Ammonia and Trace Gas Emissions from Organic Fertilizers Amended with Gypsum

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Abstract

More than 2/3 of anthropogenic ammonia emissions (NH3) result from animal operations with most NH3 deriving from urea excreted from cattle and swine and uric acid from poultry. NH3 emissions are accompanied by emissions of nitrous oxide (N2O) and methane (CH4), trace gases with high impact on global warming and destruction of the stratospheric ozone layer. From experiments on paddy rice fields the inhibiting effect of sulfate on CH_4 emissions is known. In field trials as well negative correlations between N_2O emissions from soils and soils sulfate contents were found. From this correlations the possibility of emission reduction through sulfate was deduced. First experiments about the general influence of gypsum (calcium sulfate) on both NH3 and trace gas emissions from animal wastes were carried out. Emissions of these gases were measured in a lab experiment while broiler manure and liquid swine manure were stored in open vessels. Gas fluxes were measured daily with a multigas monitor. Contents of dry matter, NH_4-N, and total N were determined from the animal wastes.

After 10 days of storage cumulative emissions from liquid swine manure reached 2,350 g NH_3, 0.56 g N_2O, and 5,680 g CH_4 per kg dry matter at maximum. Reduction of N_2O and CH_4 emissions by addition of gypsum was as high as 62 % and 26 %, respectively.

From poultry manure cumulative fluxes after 10 days of storage were 487 g NH_3, 25 g N_2O, and 8,593 g CH_4 per kg dry matter at maximum. Reduction of NH_3 and CH_4 emissions was as high as 7 % both.

Emissions of N_2O and CH_4 were up to 45times higher from poultry manure than from liquid swine manure while emission of NH_3 was more than 5times higher from liquid swine manure than from poultry manure (emissions per kg dry matter).

Effects in reduction are related to the dry matter contents of the investigated materials and the dry matter dependent existence of anaerobic microsites. High reduction effects in liquid swine manure which derive from addition of gypsum may be caused by anaerobic CH4 oxidation and its connection to denitrifying processes including N_2O formation and anaerobic NH_3 oxidation. Above all, it seems to be possible to reduce NH3 and trace gas emissions from animal wastes by addition of gypsum.

Introduction

Because of the clean air acts SO_2 emissions in western Europe are decreased drastically (Dämmgen et al., 1998). Thus macroscopic sulfur (S) has become a major limiting factor for plant production in industrialized as well as remote rural areas (Schnug & Haneklaus, 1998). On the other hand recent research has shown that sulfate reduces CH4 formation because of substrat competition between sulfate reducing microorganisms and Methanogens (Corton et al., 2000; Wassmann et al., 2000; Gauci et al., 2004). Furthermore sulfate as part of sulfuric acid is used in waste air treatment systems to reduce NH3 emissions from animal housing (Hahne & Vorlop, 2001). Model (2004) has found a positive relation between nitrate sulfate ratio in soils and nitrous oxide emissions from organic farming systems. That means that the more sulfate in relation to nitrate is found the less N_2O is emitted.

With respect to all this positive impacts of sulfate in reducing gaseous emissions lab experiments were carried out to investigate the general influence of gypsum (calcium sulfate) on both NH3 and trace gas emissions from animal wastes. Gypsum is one of a few mineral fertilizers allowed to use in organic farming.

Methods

Experiment I - Material

Broiler manure (feces-litter-mixture) was taken from a broiler house with 29,000 animals at all at day 35 of fattening. 8 vessels with a volume of 65 liter each were filled with 2 kg of this mixture respectively. In four of them gypsum (50 g per kg mixture in one rate) was added. This two variants were examined over a period of two weeks.

Experiment II - Material

Liquid manure from fattening pigs was taken from a housing system with 8,000 animals at all. Two variants were examined with 100 Liter each over a period of four weeks. Gypsum was added with 12 g per kg liquid manure in three rates one day before starting the measurements and at day 8 and 22 of the investigation period.

Trace Gas Measurement

Broiler manure and liquid swine manure, respectively, were stored in open vessels which were closed only for gas measurement. Gas measurement was done with a multigas monitor three times per week at minimum. Cumulative gas fluxes were calculated in relation to the dry matter content of the feces-litter mixture for a period of 10 days of each experiment.

Results and Discussion

Experiment I

NH_3 emission rates ranged between 3.3 and 1.6 g per kg dry matter and day in both variants. The emission from gypsum amended variant was constant lower than from control variant at least up to 11 % (Figure 1A). Cumulative fluxes after 10 days of storage were 487 g NH_3 from control variant and 452 g NH_3 per kg dry matter from gypsum amended variant, respectively (Figure 3). Thus, reduction of NH_3 emission was as high as 7 %.

CH_4 emitted on a constant high level from the first untill the last day of the investigation period (Figure 1B). Emission rates ranged between 42 g and 31 g CH_4 per kg dry matter and day with constant higher rates from control variant (up to 9.2 % per day). Constant high emission rates indicate a full microbial activity untill the last day of measurement and thus the need for a longer investigation period. Cumulative fluxes after 10 days of storage were 8,593 g CH_4 from control variant and 7,977 g CH_4 per kg dry matter from gypsum amended variant (Figure 3). At least a reduction of CH_4 emission was observed as high as 7 %, too.

In opposite to NH_3 and CH_4 emissions highest N_2O emission rates were observed at the last two days of investigation period (Figure 1C). At least N_2O emission rates ranged between 102 and 89 mg per kg dry matter and day in both variants. Constant lower emission was observed from control variant (up to 14 % per day). 10 days after storage cumulative fluxes were 22 g N_2O from control variant and 25 g N_2O per kg dry matter from gypsum amended variant (Figure 3). In this case a reduction of N_2O emission was not observed.

It's important to notice that cumulative N_2O emission was orders of magnitude lower than CH_4 and NH_3 emissions, while NH_3 emission was only one order of magnitude lower than CH_4 emission. CH_4 and NH_3 emissions were highly positively correlated ($R = 0.884$, $p < 0.000$). On the other hand both CH_4 and NH_3 emissions were negatively correlated with N_2O emission ($R = -0.424$, $p < 0.001$ and $R = -0.404$, $p < 0.001$, respectively).

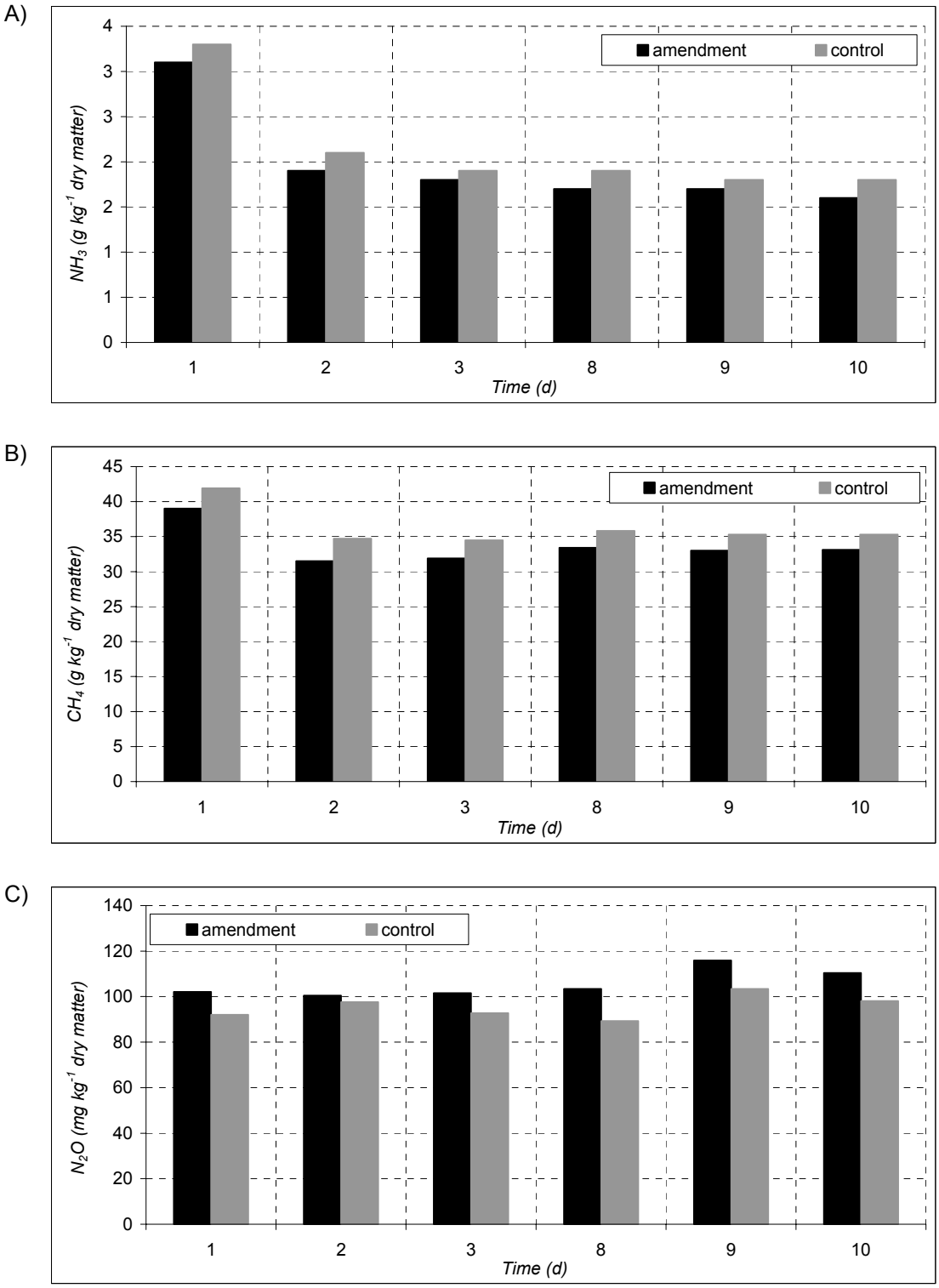

Figure 1: Gas fluxes from broiler manure

Experiment II:

With respect to results in Experiment I gas flux measurement was done over a period of four weeks now. In this period NH_3 emission rates ranged between 5.0 and 20.3 g per kg dry matter and day in both variants. Only the third rate of added gypsum led to constant lower emission rates from this variant in opposite to control variant (Figure 2A). The second rate of added gypsum induced only short term effect (day 8 in Figure 2A), and the effect of the first added rate was not measurable. So a clear reduction of NH_3 emission by addition of gypsum was not found. Hence the question arises, what is the most effective application rate and in relation to which parameters it is best calculated. Cumulative fluxes after 10 days of storage were 2.3 kg NH_3 from control variant and 2.4 kg NH_3 per kg dry matter from gypsum amended variant, respectively (Figure 3). That means that NH_3 emission from liquid swine manure was about five times higher than emission from broiler manure.

As like as with broiler manure CH_4 emission was constant lower from gypsum amended variant (up to four times at day 23, see Figure 2B). In opposite to NH_3 emission the effect of added gypsum is clearly to be seen. Each first day after addition (day 1, 9, and 23 in Figure 2B) the difference between emissions from both variants is greatest and than reduces with time. At the end of the whole measuring period the reduction of CH_4 emission by addition of gypsum was as high as 27 % (8.1 kg in opposite to 11.0 kg CH_4 per kg dry matter). After 10 days of storage cumulative fluxes reached 5.7 kg CH_4 from control variant and 4.2 kg CH_4 per kg dry matter from gypsum amended variant (Figure 3). That means that CH_4 emission from liquid swine manure was nearly two times lower than from broiler manure.

In this experiment negative N_2O emission rates were calculated. In a first step technical problems in gas measurement could be excluded. In a next step it must be investigated if N_2O uptake into the manure or N_2O consumption could take place under lab conditions. Emission rates ranged between -10.5 mg and 70.0 mg N_2O per kg dry matter in both variants. With exception of the last two days the emission from gypsum amended variant was lower than from control variant. In cases of calculated N_2O consumption this was constant higher in gypsum amended variant. At the end of the whole measuring period the reduction of N_2O emission by addition of gypsum was as high as 71 % (2.5 g in opposite to 8.7 g N_2O per kg dry matter). After 10 days of storage cumulative fluxes reached 0.56 g N_2O from control variant and –0.21 g N_2O per kg dry matter from gypsum amended variant. That means that N_2O emission from liquid swine manure was negligible in comparison with broiler manure (Figure 3).

As like as with broiler manure cumulative N_2O flux was orders of magnitude lower than CH_4 and NH_3 emissions, while CH_4 and NH_3 were emitted in the same order of magnitude. CH_4 and NH_3 emissions were negatively correlated in this experiment ($R = -0.621$, $p < 0.000$). No correlation was found between CH_4 emission and N_2O flux. On the other hand N_2O and NH_3 fluxes were slight negatively correlated ($R = -0.316$, $p < 0.001$).

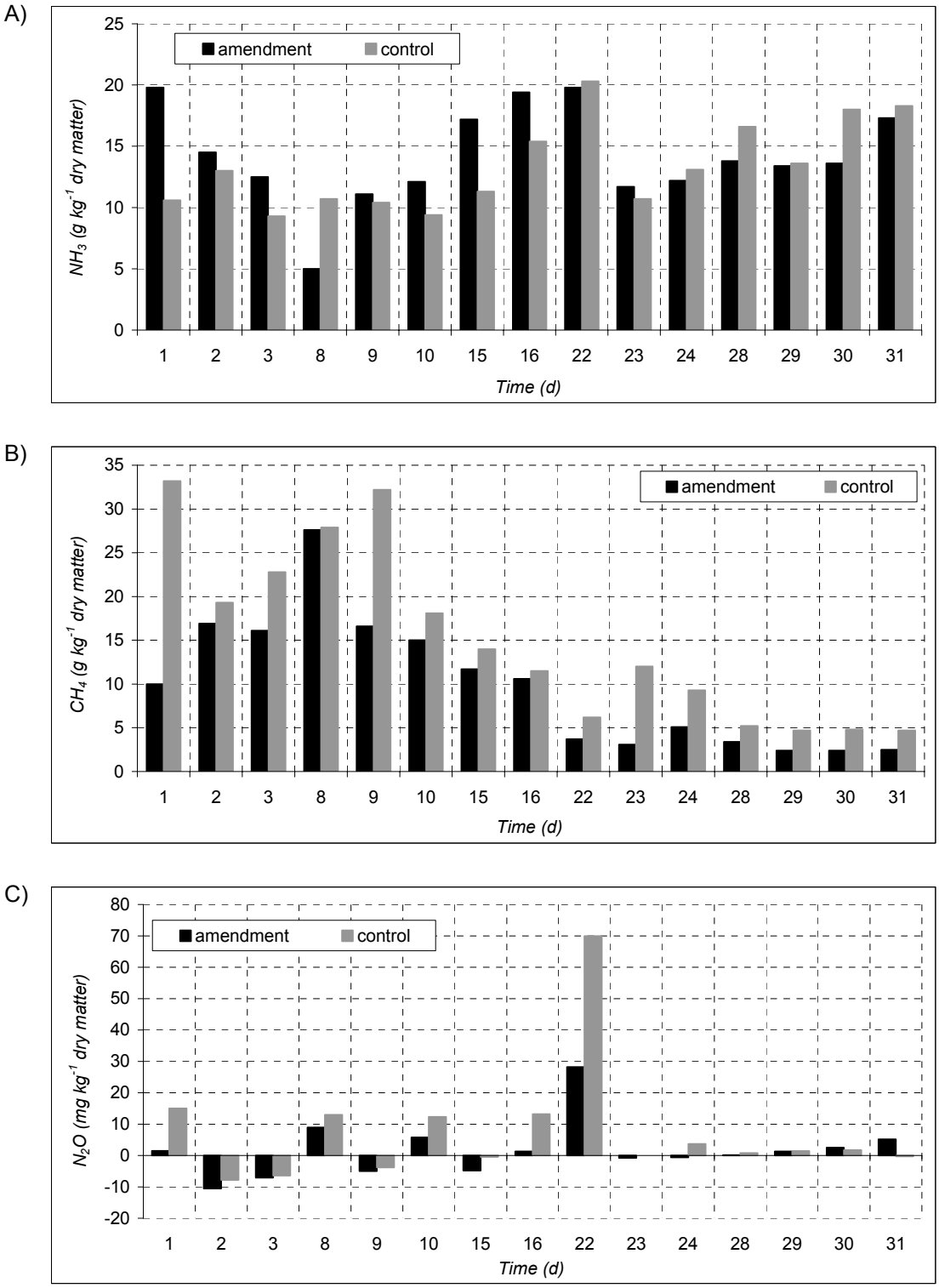

Figure 2: Gas fluxes from liquid swine manure

Comparison between both experiments:

Data from CH_4 emission measurements are in good agreement with results described by Gauci et al. (2004) and Dise & Verry (2001). Both found a reduction of methane emission in sulfate amended plots (up to 30 %). Lower CH_4 fluxes as well as lower N_2O fluxes from liquid swine manure might be caused by anaerobic CH_4 oxidation and its connection to denitrifying processes including N_2O formation. Anaerobic CH_4 oxidation was described by Nauhaus et al. (2002) in marine sediments. Model (2004) describes the possible connection between anaerobic CH_4 oxidation and N_2O formation for slurry treated soils. Because of more aerobic conditions in the broiler manure this processes might not occur with the same intensity as under anaerobic conditions in liquid swine manure. Higher NH_3 emissions from liquid swine manure are because of the higher NH_4-N content than in broiler manure (4.2 g in opposite to 2.9 g per kg manure). Independent of single results the experiments indicate the generell capability of reducing gaseous emissions from manure by addition of gypsum.

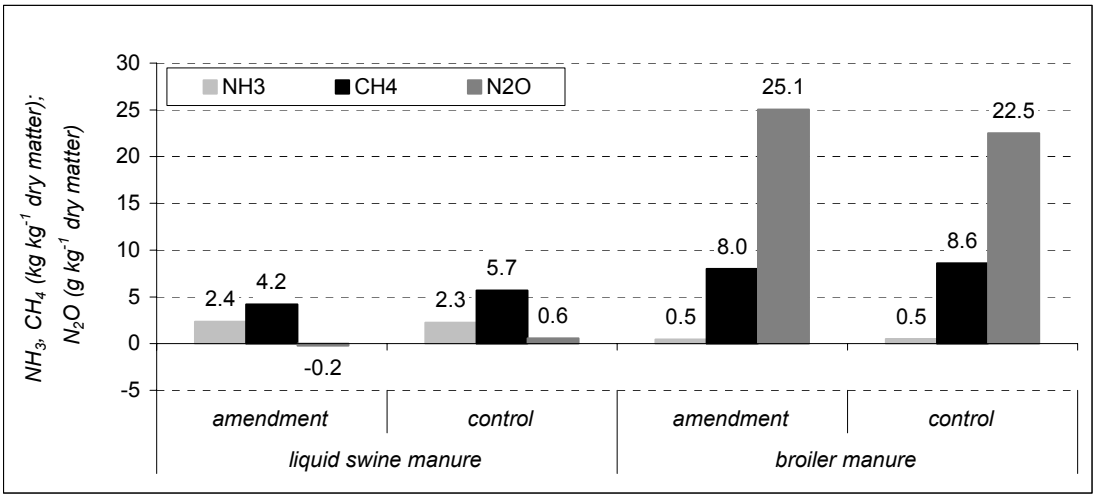

Figure 3: Cumulative gas fluxes from liquid swine manure and broiler manure 10 days after storage (take care of the different dimensions at y-axis)

Conclusions

There are already a number of investigations on mitigation strategies with most of them focussing on one gas only. They neglect the fact, that conditions reducing the emission of one trace gas might have a directly opposed effect on another (Wulf et al., 2001). By addition of gypsum it seems to be possible to reduce NH3 as well as trace gas (CH_4, N_2O) emissions from animal wastes. In further experiments it is necessary to find out optimum application rates and conditions to provide best impact of sulfate addition.

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