

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**Does soil amended with biochar and hydrochar reduce ammonia emissions following the application of pig slurry?**

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1530999> since 2015-12-14T12:27:21Z

*Published version:*

DOI:10.1111/ejss.12302

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



# UNIVERSITÀ DEGLI STUDI DI TORINO

***This is an author version of the contribution published on:***

*Questa è la versione dell'autore dell'opera:*

*European Journal of Soil Science, November 2015, 66, 1044–1053,*

*DOI 10.1111/ejss.12302*

***The definitive version is available at:***

*La versione definitiva è disponibile alla URL:*

*<http://onlinelibrary.wiley.com/doi/10.1111/ejss.12302/abstract>*

1 **Do soils amended with biochar and hydrochar reduce ammonia**  
2 **emissions following pig slurry application?**

3

4 R. SUBEDI<sup>a\*</sup>, C. KAMMANN<sup>b</sup>, S. PELISSETTI<sup>a</sup>, N. TAUPE<sup>c</sup>, C. BERTORA<sup>a</sup>, S.  
5 MONACO<sup>a</sup> & C. GRIGNANI<sup>a</sup>

6

7 <sup>a</sup>*Department of Agricultural, Forest and Food Sciences, University of Turin, 10095*

8 *Grugliasco (TO), Italy,*

9 <sup>b</sup>*Department of Plant Ecology, Justus-Liebig University, 35392 Giessen, Germany,*

10 <sup>c</sup>*Department of Chemical and Environmental Sciences, University of Limerick,*

11 *Limerick, Ireland.*

12

13 \*Correspondence: Raghunath Subedi. Email: raghunath.subedi@unito.it

14

15 **Summary**

16

17 Coupling biochar or hydrochar amendment to nitrogen (N) fertiliser can modify soil N  
18 dynamics and availability. Such behaviour suggests that these amendments would  
19 similarly influence ammonia (NH<sub>3</sub>) emissions from slurry, potentially reducing NH<sub>3</sub>  
20 volatilisation. This study measured potential NH<sub>3</sub> emissions following application of pig  
21 slurry to the surface of silt-loam and loam soils amended with biochar and hydrochar  
22 (both derived from *Miscanthus* sp.) at a rate of 3% soil dry weight (16 t ha<sup>-1</sup> soil area)  
23 and 60% water filled pore space (WFPS). The experiment was conducted in a dynamic  
24 chamber connected to a photo-acoustic trace gas analyser in a controlled climate (20 °C)  
25 for 48 hours. Statistically significant differences (P<0.05) in total emissions were

26 observed between both treatment and soil types. Surprisingly, both amendments  
27 increased  $\text{NH}_3$  emissions *versus* the control; cumulative  $\text{NH}_3$  emissions averaged 38.7%  
28 and 23.5% of applied Total Ammonium Nitrogen (TAN) for hydrochar and biochar,  
29 respectively, while it was 18.2 % for the control. The higher emission values in  
30 hydrochar-amended soils were attributed to the reduced ability to absorb  $\text{NH}_4^+$   
31 associated with increased hydrophobicity and strong pH buffering of the slurry.  
32 Furthermore, final soil extract analyses using deionised water showed significant  
33 differences ( $P < 0.05$ ) in mineral N concentration between treatments. The lower  
34 ammonium concentrations in biochar-amended soils suggest that some  $\text{NH}_4^+$ -N was  
35 immobilised by adsorption onto biochar surfaces. This study observed that biochar and  
36 hydrochar properties, as well as soil characteristics, play important roles in controlling  
37  $\text{NH}_3$  emissions from surface slurry applications. Obtained results identified  
38 circumstances where these amendments even enhance volatilisation, providing new  
39 information useful for understanding the extent and limitations of mitigation potential of  
40 biochar and hydrochar.

41

## 42 **Introduction**

43

44 Ammonia ( $\text{NH}_3$ ) emissions from field-applied animal wastes have received much  
45 attention because of post application volatilisation. Such a process not only reduces its  
46 fertiliser value by lowering N use efficiency in crop production (Misselbrook *et al.*,  
47 2005), but also causes environmental problems, such as soil acidification, surface water  
48 eutrophication, and airborne fine particulate matter (e.g. ammonium sulphate, and  
49 ammonium nitrate) formation (Monaco *et al.*, 2012). Ammonia emissions re-deposited  
50 to land or water can also lead to indirect nitrous oxide emissions. In fact, field

51 application of animal slurry (from cattle and pigs mostly) has been estimated to  
52 represent 30-40% of total  $\text{NH}_3$  emissions from European livestock production  
53 (Hutchings *et al.*, 2009). A number of factors control the extent to which  $\text{NH}_3$  is emitted  
54 from animal manure land application: physico-chemical characteristics of manure  
55 slurry, soil and soil amendment characteristics, application techniques, and  
56 environmental conditions (Beuning *et al.*, 2008).

57

58 Biochar is a carbon (C) rich solid product produced by thermo-chemical conversion  
59 (pyrolysis or gasification) of a biomass, such as wood, manure, and crop residues. Its  
60 addition to soil has occasionally resulted in increased crop productivity and soil fertility  
61 (Chan *et al.*, 2007). Furthermore, it is frequently considered an important soil  
62 amendment that improves structure, aeration and water retention of soil (Forbes *et al.*,  
63 2006), and has the potential to counteract global warming through increased carbon  
64 sequestration and often decreased nitrous oxide emission (Sohi *et al.*, 2010). The  
65 growing interest in biochar as a soil conditioner is also due to evidence that the  
66 amendment can influence soil nutrient availability (Major *et al.*, 2012). Contrary to  
67 these benefits, reports of biochar toxicity to plants and soil microbes have emerged from  
68 the detection of toxic volatile organic compounds on biochar and hydrochar surfaces  
69 (Bargmann *et al.*, 2013).

70

71 Hydrochar, also a C rich compound, differs from biochar in that its feedstock is  
72 pyrolysed under subcritical conditions (liquid water); hence, it is often called 'wet  
73 pyrolysis' (Libra *et al.*, 2011). The process mimics that of geologic brown coal or peat  
74 production whereby the feedstock is typically carbonised hydrothermally at pressures  
75 and temperatures of 15-25 MPa and 180-250 °C, respectively (Kammann *et al.*, 2012).

76 Hydrochar carbon content is lower relative to biochar as some biomass carbon is lost as  
77 dissolved organic carbon during the reaction with water. On the other hand, the gaseous  
78 loss of C and N is almost negligible compared to biochar (Libra *et al.*, 2011). It is also  
79 known that these process conditions do not approach the temperatures necessary for  
80 carbonization to be a spontaneous process and are still endothermic for hydrothermal  
81 carbonization. There is recognition that biochar research has been extensive relative to  
82 that conducted on hydrochar, which has been limited to its chemistry alone with an  
83 ongoing research interest on it (Bargmann *et al.*, 2013). Despite the depth of study, both  
84 are considered important soil amendments (McLaughlin *et al.*, 2009).

85

86 The research community continues to debate the effectiveness of biochar as a soil  
87 amendment and the extent to which it modifies the soil nitrogen cycle and reduces  $\text{NH}_3$   
88 emissions (Clough & Condon, 2010). The capacity of biochar to adsorb  $\text{NH}_4^+$  has been  
89 generally recognised (Asada *et al.*, 2006), but the physical and chemical mechanisms  
90 behind these processes are still not fully understood. Biochar surface adsorption of  
91 nutrients (such as,  $\text{NH}_4^+$  and other cations) is associated with increased cation exchange  
92 capacity (CEC), surface area, and surface attachment of acidic functional groups (such  
93 as, carboxylic groups) (Gundale & DeLuca, 2007). Some studies have found biochar  
94 can reduce N leaching (Major *et al.*, 2012), and others have shown nitrogen  
95 immobilisation may result with the use of high C:N ratio and high surface area biochars  
96 (DeLuca *et al.*, 2009). Besides these, microbial immobilisation of N on soil mixed  
97 biochars with degradable sources of carbon has also been reported (Bargmann *et al.*,  
98 2013). To our knowledge, the effect of hydrochar incorporation on  $\text{NH}_4^+$  adsorption  
99 requires further investigation.

100

101 Many studies of  $\text{NH}_3$  volatilisation from animal slurry applied to non-amended soil  
102 have been conducted (Misselbrook *et al.*, 2005; Monaco *et al.*, 2012). However,  
103 emissions from biochar- and hydrochar-amended soils fertilised with slurry have yet to  
104 be quantified. To this end,  $\text{NH}_3$  emissions after surface application of pig slurry on  
105 biochar- and hydrochar-amended soils were assessed in a laboratory experiment. We  
106 hypothesised that reduced  $\text{NH}_3$  emissions would result from the addition of biochar and  
107 hydrochar amendments due to increased surface area and porosity, and that more acidic  
108 hydrochar would further reduce emissions by lowering the soil-slurry pH. Additionally,  
109 we hypothesised that the emission rates would vary with soil type due to their differing  
110 physico-chemical properties.

111

## 112 **Material and methods**

113

### 114 *Soil collection and characterisation*

115

116 Two types of soils with contrasting texture, pH, and CEC characteristics were used for  
117 the experiment. Silt-loam soil with sub-acid pH was collected in Poirino (44° 55' N and  
118 7° 51' E) and loam soil with sub-alkaline pH was collected in Carmagnola (44° 51' N  
119 and 7° 43' E), Italy. Both soils were sampled from the top 20 cm plough layer. The  
120 samples were fully air-dried and then sieved using an electric auto-rotating sieving  
121 machine (rotating drum with 2 mm holes) (Neutron s.r.l., Autopack NTR 83). Soil  
122 texture was determined by pipet method, soil bulk density by core method and particle  
123 density by pycnometer method (Klute, 1994). Total pore volume was calculated based  
124 on bulk and particle density values obtained.

125

126 *Biochar and hydrochar production and characterisation*

127

128 Pyreg GmbH of Dorth, Germany (www.pyreg.de) produced the *Miscanthus* sp.-derived  
129 biochar employed in this study by slow pyrolysis at 600 °C by using their typical reactor  
130 technology. The hydrochar was produced from the identical feedstock by Hydrocarb  
131 (Ohmes, Germany) via hydrothermal carbonisation in steam at 200 °C under 16 bars of  
132 pressure for two hours. The hydrochar was then dried in foil inside a greenhouse to  
133 reduce its moisture content. Thereafter, a complete physico-chemical characterisation of  
134 the materials was performed at the Chemical and Environmental Science Department,  
135 University of Limerick in Ireland.

136

137 Both samples were analysed for total C and N content by total elemental analyser  
138 (Vario El Cube CNS analyser, Elementar, Germany). The pH was measured in  
139 deionised water at a 1:10 ratio of biochar to water using a pH electrode (Cyberscan 510  
140 pH meter) after mechanically shaking the mixture for 18 hours. The electrical  
141 conductivity of the same samples was measured with an EC electrode (Jenway 4510  
142 conductivity meter). Moisture, ash, and volatile matter content (on % dry weight basis)  
143 were analysed by NSAI standard testing methods (NSAI, 2009). The CEC for both  
144 samples was determined by the modified ammonium acetate compulsory displacement  
145 method (Gundale & DeLuca, 2007). Char surface acidities were determined by base  
146 adsorption as described by Cheng & Lehmann (2009). Surface areas and total pore  
147 volumes were ascertained using the Brunauer, Emmet, and Teller (BET) method with a  
148 micrometric apparatus. Each analysis was performed in triplicate.

149

150 *Pig slurry collection, storage, and characterisation*

151

152 Raw pig slurry was collected from a commercial pig farm where the pigs were raised on  
153 a fully slatted floor. The collected slurry was then stored at 4 °C to stop N  
154 mineralisation and to limit NH<sub>4</sub>-N volatilisation until the experiment. The slurry was  
155 removed from the refrigerator at least one hour before experimental start to allow it to  
156 reach ambient room temperature. Slurry pH was measured in deionised water (1:2.5  
157 ratio) using a pH electrode; Total Ammonium Nitrogen (TAN) and total N were  
158 determined by Kjeldahl distillation.

159

#### 160 *Experimental setup and treatment formulation*

161

162 The experiment was set as a randomised complete block design with three replicates.  
163 The treatments included in each block were three amendments (biochar, hydrochar, and  
164 control- no amendment) and two soil types (loam and silt-loam) organized in a factorial  
165 combination, for a total of 18 jars. ANOVA model included amendments and soil types  
166 as the fixed factors, their interaction and block as random factors. The experiment was  
167 carried out in glass jars (volume: 3200 cm<sup>3</sup>, surface area: 154 cm<sup>2</sup>). The amount of air-  
168 dried soil in the jars differed by soil type (725 g of silt-loam and 670 g of loam) in order  
169 to equate the volumes (500 cm<sup>3</sup> with 4 cm height) for the soils given their bulk density  
170 differences (Table 1) and head-air-space (2000 cm<sup>3</sup>).

171

172 Air-dried soil samples were amended with 3 g of biochar (2 mm size) or hydrochar  
173 per 100 g of dry soil. The char was manually incorporated and homogeneously mixed  
174 with the soil. This corresponded to an average biochar application rate of 16 t ha<sup>-1</sup> given  
175 the filling height of 4 cm of soil-biochar mixture inside the jar. The amended soils were

176 moistened with deionised water to reach 60% WFPS. The amount of deionised water  
177 needed to obtain the desired WFPS also differed among soil types (148 ml for loamy  
178 and 135 ml for silt-loam soil) and was calculated on the basis of soil bulk density and  
179 porosity (Table 1). The jars were then covered with punctured plastic films to allow  
180 gaseous exchange and minimize evaporation. They were pre-incubated at 20 °C for a  
181 week to activate soil micro-organisms and subside the initial water-induced CO<sub>2</sub> flush  
182 due to rewetting. After pre-incubation, pig slurry was manually spread over the soil  
183 surface at a rate of 90 g slurry per jar (equivalent to 170 kg N ha<sup>-1</sup>). Immediately, the  
184 jars were capped and connected to a measurement system, consisting of a dynamic  
185 chamber coupled with a photo-acoustic trace gas analyser (PTGA) (INNOVA 1412,  
186 LumaSense Tech., Santa Clara, USA).

187

#### 188 *Calibration procedure and possible interferences*

189

190 The PTGA model used in this experiment is equipped with five optical filters for  
191 ammonia, greenhouse gases (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>) and water vapour. The optical filter  
192 chosen for NH<sub>3</sub> determination was the model UA0976 with a center wavelength of 10.6  
193 μm, center frequency of 941 cm<sup>-1</sup> and a bandwidth of 7%. The detection limit of the  
194 system for ammonia was 0.2 ppm. Calibration is generally performed on three steps  
195 procedures (dry zero point, wet zero point and single point) for each gas with internal  
196 cross-compensation and water vapour calibration according to INNOVA procedures as  
197 mentioned in detail by Zhao *et al.* (2012). Interference bias due to different gas species  
198 (mainly CO<sub>2</sub> and water vapour) is internally compensated through mathematical  
199 correction. For any possible non-compensated interferences due to emission of volatile  
200 substances, Monaco *et al.* (2012) has done methodological comparison with standard

201 acid trap method and found a reliable assessment of emission data from PTGA with  
202 good correlation ( $R^2 = 0.959$ ,  $P < 0.01$ ,  $n = 133$ ). The instrument used for the experiment  
203 is calibrated at least once a year or whenever necessary.

204

205 *NH<sub>3</sub> volatilisation measurement*

206

207 The measurement system, fully described by Monaco *et al.* (2012), consisted of six  
208 measurement lines, each connected to an electrical air pump providing a continuous  
209 flow of air to the system (Figure 1). The flow rate of 2 l minute<sup>-1</sup> was monitored with a  
210 gauge and corresponded to an air renewal rate of one headspace volume min<sup>-1</sup> for each  
211 jar (Dinuccio *et al.*, 2008). The NH<sub>3</sub> emitted inside the volatilisation chamber  
212 (headspace of each jar) then passed into an expansion bottle (1000 cm<sup>3</sup>) for air sampling  
213 and measurement by the PTGA connected system. All input and output ports within the  
214 measurement system were tightly connected using Teflon tubes (4 mm diameter). A  
215 continuous measurement was performed for the first 30-40 minutes after fertiliser  
216 application until steady state conditions were achieved. Thereafter, measurements were  
217 done every 2, 4, 8, 12, 24, 30 and 48 hours. At the end of each measurement interval,  
218 the NH<sub>3</sub> concentration of surrounding air inside the climatic chamber measured by  
219 PTGA was referenced as a background value and deducted from the measured sample  
220 concentration to obtain the actual concentration. The output air from PTGA was located  
221 outside the climatic chamber. The measurement period, which lasted for 48 hours, was  
222 carried out at 20 °C.

223

224 *Analysis of soil extract*

225

226 At the end of the volatilisation experiment, approximately 30 g of soil were sampled  
227 from each jar and mixed with 150 ml of deionised water; they were then mechanically  
228 shaken for 30 min and filtered (through Whatman no. 4 filter paper). The filtrate was  
229 stored in a refrigerator at 4 °C until later analysis.  $\text{NH}_4^+$  concentration (ppm) in the soil  
230 extract was measured by the colorimetric method and  $\text{NO}_3^-$  concentration (ppm) was  
231 determined by ion-chromatograph (Dionex 1500, conductivity detector, AS9-HC  
232 column with 9 mM carbonate eluent at 1 ml l<sup>-1</sup> flow).

233

234 *Data processing and analysis*

235

236 Calculation of  $\text{NH}_3$  emission rate was done using following equation (Monaco *et al.*,  
237 2012):

238

$$\text{NH}_3 \text{ Flux} = \frac{CP}{RT} \times 14.01 \times \frac{Q}{A}, \quad (1)$$

239

240 where,

241  $\text{NH}_3$  flux is the emission rate ( $\text{mg NH}_3\text{-N m}^{-2} \text{ h}^{-1}$ ),

242  $C$  is the concentration of  $\text{NH}_3$  measured by PTGA ( $\mu\text{l l}^{-1}$ ),

243  $P$  is the atmospheric pressure (1013.25 Pa),

244  $R$  is the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ),

245  $T$  is the temperature inside volatilisation chamber (K),

246 14.01 is the molar mass of N ( $\text{g mol}^{-1}$ ),

247  $Q$  is the measured air flow rate ( $\text{l hour}^{-1}$ ), and

248  $A$  is the soil surface area in the jar ( $\text{m}^2$ ).

249

250 The cumulative NH<sub>3</sub> losses over time were then fitted with a sigmoidal logistic  
251 equation (Equation 2), as described by Pacholski *et al.* (2008), for effective comparison  
252 of the cumulative losses between treatments. It was also informative to use this equation  
253 to understand the trend of cumulative emission data measured with PTGA.

254

$$255 \quad Y = a \{1 - \exp(-ct)\}^\beta, \quad (2)$$

256

257 where,

258  $Y$  is the cumulative ammonia volatilisation (mg NH<sub>3</sub>-N m<sup>-2</sup>),

259  $a$  is the asymptotic maximum ammonia volatilisation (mg NH<sub>3</sub>-N m<sup>-2</sup>),

260  $c$  is the rate constant (process velocity, hour<sup>-1</sup>),

261  $t$  is the time (hours), and

262  $\beta$  is the parameter of sigmoidality (unitless). All the parameters ( $a$ ,  $c$  and  $\beta$ ) must have  
263 positive values.

264

265 A least square non-linear multiple regression (SPSS 21) with Levenberg-Marquardt  
266 algorithm was used to determine the parameters ( $a$ ,  $c$  and  $\beta$ ) from the above-mentioned  
267 equation as this approach provided the best fit to the cumulative emission data and also  
268 to minimize the residual sum of squares. The fitting was performed for each cumulative  
269 data set, separately for each combination of amendment, soil and block. Average  
270 parameter estimates for each combination of amendment per soil were calculated and  
271 average standard errors (SE) were obtained using the quadratic mean. To evaluate the  
272 goodness-of-fit of the logistic equation, the following “pseudo  $R^2$ ” was calculated:

$$273 \quad R^2 = 1 - (\text{Residual sum of squares})/(\text{Corrected sum of squares}) \quad (3)$$

274

275 Differences in physical and chemical properties between biochar and hydrochar were  
276 compared with Student's t-test. The homogeneity of variances was checked using a  
277 Levene's test and when they were not homogeneous, a t-test not assuming equal  
278 variance was applied. Two-way ANOVA for randomized complete block design was  
279 performed to test for significant effects of the amendments, soil types, their interactions  
280 and block effect considering amendments (three levels) and soil type (two levels) as two  
281 main factors. All tests were considered significant at 5% significance level. The  
282 ANOVA was performed on total cumulative  $\text{NH}_3$  volatilisation and mineral N  
283 concentration.

284

285 We decided to test the effect of amendments with a set of pre-planned orthogonal  
286 contrasts: a control *versus* char (average of biochar and hydrochar) effect and a biochar  
287 *versus* hydrochar effect to have greater insight on comparison between treatment means.  
288 The first contrast is of interest because higher surface areas of both chars could adsorb  
289 more  $\text{NH}_4^+$  ions from applied slurry. The second contrast would examine any variation  
290 in  $\text{NH}_3$  emissions between biochar and hydrochars in relation to their contrasting pH.  
291 Similar orthogonal contrast test was also proposed to assess the significant difference  
292 between amendments for mineral N concentration.

293

## 294 **Results**

295

### 296 *Soil, slurry, biochar and hydrochar characterisation*

297

298 Soils differed in texture in relation to both silt and sand content (Table 1). Silt-loam soil  
299 had higher bulk density than loam soil while the case was opposite for CEC. Silt-loam

300 soil had acidic pH while the loam had alkaline pH. Both soils had pore volume below  
301 50% as their structures were partially destroyed during sieving process. The slurry had a  
302 total N content of 0.29%, a Total Ammonium Nitrogen (TAN) of 0.20%,  $\text{pH}_{\text{H}_2\text{O}}$  7.84,  
303 and a dry matter content of 2.3%.

304

305 The C:N ratio, ash content, and pH were significantly higher ( $P < 0.05$ ) in biochar  
306 than in hydrochar, whereas the reverse was true for volatile matter content (on % dry  
307 weight basis) and surface acidity (Table 2). Surface area and pore volume of hydrochar  
308 were found to be very low compared to biochar, while average pore size was smaller in  
309 biochar than in hydrochar.

310

311 *Ammonia volatilisation*

312

313 The emission rates trended higher for the first 30–40 minutes after slurry application and  
314 then gradually fell to very low and constant levels after 40 hours (Figure 2). The  
315 average peak fluxes recorded in hydrochar-amended soils (222.2 and 288.1 mg  $\text{NH}_3\text{-N}$   
316  $\text{m}^{-2} \text{h}^{-1}$  for silt-loam and loam, respectively) and biochar amendment (208.2 for silt-loam  
317 and 332.1 for loam soil) were significantly higher ( $P < 0.05$ ) than those measured for  
318 control (165.2 for silt-loam and 249.3 for loam). In general, a rapid decrease in flux  
319 after peaking was observed in the biochar and control treatments while fluxes decreased  
320 slowly in the hydrochar treatment as shown in Figure 2. The lowest peak was measured  
321 in non-amended (control) silt-loam soil, while the highest for biochar amended loam  
322 soil.

323

324 The trends of cumulative emissions from applied slurry were well described by the  
325 equation as noticed from smooth curve fitting (Figure 3). Table 3 presents the parameter  
326 estimates of the reported logistic equations fitted to the cumulative  $\text{NH}_3$  emissions. The  
327 proportion of variance accounted for in fitting the equation ranged between 99.8 and  
328 100% among treatments. Similar values of parameter 'c' among treatments showed the  
329 similar dynamic of  $\text{NH}_3$  volatilisation process. The low values of parameter ' $\beta$ ' (0.98,  
330 on average) indicated early achievement of maximum emission rates for all treatments  
331 as seen in Figure 2. The slightly higher value ( $>1$ ) of ' $\beta$ ' for hydrochar treatment *versus*  
332 the others shows greater inflection of its cumulative curve. The average asymptotic  
333 maximum loss 'a' predicted was highest (5679.5 mg  $\text{NH}_3\text{-N m}^{-2}$ ) for hydrochar-  
334 amended loam soil and lowest (2154.0 mg  $\text{NH}_3\text{-N m}^{-2}$ ) for the control silt-loam soil  
335 (Table 3).

336  
337 The summary output from ANOVA showed the significant effects of both treatments  
338 and soil types on total cumulative  $\text{NH}_3$  volatilisations, while the interaction effect  
339 between them was not significant (Table 4). Results of orthogonal contrast showed that  
340 total losses were significantly higher ( $P<0.05$ ) for char treatments (average of biochar  
341 and hydrochar) compared to the control (Table 5). The contrasts for biochar *versus*  
342 hydrochar effect on total losses were also significant indicating higher emissions  
343 associated with hydrochar treatment. Total  $\text{NH}_3\text{-N}$  losses among treatments accounted  
344 for 86-93% of the asymptotic maximum loss.

345  
346 The highest total  $\text{NH}_3\text{-N}$  emissions resulted with hydrochar amendment, 3788.4 mg  
347  $\text{NH}_3\text{-N m}^{-2}$  (32.4% of applied TAN, on average) in silt-loam soil and 5272.6 mg  $\text{NH}_3\text{-N}$   
348  $\text{m}^{-2}$  (45.1% of applied TAN, on average) in loam soil (Figure 4). Alternatively, the

349 lowest total emissions were recorded for the control treatments at 1967.1 mg NH<sub>3</sub>-N m<sup>-2</sup>  
350 (16.8% of applied TAN, on average) in silt-loam soil and 2291.3 mg NH<sub>3</sub>-N m<sup>-2</sup> (19.6%  
351 of applied TAN, on average) in loam soil. The average total overall emission from silt-  
352 loam soil (2749.2 mg NH<sub>3</sub>-N m<sup>-2</sup>, 23.5% of applied TAN, on average) was significantly  
353 lower ( $P<0.05$ ) compared to loam soil (3521.1 mg NH<sub>3</sub>-N m<sup>-2</sup>, 30.1% of applied TAN,  
354 on average) (Figure 4).

355

#### 356 *Soil mineral nitrogen content*

357

358 The ANOVA summary of Table 6 showed a significant effect ( $P<0.05$ ) of both  
359 amendment and soil type on mineral N concentration in the soil extracted with  
360 deionised water at the end of the experiment. These data represents the easily available  
361 mineral N (mainly from the soil solution) for the plants as deionised water is recognized  
362 as a weak extractant. The interaction effect between soil and amendment was significant  
363 only for the NO<sub>3</sub><sup>-</sup>-N (Table 6). The contrast between control *versus* char was significant  
364 for the NH<sub>4</sub><sup>+</sup>-N concentration for both soils, while this was not significant for biochar  
365 *versus* hydrochar (Table 7). The concentration of N-NH<sub>4</sub><sup>+</sup> in both chars amended soils  
366 was significantly lower ( $P<0.05$ ) compared to control. The N-NO<sub>3</sub><sup>-</sup> concentrations were  
367 significantly lower in hydrochar treatments compared with the control and biochar  
368 treatments. The NO<sub>3</sub><sup>-</sup>-N concentrations were much lower than the NH<sub>4</sub><sup>+</sup>-N concentration  
369 in both soils. The orthogonal contrast for the total mineral N concentration was  
370 significant ( $P<0.05$ ) for both control *versus* char effect and biochar *versus* hydrochar  
371 effect (Table 7).

372

#### 373 **Discussion**

374

375 *Biochar and hydrochar properties relevant for NH<sub>3</sub> emission*

376

377 This research intended to use biochar and hydrochar amendment to reduce NH<sub>3</sub>  
378 volatilization following slurry application. Expected properties responsible for this  
379 mitigation action were high surface area, CEC and porosity of both chars coupled with  
380 low pH for hydrochar (Budai *et al.*, 2014). The high surface area and porosity of biochar  
381 may be explained by volatilisation of the organic molecules present on char surfaces at  
382 temperatures of about 600 °C that otherwise can clog biochar pores, as borne out in  
383 reported hydrochar values (Lee *et al.*, 2010). Results showed that CEC values were high  
384 for both chars but failed to show significant difference between them. However,  
385 previous researchers have put forth that higher CEC of biochars can be linked to the  
386 presence of acidic functional groups as well as to pyrolysis temperature (Mukherjee *et*  
387 *al.*, 2011).

388

389 The high pH of biochar is attributed to higher ash content while the low pH of  
390 hydrochar is mainly due to its more numerous acidic functional groups (such as,  
391 carboxylic acid groups) and lower ash content likely due to mineral loss in the liquid  
392 phase of hydrothermal carbonisation (Fuentes *et al.*, 2010). Another property found  
393 different for the two chars that might influence N dynamics leading to NH<sub>3</sub> emissions is  
394 the volatile matter content which is higher in hydrochar than biochar as higher labile C  
395 compounds were maintained at lower temperature during hydrothermal carbonisation  
396 (Kammann *et al.*, 2012). An effect of volatile matter on NH<sub>3</sub> emissions from applied  
397 slurry begs further investigation.

398

399 *NH<sub>3</sub> volatilisation and emission factor*

400

401 The proposed equation (model) fitted well with good agreement to emission data  
402 from slurry measured in dynamic chambers in this experiment as shown by the higher  
403 coefficient of determination (>0.998). This also showed a good possibility of using it  
404 and fitting the cumulated emission data from slurry measured with PTGA at laboratory  
405 scale for better understanding the emission trend. Total emission results demonstrated  
406 that the reverse of our proposed hypothesis occurred in this experiment; that is, higher  
407 NH<sub>3</sub> were emitted from soil amended with biochar relative to the control, and even  
408 higher emissions were released from hydrochar-amended soil. Emissions from biochar-  
409 amended soils at levels above those observed in the control treatment could be linked to  
410 alkaline pH of biochar.

411

412 The highest NH<sub>3</sub> volatilisation from soils amended with hydrochar may have arisen  
413 from three factors: (i) reduced slurry infiltration after surface spreading due to increased  
414 hydrophobicity (Beuning *et al.*, 2008; Libra *et al.*, 2011); (ii) low adsorption of NH<sub>4</sub><sup>+</sup> to  
415 soil particles due to reduced slurry infiltration (Brockhoff *et al.*, 2010); and (iii) strong  
416 pH buffering action from slurry invalidating the potential acidifying effect of hydrochar  
417 (Genermont & Cellier, 1997). In addition to this, difference in pore sizes between soil  
418 and amendment materials associated with different soil packing arrangement would  
419 have resulted in different Bernoulli forces within the soil-hydrochar-slurry system. This  
420 could have affected the slurry water movement through the soil column (Brockhoff *et*  
421 *al.*, 2010).

422

423 Hydrochar is a fibrous, more hydrophobic material than biochar. These properties  
424 make it able to repel slurry water, temporarily increase slurry viscosity, raise the water  
425 holding capacity at the surface of the soil-hydrochar mixture, and finally, impede  
426 infiltration as well as outweigh the cation adsorption capability of acidic hydrochar  
427 itself (Misselbrook *et al.*, 2005). Emissions at levels above those observed in the control  
428 treatment could be linked to biochar due to its alkaline pH.

429

430 Slurry, soil surface, and amendment material (biochar and hydrochar) pH values are  
431 each considered as important in NH<sub>3</sub> emission. The soil-surface pH changes greatly  
432 when slurry is applied to it, arising principally from the different buffering capacities of  
433 the soil and slurry (Sommer & Husted, 1995). Buffering substances such as bicarbonate  
434 ions present in the soil-slurry solution can easily neutralise acidic cation H<sup>+</sup> and result in  
435 a temporary soil surface pH increase. Such a pH rise may further enhance NH<sub>3</sub>  
436 volatilisation as it drives to acid-base equilibrium. In this study, slurry accumulation in  
437 hydrochar-amended soils due to increased hydrophobicity might have produced slurry  
438 ponding and consequently masked the pH effect of hydrochar (Genermont & Cellier,  
439 1997; Libra *et al.*, 2011).

440

441 Vandre & Clemens (1997) found that soil-slurry pH rose by approximately 0.5 units  
442 following cattle slurry application, and that the increase continued for at least 72 hours  
443 within the soil-slurry system resulting initial flux increase up to 40%. Although we did  
444 not measure pH change in our experiment, it was observed that the overall loam soil  
445 average emission was significantly higher ( $P < 0.05$ ) than for silt-loam. This outcome  
446 might mainly emanate from the alkaline pH of loam soil that could have triggered an

447 emission contributing to increased soil-slurry pH as evidenced in previous studies  
448 (Genermont & Cellier, 1997; Beuning *et al.*, 2008).

449

450 Emission factors obtained in this study are within the range reported by previous  
451 authors. For control and biochar-amended soils, the average total ammonia losses were  
452 18.2% and 23.5% of applied TAN, respectively. Studies carried out by Monaco *et al.*  
453 (2012) and Misselbrook *et al.* (2005) gave similar values for field applied raw pig slurry  
454 with low dry matter content on loam soil. The higher emission factor (38.8%, on  
455 average) associated with hydrochar amendment for both soil types was also within the  
456 range of 20-80% as indicated in the emission inventory guidebook (Hutchings *et al.*,  
457 2009).

458

459 *Soil mineral nitrogen content*

460

461 The low  $\text{NH}_4^+$  concentration of hydrochar-amended soils may result primarily from  
462 increased  $\text{NH}_3$  losses through surface applied slurry volatilisation. The low  $\text{NH}_4^+$   
463 concentration in biochar-amended soil may stem from partial ion immobilisation due to  
464 biochar surface adsorption. DeLuca *et al.* (2009) has shown this latter phenomenon is  
465 mainly associated with high surface area and porosity in addition to C:N ratio.

466

467 The low  $\text{NO}_3^-$  concentrations in the hydrochar-amended soils of this study might  
468 come from microbial immobilisation of  $\text{NO}_3^-$ -N due to the significant amount of labile  
469 carbon contained in hydrochar, as suggested by Bargmann *et al.* (2013). Alternatively,  
470 He also reported poor barley seed germination in hydrochar-amended soils was likely  
471 caused by the presence of phytotoxic chemicals (phenols and hydroxymethylforfural)

472 that may eventually have influenced the nitrifying community in soil (Wardle *et al.*,  
473 1998). As deionised water is a weak extractant, mineral N concentration results obtained  
474 do not definitively explain the cause(s) responsible for the observed emission rates.  
475 These data solely give an estimation of mineral N concentration mainly from the soil  
476 solutions that are quickly available for the plants. It seems that hydrochar is less stable  
477 than biochar and its potential for nitrogen immobilisation and NH<sub>3</sub> volatilisation needs  
478 further investigation.

479

## 480 **Conclusions**

481

482 This study observed that biochar and hydrochar properties, as well as soil  
483 characteristics, play important roles in controlling NH<sub>3</sub> emissions from surface slurry  
484 applications. Nevertheless, properties that were expected to be relevant for reducing  
485 volatilization (i.e. surface area and porosity) actually did not produce any hypothesized  
486 effect while other unexpected reasons even produced the opposite results increasing  
487 NH<sub>3</sub> emissions. Specific further investigations are necessary to validate assumed  
488 hydrochar- induced hydrophobicity and subsequent retardation of slurry infiltration in  
489 soil, for better elucidating with possible reasons of observed emission dynamics.

490

491 Valid expectations of the effect of pyrolysed amendments need to consider many  
492 different properties of chars in different environment for longer time periods. The  
493 assumptions that any type of char is effective for reducing NH<sub>3</sub> emissions are  
494 unrealistic. Obtained results in fact identified circumstances where these amendments  
495 even enhance volatilization, thus providing new information useful for understanding  
496 the extent and limitations of mitigation potential of biochar and hydrochar.

497

498 **Acknowledgement**

499

500 The research leading to these results has received funding from the People Programme  
501 (Marie Curie Actions) of the European Union Seventh Framework Programme  
502 FP7/2007-2013/ under REA grant agreement n° 289887. Special thanks go to Dario  
503 Sacco for his assistance in statistical analysis of the data. We also greatly acknowledge  
504 the constructive comments and feedbacks from two anonymous reviewers for  
505 improving the quality of the manuscript.

506

507 **References**

508

509 Asada, T., Ohkubo, T., Kawata, K. & Oikawa, K. 2006. Ammonia adsorption on  
510 bamboo charcoal with acid treatment. *Journal of Health Science*, **52**, 585–589.

511

512 Bargmann, I., Rillig, M.C., Buss, W., Kruse, A. & Kucke, M. 2013. Hydrochar and  
513 biochar effects on germination of spring barley. *Journal of Agronomy & Crop Science*,  
514 **199**, 360–373.

515

516 Beuning, J.D., Pattey, E., Edwards, G. & Van Heyst, B.J. 2008. Improved temporal  
517 resolution in process-based modelling of agricultural soil ammonia emissions.  
518 *Atmospheric Environment*, **42**, 3253–3265.

519

520 Brockhoff, S.R., Christians, N.E., Killorn, R.J, Horton, R. & Davis, D.D. 2010. Physical  
521 and mineral-nutrition properties of sand-based turfgrass root zones amended with  
522 biochar. *Agronomy Journal*, **102**, 1627–1631.

523

524 Budai, A., Wang, L., Gronli, M.G., Strand, L.T., Antal, M.J., Abiven, S. *et al.* 2014.  
525 Surface properties and chemical composition of corncob and miscanthus biochars:  
526 Effects of production temperature and method. *Journal of Agricultural & Food*  
527 *Chemistry*, **62**, 3791–3799.

528

529 Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A. & Joseph S. 2007. Agronomic  
530 values of green waste biochar as a soil amendment. *Australian Journal of Soil Research*,  
531 **45**, 629–634.

532

533 Cheng, C. H. & Lehmann, J. 2009. Ageing of black Carbon along a temperature  
534 gradient. *Chemosphere*, **75**, 1021–1027.

535

536 Clough, T.J. & Condon, L.M. 2010. Biochar and the nitrogen cycle: Introduction.  
537 *Journal of Environmental Quality*, **39**, 1218–1223.

538

539 DeLuca, T.H., MacKenzie, M.D. & Gundale, M.J. 2009. Biochar effects on soil nutrient  
540 transformation. In: *Biochar for Environmental Management: Science and Technology*  
541 (eds J. Lehmann & S. Joseph), pp. 251–270. Earthscan, London, U. K.

542

543 Dinuccio, E., Berg, W. & Balsari, P. 2008. Gaseous emissions from the storage of  
544 untreated slurries and the fractions obtained after mechanical separation. *Atmospheric*  
545 *Environment*, **42**, 2448–2459.

546

547 Forbes, M.S., Raisan, R.J. & Skjrmstad, J.O. 2006. Formation, transformation and  
548 transport of black carbon in terrestrial and aquatic ecosystems. *Science of the Total*  
549 *Environment*, **370**, 190–206.

550

551 Fuertes, A.B., Arbestain, M.C., Sevilla, M., Macia-Agullo, J.A., Fiol, S., Lopez, R. *et*  
552 *al.* 2010. Chemical and structural properties of carbonaceous products obtained by  
553 pyrolysis and hydrothermal carbonisation of corn stover. *Australian Journal of Soil*  
554 *Research*, **48**, 618–626.

555

556 Genermont, S. & Cellier, P. 1997. A mechanistic model for estimating ammonia  
557 volatilization from slurry applied to bare soil. *Agricultural & Forest Meteorology*, **88**,  
558 145–167.

559

560 Gundale, M. J. & DeLuca, T. H. 2007. Charcoal effects on soil solution chemistry and  
561 growth of *Koeleria macrantha* in the ponderosa pine/Douglas-fir ecosystem. *Biology &*  
562 *Fertility of Soils*, **43**, 303–311.

563

564 Hutchings, N., Amon, B., Dammgen, U. & Webb, J. 2009. *Animal Husbandry and*  
565 *Manure Management*. Air Pollutant Emission Inventory Guide Book, chapter 4B. pp. 1–  
566 73. European Environmental Agency, Copenhagen, Denmark.

567

- 568 Kammann, C., Ratering, S., Eckhard, C. & Muller, C. 2012. Biochar and hydrochar  
569 effects on greenhouse gas fluxes from soils. *Journal of Environmental Quality*, **41**,  
570 1052–1066.
- 571
- 572 Klute, A. 1994. *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*.  
573 Soil Science Society of America– Agronomy Monograph no. 9 (2<sup>nd</sup> ed.), pp. 399–408.  
574 Madison, USA.
- 575
- 576 Lee, J.W., Kidder, M., Evans, B.R., Paik, S., Buchanan, A.C., Garten, C.T. *et al.* 2010.  
577 Characterization of biochars produced from corn stovers for soil amendment.  
578 *Environmental Science & Technology*, **44**, 7970–7974.
- 579
- 580 Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., Tritici,  
581 M.M. *et al.* 2011. Hydrothermal carbonization of biomass residuals: a comparative  
582 review of the chemistry, processes and applications of wet and dry pyrolysis. *Biofuels*,  
583 **2**, 71–106.
- 584
- 585 Major, J., Rondon, M., Molina, D., Riha, S.J. & Lehmann, J. 2012. Nutrient leaching in  
586 a Columbian savanna Oxisol amended with biochar. *Journal of Environmental Quality*,  
587 **41**, 1076–1086.
- 588
- 589 McLaughlin, H., Anderson, P.S., Shields, F.E. & Reed, T.B. 2009. All biochars are not  
590 created equal and how to tell them apart. *Proceedings of the North American Biochar*  
591 *Conference*, **2**, 1–36.
- 592

- 593 Misselbrook, T.H., Nicholson, F.A. & Chambers, B.J. 2005. Predicting ammonia losses  
594 following the application of livestock manure to land. *Bioresource Technology*, **96**,  
595 159–168.
- 596
- 597 Mokome, F.N.D., Zhang, X., Silva, L.C.R., Six, J. & Parikh, S.J. 2013. Use of chemical  
598 and physical characteristics to investigate trends in biochar feedstocks. *Journal of*  
599 *Agricultural & Food Chemistry*, **61**, 2196–2204.
- 600
- 601 Monaco, S., Sacco, D., Pelisetti, S., Dinuccio, E., Balsari, P., Rostami, M. *et al.* 2012.  
602 Laboratory assessment of ammonia emissions after soil application of treated and  
603 untreated manures. *Journal of Agricultural Science*, **150**, 65–73.
- 604
- 605 Mukherjee, A., Zimmerman, A.R. & Harris, W. 2011. Surface chemistry variations  
606 among a series of laboratory-produced biochars. *Geoderma*, **163**, 247–255.
- 607
- 608 NSAI. 2009. *Solid biofuels- determination of ash and volatile matter content*. pp. 1–10.  
609 National Standard Authority of Ireland (NSAI), I.S. EN14775:2009.
- 610
- 611 Pacholski, A., Cai, G.X., Fan, X.H., Ding, H., Chen, D., Nieder, R. *et al.* 2008.  
612 Comparison of different methods for the measurement of ammonia volatilization after  
613 urea application in Henan Province, China, *Journal of Plant Nutrition & Soil Science*,  
614 **171**, 361–369.
- 615
- 616 Sohi, S.P., Krull, E., Lopez-Capel, E. & Bol, R. 2010. A review of biochar and its use  
617 and function in soil. *Advances in Agronomy*, **105**, 47–82.

618

619 Sommer, S.G. & Husted, S. 1995. The chemical buffer system in raw and digested  
620 animal slurry. *Journal of Agricultural Science*, **124**, 45–53.

621

622 USDA. 2013. Soil Texture Calculator. United States Department of Agriculture. Natural  
623 Resources Conservation Service. In:

624 [http://www.nrcs.usda.gov/wps/portal/nrcs/detail/?cid=nrcs142p2\\_054167](http://www.nrcs.usda.gov/wps/portal/nrcs/detail/?cid=nrcs142p2_054167) (Accessed  
625 on: 12–04–2013).

626

627 Vandre, R. & Clemens, J. 1997. Studies on the relationship between slurry pH,  
628 volatilization processes and the influence of acidifying additives. *Nutrient  
629 Cycling in Agroecosystems*, **47**, 157–165.

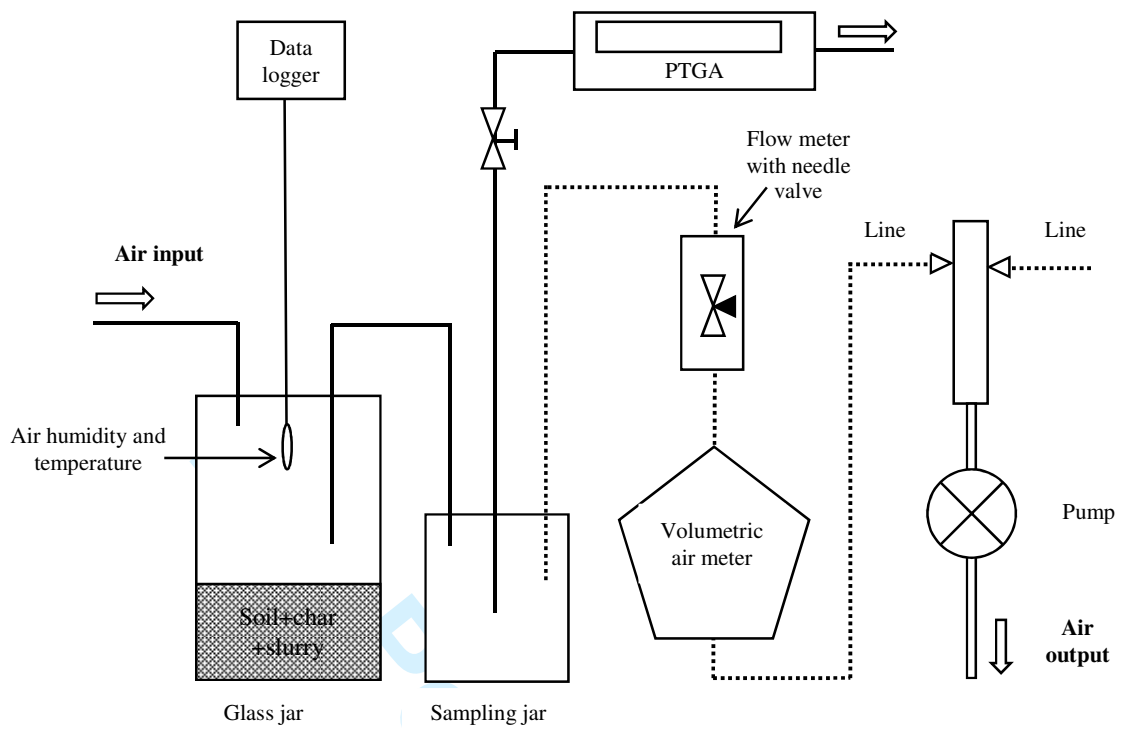
630

631 Wardle, D.A., Zackrisson, O. & Nilsson, M.C. 1998. The charcoal effect in Boreal  
632 forests: mechanisms and ecological consequences. *Oecologia*, **115**, 419–426.

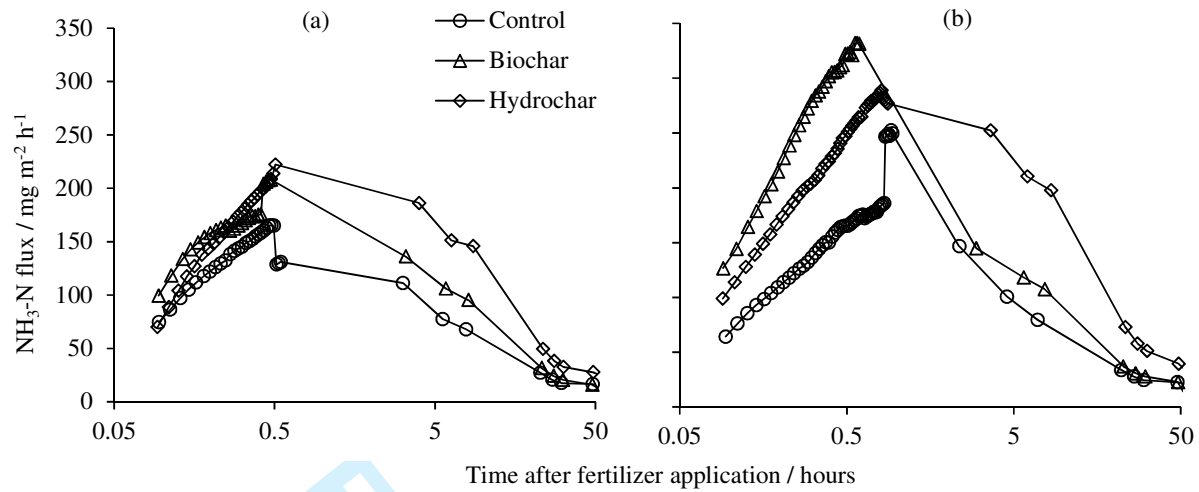
633

634 Zhao, Y., Pan, Y., Rutherford, J. & Mitloehner, F.M. 2012. Estimation of the  
635 interference in multi-gas measurements using infrared photo-acoustic analysers.

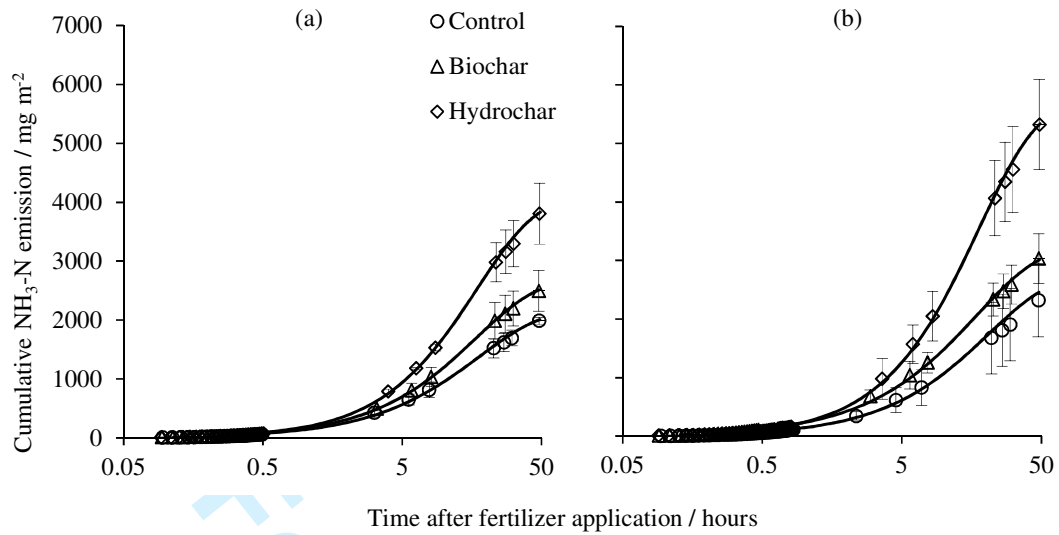
636 *Atmosphere*, **3**, 246–265.



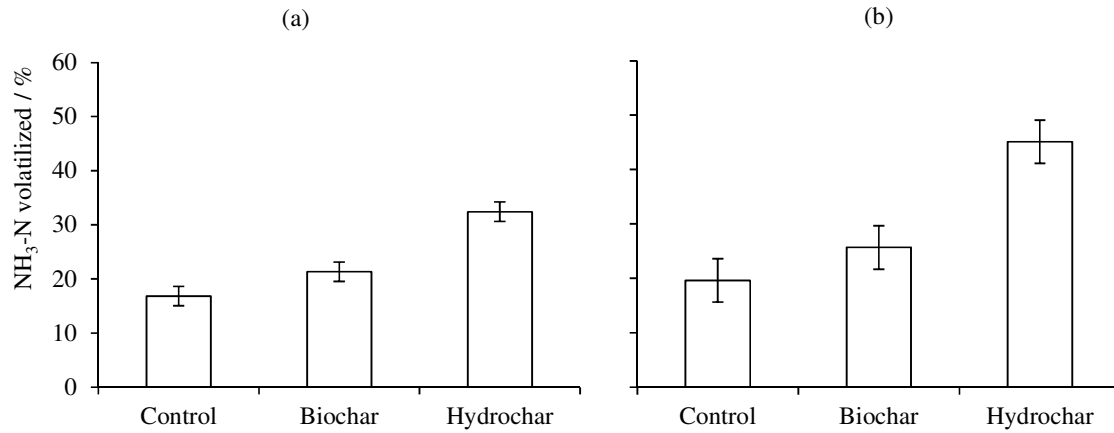
**Figure 1** Measurement system (dynamic chamber method) used in the experiment. Continuous and dotted lines represent Teflon and nylon tubes respectively.



**Figure 2** Ammonia fluxes (mean values over blocks,  $n=3$ ) measured with dynamic chambers combined with photo-acoustic trace gas analyser for (a) silt-loam and (b) loam soils treated with different amendments. The values in X-axis are in logarithmic scale in order that the temporal courses of the emissions at the beginning are properly visualised. Error bars are omitted for better visibility.



**Figure 3** Cumulative  $\text{NH}_3\text{-N}$  emissions after surface application of pig slurry for (a) silt-loam and (b) loam soils with different treatments over 48 hours. The solid lines represent the fitted sigmoidal logistic equation. The values in X-axis are in logarithmic scale for better illustration of curve shape. Error bars represent standard deviation from the mean over blocks (n=3).



**Figure 4** Effect of soil treatments on total  $\text{NH}_3\text{-N}$  volatilisation expressed as % of applied TAN with pig slurry for (a) silt-loam and (b) loam soils. Error bars represent standard error of the means (n=3).

**Table 1** Properties of soils used in the experiment

Soil type	Sand	Silt	Clay	Porosity	TOC	Total N	C:N	BD	pH	CEC
	----- / % -----							/ gcm <sup>-3</sup>		/ cmol <sub>c</sub> kg <sup>-1</sup>
Silt-loam	15.8	75.6	8.6	45.2	0.84	0.081	10.4	1.45	6.1	12.5
Loam	48.4	43.1	8.5	49.3	0.83	0.083	10.0	1.34	8.2	8.2

TOC- total organic carbon, BD- bulk density, CEC- cation exchange capacity, texture based on USDA (2013).

For Peer Review

**Table 2** Physico-chemical characteristics of biochar and hydrochar (mean values, n=3) utilised in the experiment

	C	N	Moisture	Ash	VM	pH	CEC	EC <sup>b</sup>	Surface acidity	Surface area	Pore volume	Average pore size
	- - - - - / %		dry wt. basis	- - - - -			/ cmol <sub>c</sub> kg <sup>-1</sup>	/ mS m <sup>-1</sup>	/ mmol H <sup>+</sup> g <sup>-1</sup>	/ m <sup>2</sup> g <sup>-1</sup>	/ mm <sup>3</sup> g <sup>-1</sup>	/ nm
Biochar	73.6	0.26	6.10	20.83	14.1	10.1	32.0	1.63 ± 0.02	0.93	249.9	138.2	2.5
Hydrochar	51.6	0.23	4.42	6.24	75.8	5.61	31.6	1.09 ± 0.001	3.35	5.9	2.4	3.3
SE	0.74	0.004	0.048	0.31	1.66	0.04	1.40	-	0.24	10.45	8.68	0.39
<i>P</i> value <sup>a</sup>	<b>&lt; 0.001</b>	0.067	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	0.807	<b>0.001</b>	<b>0.001</b>	<b>&lt; 0.001</b>	<b>&lt; 0.001</b>	0.496

EC- electrical conductivity, CEC- cation exchange capacity, VM- volatile matter, SE- standard error of the mean

<sup>a</sup>Values, the significance level of the t-test, in italics are significant at the 0.05 level.

<sup>b</sup>The assumption of equal variances were not fulfilled.

**Table 3** Parameter estimates (mean values, n=3) derived with sigmoidal logistic equation,  $Y = a \{1 - \exp(-ct)\}^\beta$  fitted to cumulative  $\text{NH}_3\text{-N}$  emission data for surface applied pig slurry with different treatments

Treatments	Parameter	Estimate	Standard error	Average $R^2$
Silt-loam soil				
Control	$a$	2154.0	44.0	0.998
	$c$	0.05	0.003	
	$\beta$	0.93	0.026	
Biochar	$a$	2673.0	26.4	1.000
	$c$	0.06	0.002	
	$\beta$	0.97	0.019	
Hydrochar	$a$	4058.3	40.6	0.999
	$c$	0.06	0.002	
	$\beta$	1.09	0.022	
Loam soil				
Control	$a$	2740.4	123.9	0.998
	$c$	0.05	0.003	
	$\beta$	0.95	0.021	
Biochar	$a$	3219.8	57.2	0.998
	$c$	0.05	0.003	
	$\beta$	0.89	0.024	
Hydrochar	$a$	5679.5	52.7	1.000
	$c$	0.06	0.002	
	$\beta$	1.11	0.018	

$a$ - asymptotic maximum loss,  $c$ - rate constant,  $\beta$ - degree of sigmoidality,  $R^2$ - calculated as  $1 - (\text{Residual sum of squares} / \text{Total sum of squares})$ .

**Table 4** Summary of the analysis of variance for the total NH<sub>3</sub>-N volatilisation loss for the surface applied pig slurry with different treatments

Model	Degrees of freedom	Sum of squares	Mean square	F value	<i>P</i> value <sup>a</sup>
Soil type	1	2681786.1	2681786.1	5.70	<b><i>0.038</i></b>
Treatment	2	18655933.4	9327966.7	19.8	<b><i>&lt;0.001</i></b>
Block	2	6425.0	3212.5	0.01	0.993
Soil × treatment	2	1167641.2	583820.6	1.24	0.330
Error	10	4706628.5	470662.8		
Total	17	27218414.2	1601083.2		

<sup>a</sup>Values shown in italics are significant at the 0.05 level.

For Peer Review

**Table 5** Orthogonal contrasts of amendment effects for the mean values (n=3) of the total NH<sub>3</sub>-N volatilisation loss at the end of the experiment

Contrast		Average 1	Average 2	Standard error	<i>P</i> value <sup>a</sup>
1	vs 2	- - mg NH <sub>3</sub> -N m <sup>-2</sup> - -			
Control	vs Chars	2128.8	3638.3	343.0	<i>0.001</i>
Biochar	vs Hydrochar	2746.6	4530.0	396.1	<i>&lt;0.001</i>

<sup>a</sup>Values shown in italics are significant at the 0.05 level.

For Peer Review

**Table 6** Summary of the analysis of variance of the soil mineral N concentrations ( $\text{mg kg}^{-1}$ ) at the end of the experiment

	Model	Degrees of freedom	Sum of squares	Mean Square	F value	P value <sup>a</sup>
$\text{NH}_4^+$ -N	Soil type	1	392.0	392.0	10.8	<i><b>0.008</b></i>
	Treatment	2	4091.0	2045.5	56.5	<i><b>&lt;0.001</b></i>
	Block	2	177.0	88.5	2.44	0.137
	Soil type x treatment	2	107.1	53.5	1.48	0.274
	Error	10	362.3	36.2		
	Total	17	5129.3			
$\text{NO}_3^-$ -N	Soil type	1	1.6	1.6	0.49	0.501
	Treatment	2	529.0	264.5	79.7	<i><b>&lt;0.001</b></i>
	Block	2	1.7	0.8	0.25	0.784
	Soil type x treatment	2	37.4	18.7	5.63	<i><b>0.023</b></i>
	Error	10	33.2	3.3		
	Total	17	602.8			
Total $\text{N}_{\text{min}}$ <sup>b</sup>	Soil type	1	445.0	445.0	9.57	<i><b>0.011</b></i>
	Treatment	2	6544.2	3272.1	70.4	<i><b>&lt;0.001</b></i>
	Block	2	174.8	87.4	1.88	0.203
	Soil type x treatment	2	102.7	51.4	1.11	0.369
	Error	10	465.1	46.5		
	Total	17	7731.9			

<sup>a</sup>Values shown in italics are significant at the 0.05 level.

<sup>b</sup>( $\text{NH}_4^+$ -N +  $\text{NO}_3^-$ -N).

**Table 7** Orthogonal contrasts of amendment effects for the mean values (n=3) of the mineral N concentrations in soil extracts with deionised water at the end of the experiment

Contrast			Average 1	Average 2	Standard error	P value <sup>a</sup>
1	vs	2	- - - mg kg <sup>-1</sup> - - -			
NH <sub>4</sub> <sup>+</sup> -N						
Control	vs	Char	69.2	37.8	3.01	<i>&lt;0.001</i>
Biochar	vs	Hydrochar	41.4	34.2	3.48	0.065
NO <sub>3</sub> <sup>-</sup> -N						
Control	vs	Char	12.8	7.07	0.91	<i>&lt;0.001</i>
Biochar	vs	Hydrochar	12.8	1.30	1.05	<i>&lt;0.001</i>
Total N <sub>min</sub> <sup>b</sup>						
Control	vs	Char	82.0	44.9	3.41	<i>&lt;0.001</i>
Biochar	vs	Hydrochar	54.3	35.6	3.94	<i>0.001</i>

<sup>a</sup>Values shown in italics are significant at the 0.05 level.

<sup>b</sup>(NH<sub>4</sub><sup>+</sup>-N + NO<sub>3</sub><sup>-</sup>-N).