

Effect of acidification and soil injection of animal slurry on ammonia and odour emission

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Abstract

Laboratory and field experiments examined ammonia (NH₃) emissions after application of slurry on packed soil or fields. Acidified slurry reduced NH₃ emissions significantly, and the greatest effect was obtained by lowering the pH from 7.8 to 6.8. The field trial demonstrated two acidification techniques to lower the slurry pH with good reduction of NH₃ emission. NH₃ emission was at the same level with soil injection of un-acidified slurry as acidified slurry applied by trailing hoses. In addition, we tested the development of some odorous compounds by covering the fields after application of un-treated or treated slurry with static chambers and measured the development of some odorous compound by proton-transfer-reaction mass spectrometry (PTR-MS).

Introduction

Denmark has one of the most intensive livestock productions in Western Europe [1], and application of the produced manure on fields exposes the environment and humans to ammonia (NH₃) and odour [2]. Therefore new legislation was introduced in 2011 that aims to reduce the loss of ammoniacal nitrogen during and after application of manure to fields by banning application of liquid manure (slurry) on the soil surface of grasslands unless the slurry pH is lowered to less than 6.4 [3]. Consequently, application of slurry to grassland must be made by (i) soil injection of slurry, or (ii) surface application of acidified slurry.

Soil injection has been shown to significantly reduce NH₃ and odour emission compared to surface application [4; 5] and is a commonly used technology. However, acidification of the manure slurry is a relatively new technology. Acidification can take place in different ways: (i) acid added to the slurry in the animal housing (designated “barn acidified”), (ii) acid added to the slurry in the storage tank (designated “storage acidification”), or (iii) acid added to the slurry tanker during field application (designated “field acidification”). The acid used was concentrated sulphuric acid, ~96% (w/w). All three technologies are marketed today by different commercial companies, and around 10 per cent of the slurry applied to fields in Denmark in 2012 was acidified (Annette Vestergaard, 2013, personal communication).

The main purpose of this article is to map the total NH₃ emissions of barn and field acidified slurry versus untreated slurry, all applied with trailing hoses on two fields with different crops and compared to trail hose applied untreated slurry and with disc soil injection. Secondly, the purpose was to monitor the development of the concentrations of selected odorous compounds (odorants) in the headspace air in static boxes that were placed on the fields immediately after application of untreated slurry or acidified slurry.

Material and Method

Laboratory and field trials were conducted in the spring and summer of 2010 at Aarhus University’s agricultural research centre at Foulum.

The laboratory experiments included 8 plastic boxes (35 x 25 x 20 cm) packed with soil and used as dynamic emissions chambers. Soil was packed using a standardized method with 12 kg (~ 13 L) of soil per box, leaving a headspace in the chambers of 4.5 L. (Dorno et al., unpublished data). Untreated and acidified slurry from finishing pigs with an initial pH of 7.8 was applied evenly on the soil

surfaces. The acidified slurries were acidified with concentrated sulphuric acid until pH-values as shown in Table 1. Immediately after slurry application the boxes were closed and sealed with lids, and an air flow of 13.6 L min^{-1} was passing through each box for 70 h. The concentration of NH_3 in the air passing through the chambers was measured in the exhaust air from each box with a photo-acoustic gas detector and a multiplexer (Brüel & Kjær Photoacoustic Multi-gas Monitor, type 1312 and Multiplexer, type 1309, both Innova Air Tech Instruments A/S, Denmark).

Two fields at Aarhus University, Foulum ($56^\circ 29' \text{ N}$, $9^\circ 34' \text{ E}$, loamy sand soil, Typic Hapludult) of 20 and 25 ha each, and with little topographic variance, cropped with winter wheat and forage grass, respectively, was used for the field experiment. The field acidification system consisted of a 160-kW standard tractor and an 18-ton standard slurry tanker. The tractor was fitted with a front tank, containing a 1000-L acid container with an acid pump. The pump delivers the acid to the tanker via fixed hoses and discharge pipes. Acidification in the barn is described in detail elsewhere [6]. Field acidification consumed 1.9 to 2.9 L of concentrated sulphuric acid per ton of slurry, and the consumption at barn acidification was 3.3 l per ton slurry. This difference between the acidification systems resulted in pH differences between the slurries with pH 5.9-6.3 in barn acidified, and 6.1-6.7 in field acidified slurry. Soil injection of slurry was performed with an experimental double disc injector (400 mm disc diameter) with a spacing of 300 mm between the discs. A more detailed description is given in Nyord et al. [7].

Slurry corresponding to 30 tons slurry per ha was applied on the experimental plots (36 x 36 m). The plots were located with a minimum of 100 m apart and more than 200 m from hedges and forest. NH_3 emission was determined by the micrometeorological mass-balance method [8]. More detailed description of the method can be seen in Nyord et al. [9]. NH_3 was collected in 7 consecutive periods: 0-1, 1-3, 3-8, 8-22, 22-48, 48-78, 78-102 h after application of the slurry. In the same grass field as above mentioned, 3 experimental plots (12 x 30 m each) were used to measure concentration of odour components in the air, following the application of the (i) un-acidified slurry, (ii) field acidified slurry, and (iii) field acidified slurry plus 0.50 L 42% (w/w; $177 \text{ g Fe}^{3+} \text{ L}^{-1}$) iron(III) sulphate (FeSO_4) was added per ton slurry. Unfortunately, the acidification system did not function in the latter with only addition of iron sulphate as a result.

Static chambers made of polyethylene covered with aluminium foil (ground area: 1.85 m^2 , volume: 0.8 m^3) were placed on the grass sward and the development of various odorants were measured by a high-sensitivity Proton-Transfer-Reaction Mass Spectrometer (PTR-MS, Ionicon Analytik, Innsbruck, Austria) immediately after the slurry was applied in the experimental plots. The PTR-MS was operated under standard drift-tube conditions (drift-tube pressure 2.1~2.2 mbar, voltage 600 V, temperature 60° C). Each measurement was run around 25 min immediately after the slurry application under selected ions monitor mode (42 masses in total). The selection of monitored ions was based on the scan measurements before the field experiments.

Results and discussion

Main results of NH_3 emission from the laboratory and the field experiments are shown in table 1. The results of the laboratory study showed a clear reducing effect on NH_3 emission following surface application of slurry by reducing the pH of the slurry ($p < 0.0001$). However, for the slurry used in this experiment, it seems that reducing pH to less than 6.8 did not result in significantly lower NH_3 emission, whereas the effect of reducing the pH from 7.8 to 6.8 resulted in more than a halving of the emission. A reduction of the pH from 7.8 to 6.8 reduces the liquid NH_3 concentration significantly in the slurry and accordingly the NH_3 emission.

The field experiment showed that the effect of barn and field acidification significantly reduced NH_3 emission following field application. The results from micro-metrological measurements were supported by the PTR-MS measurements, see figure 1. The NH_3 emission from field acidified slurry applied by trailing hoses was at the same level as soil injection of untreated slurry. The pH difference between barn and field acidification did not result in significantly different NH_3 emission contrary to expected that the lower pH of the barn acidified compared to the field acidified slurry would result in

less NH₃ emission. However, there is a weak tendency to lower emissions when slurry is barn acidified compared to field acidified.

Table 1. Average NH₃ emission for all treatments in the laboratory (*n*=2) and the field experiment (*n*=4-7). Letters indicate significant difference at 95% level.

Laboratory experiment		Field experiments	
Treatment	Total NH ₃ emission (±95% CI) as percentage of applied TAN)	Treatment	Total NH ₃ emission (±95% CI) as percentage of applied TAN)
pH 7.8	35.2 ^a ± 2.1	Untreated, trailing hose	20.1 ^a ± 1.9
pH 7.3	31.3 ^b ± 0.6	Untreated, soil injected	8.6 ^b ± 2.6
pH 6.8	14.8 ^c ± 5.5	Barn acidified, trailing hose	6.1 ^b ± 2.2
pH 6.2	12.3 ^c ± 5.3	Field acidified, trailing hose	6.9 ^b ± 2.2

The development of two significant odorants, hydrogen sulphide (H₂S) and 4-methylphenol (p-cresol), in the static chamber placed above the grass field plots immediately after application of slurries is shown in figure 2. These compounds are found to be significant odorants from pig production [10]. Hydrogen sulphide (figure 2a) showed an emission peak (1000 - 2000 ppbv) within a few minutes after application of un-acidified and field acidified slurry as well as iron sulphate treated slurry. This indicates that some removal processes take place in the chambers since a stable equilibrium between liquid and gas phase is expected. The removal process can be ascribed to (i) absorption into grass/soil surface, (ii) adsorption onto the chamber walls, (iii) absorption into liquid water condensing at the chamber walls, (iv) catalytic degradation at surfaces, and (v) loss to the outside air [5]. For 4-methylphenol a stable plateau of ca. 15 ppbv was reached between 5 and 15 min for un-acidified slurry, and for field acidified slurry a plateau of ca. 6 ppbv from 1 to 20 min. In contrast, un-acidified slurry with addition of iron sulphate did not develop any 4-methylphenol for the first 10 min, whereupon a linear development up to ca. 10 ppbv after 25 min took place. It is expected that iron(II) ion will react with sulphide and form iron sulphide (e.g. FeS) and thus reduce the concentration and emission of liquid H₂S. However, since the formation of a foam layer was observed when applying the iron sulphate enriched slurry, an alternative or complementary explanation could be that the surface was covered by foam during the 5 min. This explanation is supported by the development of NH₃ from the iron sulphate enriched slurry where little NH₃ was seen during the first 5 min (Figure 1). The decline in concentration for NH₃ (figure 1) and 4-methylphenol (figure 2b) from the un-acidified slurry after around 15 min can be ascribed to infiltration of the slurry into the soils as well as the previous mentioned removal processes. Even though the use of static chambers can give valuable information about the development of odorants, it is important to notice their limitation due to severe losses of important odorants, e.g. hydrogen sulphide [5]. Whether this reflects the real emission when applying slurry on fields is so far unknown, but the fast removal of H₂S and methanethiol (not shown) suggests that these compounds will be severely underestimated if the concentration is sampled and measured after e.g. 20 min pre-concentration as recommended in the VERA protocol [11].

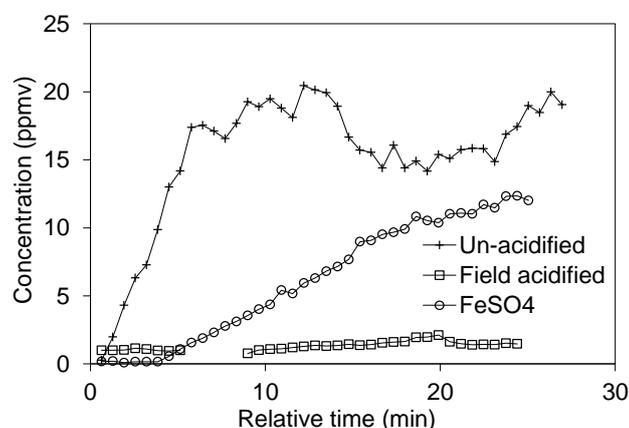


Figure 1. Development of NH₃ in static chambers measured by PTR-MS after applications of slurry by trailing hoses to the plots in the grass field experiment.

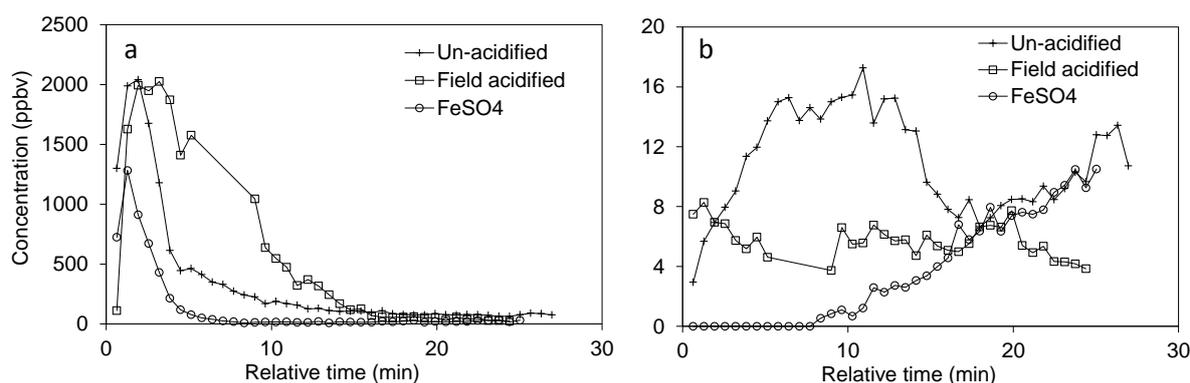


Figure 2. Development of two selected odorants (a) hydrogen sulphide, and (b) 4-methylphenol measured by PTR-MS in static chamber placed above the grass field plots immediately after applications of slurries.

Conclusion and perspectives

Laboratory and field experiments examined ammonia (NH_3) emissions after application of slurry on packed soil in lab-scale boxes or fields. Acidified slurry reduced NH_3 emissions significantly, and the greatest effect was obtained by lowering the pH from 7.8 to 6.8. The field trial demonstrated two acidification techniques to lower the slurry pH with good reduction of NH_3 emission. NH_3 emission was at the same level with soil injection of un-acidified slurry as acidified slurry applied by trailing hoses. In addition, we tested the development of some odorous compounds by covering the fields after application of un-treated or treated slurry with static chambers and measured the development of some odorous compound by PTR-MS. Hydrogen sulphide and methanethiol showed a rapid increase in concentration followed by a little slower decline ending in around 0 ppbv. The use of static chambers to evaluate development of odorous compounds cannot be recommended.

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