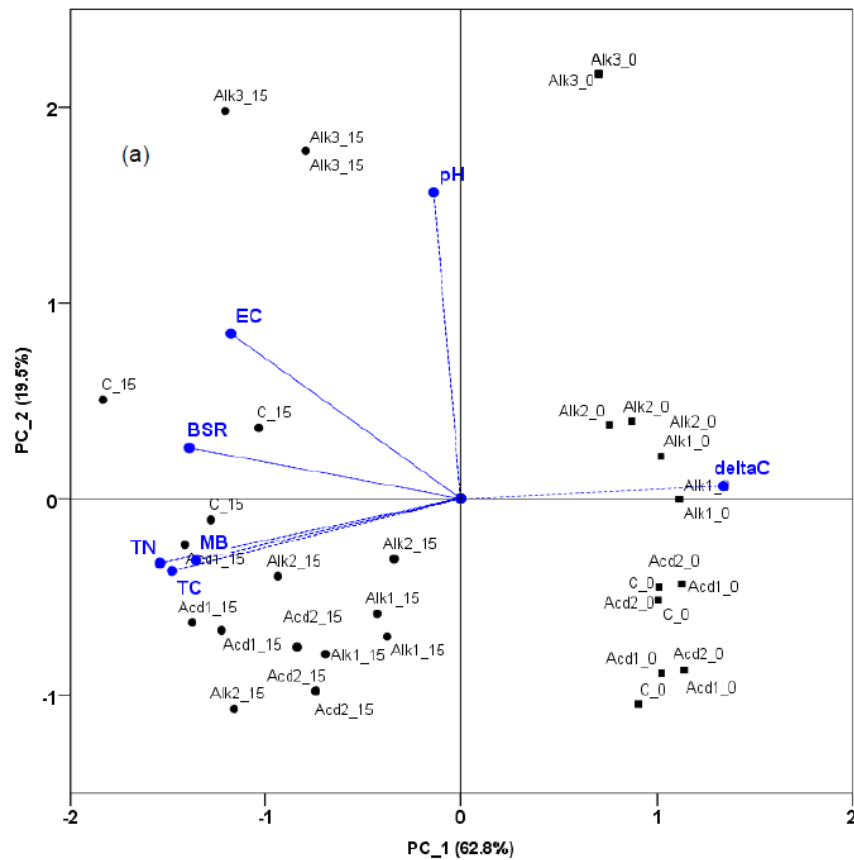
377 graph



378

379 Fig 3 Impact of acidic or alkaline coal fly ash additions on (a) total carbon (TC), (b) total N (TN), (c)  
 380 basal microbial respiration rate (BSR), and (d) microbial biomass in soil supplied with 0 or 15% w/w  
 381 of sheep manure after three-month incubation. The mean ( $\pm$  standard errors) values for 0 and 15%  
 382 manure additions are given.

383



386 Fig 4 Biplots from principal component analysis showing vector loadings for relationships amongst (a) coal fly ash characteristics and TC (total C) and TN  
 387 (total N) measured, and (b) measured soil variables, after 3 month incubation The ash treatments are expressed as either acidic (Acd1, Acd2) or alkaline  
 388 (Alk1, Alk2, Alk3) applied to either unmaured (\_0) or manured (\_15) soil; other notations are BSR (basal respiration rate), MB (microbial biomass), and  
 389 deltaC ( $\delta^{13}\text{C}$ )