AMENDMENT OF BIOCHAR TO SLURRY: A POSSIBILITY TO MITIGATE AMMONIA EMISSIONS?

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ABSTRACT Amendments of biochar (BC) to slurry potentially reduces NH_3 losses in animal housings and during storage. In this study, we report on an investigation on the effect of adding biochar to slurry during storage.
Two untreated biochars, with strong alkaline (BC22) and neutral (BC24) pH respectively, and one acidified biochar (BC24 treated with a phosphoric acid solution) are added to fresh slurry from dairy cows. Ammonia emissions are measured using a Dynamic Chamber system in conjunction with a HT-CIMS and a Cavity Ring down NH3 analyzer.
The addition of the untreated biochar alter the ammonia emission in both directions (BC24 to roughly 75% – 100% and BC22 to roughly 95% – 105% of the control sample), whereas the acidified biochar reduces emissions significantly (< 3% of the control sample).
The results indicate that not the pH of BC alone, but a combination of BC characteristics influences the ammonium adsorption potential of untreated biochar.

Keywords: NH3, Slurry, Cattle, Storage, Mitigation strategy

INTRODUCTION Biochar, a pyrolysis product of organic material, is an amendment for agricultural systems to improve soil fertility, sequester CO_2 and reduce greenhouse gas emissions (Lehmann and Joseph, 2009; Clough and Condron, 2010; Atkinson et al., 2010). It is an efficient adsorbent for NH_3 in the gas phase (e.g. Asada et al., 2002; Asada et al., 2006; Iyobe et al., 2004). Further, when added to composting material, BC lowers ammonia emissions (Steiner et al., 2009; Chen et al., 2010; Hua et al., 2008), and Taghizadeh-Toosi et al. (2011) found that BC, incorporated into soil, reduces the NH_3 cumulative loss after urine application. Here we focus on the NH_3 emission reduction during slurry storage without looking at potential later losses/consequences.

1. MATERIAL AND METHODS Measurements have been carried out using two different types of BC (Table 1). BC24, a pyrolysed mix of 20% hardwood and 80% softwood, has a neutral pH, and BC22, which has its origin in sieve residues from forest material, is alkaline with a relatively high pH of 12.4. Both BC were stored for one year before measurements. In a first measurement series (V1), the effect of the addition of the two untreated biochars BC22 and BC24 has been compared to a slurry control sample. In a second series (V2), BC24 was acidified with phosphoric acid by soaking in 5% orthophosphoric acid solution for 5 days. This acidic biochar (PSBC24) has been compared to the untreated BC24 (BC24-2), the same amount of acid added to the control sample (PS), and a slurry control sample (Control-2). For each sample, a 6L bucket with 5L of dairy cow slurry was used. BC was added to the BC samples and mixed for 2 min (with a kitchen mixer), immediately before the experiment started. Each BC sample contained 200 g of biochar,

Table 1. Elementary composition, BET surface area (N_2 adsorption) and pH of the investigated BC. (20L80N: 20% hard-/80% softwood. SR-W: sieve residues forest.)

	Material	C (g/kg)	N (g/kg)	O (g/kg)	H (g/kg)	BET SA (m^2/g)	pH (in $CaCl_2$)
BC24	20L80N	799.2	4.6	89.2	18.9	109	7.0
BC22	SR-W	767.2	6.4	62.0	6.3	123	12.4

The slurry was collected directly from the stable and stored at 4°C until the start of the measurements. Before the experiments started, the slurry was diluted with water at a ratio of 1:2, slurry to water. Table 2 gives the characteristics of the control slurries.

Table 2. Characteristics of the dairy cow slurry for the two measurement series V1 & V2. (OM: Organic Matter. TAN: total ammoniacal nitrogen.)

	DM (g/L)	Ash (g/L)	OM (g/L)	N_{tot} (g/L)	P_2O_5 (g/L)	KO_2 (g/L)	Ca (g/L)	Mg (g/L)	Na (g/L)	TAN (g/L)	Density (g/L)	pH
V1	59.1	15.9	43.2	2.79	1.15	3.07	1.12	0.53	0.33	1.33	1020	7.1
V2	58.7	15.8	42.9	2.86	1.10	3.07	1.02	0.50	0.36	1.45	1020	6.7

The measurements were carried out using a Dynamic Chamber (DC) system (Pape et al., 2009) in a large environmental chamber with regulated temperature and humidity. Both, temperature and humidity were held constant at 20°C and 60%, respectively. The ingoing concentration of the DC was measured with a Cavity Ring-Down spectrometer, the outgoing concentration was measured with a HT-CIMS (Sintermann et al, 2011). The inflow to the DC was held constant at 60 L/min. The samples were measured in turn, for approx. one hour each. Before the samples were placed in the DC for emission measurements, they had been mixed for 2 min. In between the measuring intervals, the samples were stored in a separate environmental chamber at the same temperature and relative humidity.

2. RESULTS AND DISCUSSION Flux measurements in a Dynamic Chamber reflect a potential emission flux due to the high air exchange rate and the enhanced turbulent transport from the slurry surface. This flux will exceed the e effective flux from a storage system. Flux measurements did not show a major enhancement in the average NH_3 emissions due to BC addition (Figure 1), as might have been expected from the pH characteristics of the BCs. When adding BC24 to slurry, there was even a small reduction by 5-10% compared to the control sample. N-Budget calculations (covering 20 days of slurry storage) supported these findings in emission reduction due to BC addition, for both BC types. For the acidified BC and the direct amendment of acid the reduction was almost 100%, due to the very low pH established in the samples. Integrated over the whole observation time, the acid only was the most effective mitigation strategy, acting in high ambient concentration periods even as a sink for ammonia. The addition of acidified BC resulted in higher, although still very low, emissions of NH3.

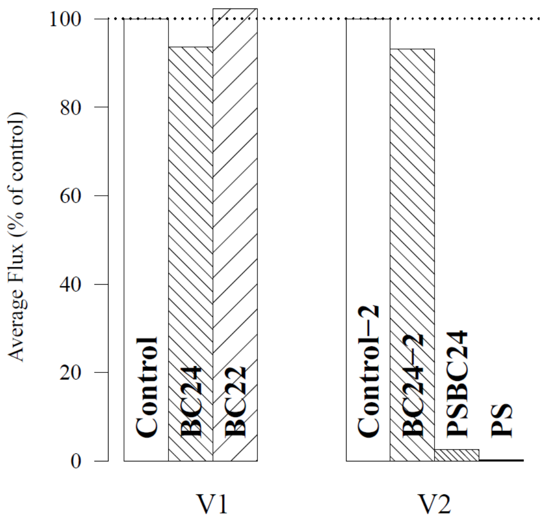

Figure 1. Overall average of the measured flux in % of control sample. (measurement series V1 & V2.)

Figure 2 shows the average measured flux for the 8 measuring events in series V1. The absolute NH_3 emission decreased from roughly 200 µg m^{-2} s^{-1} in the first event, to about 90 µg m^{-2} s^{-1} in the last event. This decrease in the flux goes parallel with a decrease in slurry pH from 7.9 to 6.9 in all the samples. The temporal dynamics of the emission reduction is characterized by a higher reduction at the beginning of the experiments (measuring event 1 and 2) and a decreasing reduction after a few days of storage.

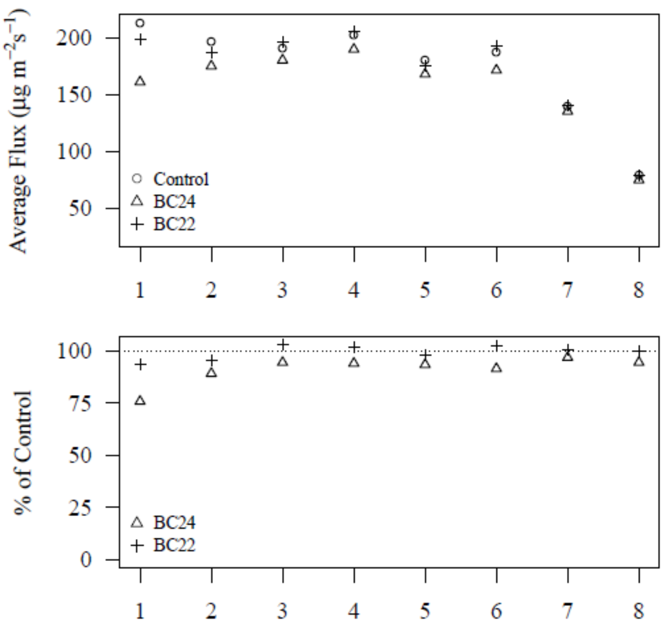

Figure 2. Measured average flux. Absolute (top) and relative to control sample (bottom). (8 measuring events in measurement series V1.)

3. CONCLUSION Amendment of BC to slurry during storage may reduce ammonia emissions, depending on the characteristics of the BC added. The reduction in NH_3 loss takes mainly place directly after adding BC to the slurry. The results of this study indicate that not the pH of BC alone, but an interaction of BC characteristics determines its ammonium adsorption potential. This means that a variety of NH_3 emission reduction behaviours can be expected depending on the source material, the pyrolysis process and the post-treatment of the biochar.

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