Use of biochar and hydrochar to reduce ammonia emissions from soils fertilized with pig slurry

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Abstract
Ammonia (NH_3) volatilization caused by animal manure application to agricultural soils leads to high amounts of nitrogen (N) losses. The use of biochar and hydrochar by-products as soil amendments modifies the dynamic of N in soil and may also influence NH_3 emissions and nitrates leaching. The present study assessed the potential NH_3 emissions after surface application of pig slurry on soils amended with a biochar (from pyrolysis) and an hydrochar (from hydrothermal carbonization) of *Miscanthus* sp. in a laboratory experiment. The experiment was carried out in a dynamic chambers coupled with a photo-acoustic trace gas analyzer in a controlled environment for 48 hours. Statistical results showed significant differences among treatments. Total emissions of NH_3 and total inorganic N concentrations in the soil extracts were related to type of soil amendment and not to soil type.

Introduction
Intensive animal production and increased size of animal production units in developed countries have resulted into production of large quantities of animal wastes in some regions, which if not properly managed can create a lot of environmental problems due to nutrient losses, such as leaching of nitrates (NO_3^-), emissions of greenhouse gases (CO_2, CH_4, N_2O, etc.) and volatilization of ammonia (NH_3) [1]. It has been estimated that more than 1.5 Gt of animal manures, mostly from cattle and pig livestock, are generated every year within EU 27 countries [1,2]. It has also been rated that more than 80% of total NH_3 emissions (i.e. approximately 2.9 Mt/year) is generated from European agriculture, mainly due to animal husbandry and manure management practices [2,3]. Application of animal manures in the field accounts for 30-40% of these losses [3,4]. However, NH_3 emissions from manure application to the soil are greatly affected by several variables such as physico-chemical characteristics of slurry, soil and soil amendments, application techniques and environmental conditions [5,6].
Biochars are carbon rich solid by-products obtained after heating biomass in an oxygen limited environment [7]. Hydrochars are produced by hydrothermal carbonization of feedstock: the process mimics the formation of brown coal, with pressure and temperature adjustment of 15-25 MPa and 180-250 °C respectively [8,9]. The uses of biochars and hydrochars as soil amendments can modify the dynamic of nitrogen (N) in soil after the application of fertilizers and may also influence NH_3 emissions. There have been lots of debates among researchers in relation to effectiveness of biochar and hydrochar as soil amendments and its contribution to soil N cycle [10]. The capacity of these materials to absorb ammonium (NH_4^+) during soil N transformation may reduce NH_3 emission but the mechanisms behind these processes are not completely investigated [11]. In the present paper in laboratory potential NH_3 emission after surface application of pig slurry on soils amended with a biochar and an hydrochar is evaluated.

Material and Methods
Treatments and experimental setup
The experiment was carried out in glass jars (3.2 L capacity) intended to mimic the plough layer (0-30 cm) of two agricultural soils (NW Italy) with different physico-chemical characteristics: 1) a silt-loamy soil with sub-acid pH and 2) a loam soil with sub-alkaline pH (Table 1). The biochar (from pyrolysis at 600 °C) and hydrochar (from hydrothermal carbonization at 200 °C under pressure of 16 bars for 2 hours) from *Miscanthus* sp. were imported from Justus-Liebig University (Germany) (Table 1). The whole experiment was designed with randomized complete block design with three soil treatments (biochar, hydrochar and control) and two soil types (Loam and silty-loam) as main effects.

The amount of air-dried soil in the jar differed among soil types (726 g of loam and 672 g of silty-loam sieved at 2 mm) in order to reach the same volumes of 500 cm^3 of soil samples and an head-air space of 2000 cm^3 in the jar. Air-dried soil samples were amended with incorporation of 3 g of biochar or hydrochar per 100 g of dry soil and moistened with deionized water in order to reach 60% of water filled pore space. Jars with unamended soils were also prepared as controls. The jars were then covered with parafilm to minimize water losses during the pre-incubation, which lasted one week at 20 °C. The moisture content of the soil was checked on daily basis by re-weighting the jars.

After pre-incubation, jars were manually fertilized with pig slurry (0.29% of total N and 0.2% of TAN) on the soil surface at a rate of 17 g of N per m^2 (i.e. 170 kg N ha^{-1}) and immediately connected to the measurement system, which consisted in a dymanic chamber coupled with a photo-acoustic trace gas analyzer (PTGA) (INNOVA 1412, LumaSense Tech.).

Table 1. Physico-chemical characteristics of materials (soils, biochar and hydrochar, pig slurry) utilized in the experiment.

	Sand %	Silt %	Clay %	Bulk density g/cm^3	CEC meq /100 g	pH	EC mS/cm	Dry matter %	Total C % of DM	Total N % of DM
Loam	15.8	75.6	8.7	1.34	16.7	6.2	-	-	0.83	0.83
Silty-loam	48.4	43.1	8.5	1.45	12.4	7.9	-	-	0.84	0.81
Biochar	-	-	-	na	na	10.3	1.59	95.3	75.6	0.24
Hydrochar	-	-	-	na	na	5.3	2.88	95.4	51.1	0.25
Pig slurry	-	-	-	-	-	7.8	2.41	2.3	-	-

na- not available

NH_3 Volatilization measurement

NH_3 emission at 20 ºC and air flow rate of 2 litres min^{-1} was measured for 48 hours. The NH_3 emitted in volatilization chamber (i.e. head space of each jar) was sampled from an expansion bottle (1 L capacity) and analyzed with PTGA connected with the volatilization system.

Analysis of soil extract

At the end of the volatilization experiment (48 h), 30 g of soil samples from each was mixed with 150 ml of deionized water and shaken for half an hour. Soil extracts were then filtered and analysed for inorganic N (NH_4^+ and NO_3^-) concentration using colorimetric method.

Data analysis and processing

The procedure for calculating the emission rates and total amount of NH_3 emitted were fully described by [3]. Two way ANOVA test was performed using SPSS software (version 19).

Results and discussion

Statistical analysis showed significant differences among soil treatments, while no differences were observed between soil types in terms of total NH_3 emissions (Table 2). Unexpectedly, NH_3 emissions from soils amended with biochar (2201 mg N-NH_3/m^2 or 18.8 % of TAN) showed no differences with respect to control (2159 mg N-NH_3/m^2 or 18.5% of TAN), while hydrochar even showed a higher total NH_3 emission (4239 mg N-NH_3/m^2 or 36.3% of TAN) compared with control (Figure 1). This contradicts the initial hypothesis that NH_4^+ absorption on chars can reduce NH_3 emissions. Also the pH effect of added materials for amendment on NH_3 emissions, i.e. alkaline for biochar and acidic for hydrochar, was reversed.

Analysis of soil extracts with deionized water at the end of volatilization experiment showed significant effect of soil treatment for total inorganic and highly significant for N-NO_3^- concentrations (Figure 2). In particular, unamended soil had highest inorganic N concentration (68.4 ± 5.6 mg N/kg) compared with soil amended with biochar (47.1 mg N /kg) and hydrochar (50.2 mg N/kg). Moreover, hydrochar, which had no significant difference on total inorganic N concentration, compared with biochar amendment, showed lower N-NO_3^- concentrations compared with all the other treatments.

Table 2. Level of probability for soil treatment, soil type and the interaction between effect derived from the ANOVA of the measured variables.

Effects	Total NH_3 emissions	N - (NH_4^+ + NO_3^-) in soil extracts	N-NH_4^+ in soil extracts	N-NO_3^- in soil extracts
Soil treatment	0.006**	0.048*	0.066	0.000**
Soil type	0.322	0.514	0.614	0.328
Soil type x Treat.	0.135	0.464	0.428	0.047*

*significant at P(F) <0.05

** highly significant at P(F) <0.01

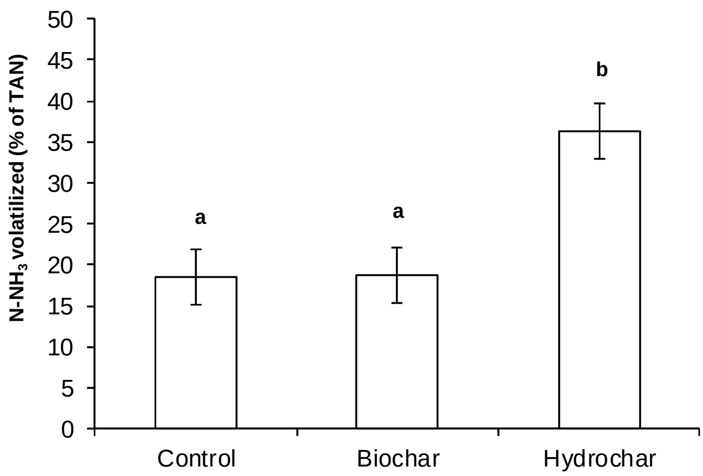

Figure 1. Effect of soil treatment on total NH_3 volatilization expressed as % of applied TAN with pig slurry. Error bars represent standard error of the mean. Letters show significant difference (Bonferroni test at P<0.05)

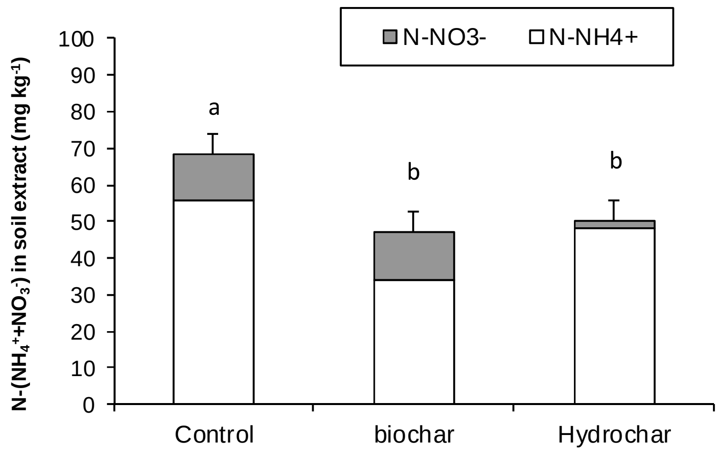

Figure 2. Effect of soil treatment on total inorganic N in soil extracts with water and N concentrations in soil extracts as N-NO_3^- and N-NH_4^+. Error bars represent standard error of the mean for total inorganic N. Letters show significant difference (Bonferroni test at P<0.05).

In order to explain the results some preliminary hypothesis can be formulated. Results on NH_3 emissions could probably be explained by the fact that slurry infiltration process could mask the effect of NH_4^+ absorption on biochar and hydrochar and pH effect. This could clarify the reason of not differences between control (unamended) and biochar amendment. This is also congruent with the results of total inorganic N concentrations in soil extracts, which showed a significant effect of amendment with biochar and hydrochar in reducing the amount of inorganic N extracted from the soil.
With respect with hydrochar amendment effect on increasing NH_3 emissions, two hypothesis could be formulated: 1) the higher fibrous nature of hydrochar than biochar might have influenced the NH_3

emissions from slurry due to a mulching effect that increased retention of ammonium on the soil surface and 2) hydrochar reduced nitrification rates in the soil as shown by the significant lower N-NO_3^- concentrations, thus increasing the NH_4^+ that could be converted in NH_3 during the volatilization experiment.

Nevertheless, the emission values obtained are within the range reported by [12,13] for field application of swine slurry with lower dry matter content. Not enough scientific descriptions have been found in relation to the change slurry-soil pH as the mechanisms behind these are still unclear and need to be further investigated. Moreover, a study conducted by [14] reported pH increase of approximately 0.5 units following slurry application and an increased pH can be maintained in the soil surface for at least 72 hours. In this case, the pH effect of biochar in soils and applied slurry might not be so visible and effective in a very short period (48 hours).

Conclusion and perspectives

Total emissions of NH_3 and total inorganic N concentration in the soil extracts were related to type of soil amendment and not to soil type. In depth research study on processes and mechanisms associated to these effects are necessary for better understanding and also exploring further use of biochar and hydrochar properties in order to meet the new mitigation strategies.

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