Ammonia emissions from field applied digestates and related cross media effects

Döhler Helmut[1], Möller Kurt[1], Sebastian Wulf[1]
(1) KTBL, Association for Technology and Structures in Agriculture, 64289 Darmstadt, DE
**Corresponding author: h.doehler@ktbl.de*

Abstract
Anaerobic digestion (AD) leads to changes in the composition of animal manures, which are relevant for manure carbon and nitrogen turnover after field application. Already in the mid-eighties and in recent years an increasing number of experiments were carried out to assess the effects of digestate application on emissions. AD leads to a higher pH and ammonium content in digestates, which counteracts the effects of the decreased viscosity on ammonia volatilization, due to the lower dry matter content. Most studies indicated a high potential for N_2O emissions during handling of digestates, however lower soil N_2O emissions after field application can be expected due to the lower biodegradability of digestates.

Introduction
Anaerobic digestion (AD) for biogas production leads to several changes in the composition of the resulting digestates compared to the original feedstock (ammonium content, pH, carbon to nitrogen ratio, etc.), which are potentially relevant for gaseous emissions of ammonia and for other N species. This review discusses the current state of knowledge on the effects of AD on organic compounds in digestates and the most important processes influencing N emissions in the field.

Material and Methods
A compilation of the available information and data on the effects of AD on manure characteristics and fertilizer effects from laboratory and field trials was carried out, including publications in peer-reviewed journals as well as in "grey literature".

Results
Impact of AD on ammonia volatilization from field applied manures
From German research of the eighties it is known, that digestates (biogas slurry digestate from mono-digestion of manure) show higher ammonium (NH_4^+):total nitrogen (N) ratios, decreased organic matter contents, decreased total and organic carbon contents, reduced biological oxygen demands, elevated pH values, smaller carbon to nitrogen ratios, and reduced viscosities than undigested animal manures [1] [2] [3]. It is further known, that the release of ammonia from manure and is not significantly different. Two research groups determined for cattle biogas slurry slightly higher losses after fermentation (29% instead of 24% and 37% instead of 33% NH_3-N losses relative to the applied TAN), in a further experiment something higher losses in the raw slurry. The tests for swine manure rendered in any case lower release rates in the biogas slurry. Due to the higher pH of the biogas slurry changed kinetics so that the release was increased shortly after application of fermented manure compared to the raw slurry. Due to the more fluid consistency and therefore more rapid and deeper infiltration into the soil, the cumulative NH_3 emission rates were somewhat lower [1] [2] [3].
Contradictory results regarding the effects of AD on ammonia volatilization have been reported later in literature: Some researchers report a decrease of ammonia losses after AD of animal manures, others report an increase of losses, and others did not found any effect or ambiguous effects (Table 1). Other research groups compared volatilization after spreading of undigested slurry and a digestate derived from slurry plus other feedstocks[4] [5], an approach which did not allow for the assessment of the effect of AD on NH_3 volatilization itself. In two of the cited publications digestates were used which lost considerable amounts of N during AD or the following manure storage, a situation which does not match current state of the art, and probably reduced the NH_3-losses after digestate field spreading. From the cited investigations it became obvious that the higher pH and ammonia content in digestates counteracts the effects of the decreased viscosity.

Reliable NH_3 emission estimates could potentially be derived from mathematical models based on the physico-chemical processes controlling NH_3 volatilization from manures and their interactions with soil, canopy and atmospheric variables. Gericke et al. [6] modeled ammonia volatilization after digestate field application using a linear model. According to their model, a change of the temperature by +1 K or of the pH by +0.1 pH units ammonia volatilization will increase by about 1% or 1.6% of the total applied NH_4^+-N, respectively. However, the increasing dissociation of NH_4 + to NH_3 ($H_3O^+ + NH_3 \leftrightarrow H_2O + NH_4^+$) with increasing pH is an exponential function, and the acid dissociation constant (pKa) of NH_4^+/NH_3 is 9.25. The pH range considered in their measurements ranged between 6.9 and 7.7 and total ammonium- N ranged between 1.75 and 2.72 kg NH_4^+-N Mg^{-1} [6]. Digestates can have considerable higher NH_4^+-N concentrations of up to 6.8 kg Mg^{-1} and pH values up to 9 [7]. Therefore, the model of Gericke et al. (2012) is an approach to assess ammonia losses in a pH range of most digestates available in practice (e.g. with cattle slurry or silage maize as feedstocks), but it is probably not able to assess NH_3-losses from digestates with very high NH_4^+-N concentrations, which are simultaneously characterized by very high pH values (e.g. digestates from poultry or/and pig manures, cereal grains, kitchen wastes and other digestates derived from N rich feedstocks with a high bio-degradability). The combination of both characteristics strongly increases the potential for ammonia losses. There are only very few publication available about the combination of AD with other treatments (separation, acidification, flocculation, etc.) on ammonia volatilization after field application.

Table 1: Effects of AD on ammonia N losses after surface application of digestates [4] [5] [9] [10] [11] [12] [13]

feedstocks used	further sources of variation in the experimental design	application rates based on equivalent	effects on NH_3 volatili-zation (%) [1)]	reference
decanted pig slurry	no	total N total NH_4^+- N	- 0.9 (- 4.7) - 2.5 (- 9.7)	Chantigny et al., 2007
pig slurry	no	total N	-2.5 (- 16.5)	Chantigny et al., 2009
pig slurry	no	amounts of fresh matter	no significant	Chantigny et al., 2004
cattle slurry	no	total N amount	+ 1.2 (+ 9,2)	Möller and Stinner, 2009
cattle & pig slurry + others	reference treatments did not meet feedstocks for AD	total N amount	+10 (+71)	Ni et al., 2012
cattle slurry	NH_4^+-N losses during AD, before field application	amounts of fresh matter	no significant	Pain et al., 1990
cattle slurry	NH_4^+-N losses during AD, before field application	total NH_4^+- N total N	- 4.0 (11.6) +2.0 (+10.3)	Rubæk et al., 1996
cattle slurry & urban bio-wastes	reference treatments did not meet feedstocks for AD	total NH_4^+- N	arable land: + 5.0 (14.7) grassland: + 13.0 (33.3)	Wulf et al., 2002a
pig slurry	separation of liquids and solids before AD	total N total NH_4^+- N	- 4.2 (- 18.8) - 10.6 (- 31.2)	Chantigny et al., 2007

Impact of anaerobic digestion on N_2O emissions from field applied manures

Due to the decomposition of the easily degradable C compounds during AD, the viscosity of manures becomes lower and the amounts of easily degradable C added to the soil decreased considerably. Consequently, less anoxic microsites, favorable for denitrifying activities, might emerge and it can be assumed that AD will reduce N_2O emissions after manure field spreading. Another hypothesis is that treatment technologies reducing the viscosity (e.g. due to degradation of organic matter) have the potential to reduce N_2O emissions, as dissolved C and N are dispersed into a larger soil volume, changing the balance between aerobic and anaerobic decomposition [13]. Most of the available studies confirmed lower N_2O emissions after digestate application in comparison to undigested feedstocks. However, there are also some contradictory results. A negative relationship was found [14] between soil respiration and the N_2O molar ratio, demonstrating that C availability in soil promotes the reduction of N_2O to N_2. This is in line with a conceptual model by [15] which considers the ratio between O_2 supply and O_2 consumption as the main driving variable for changing N_2/N_2O -ratios. Therefore, effects of a manure treatment, that affects its biological and chemical oxygen demand, as manure separation or AD, will depend on soil conditions at the time of application. In a relatively dry or inactive soil an increase of the N_2O fluxes can be expected by a slurry treatment such as AD, whereas a net decrease would result if the treated manure is applied to a soil where conditions are already conducive to denitrification, leading to an enhanced N_2O reduction to N_2 (and thus to a higher

N_2/N_2O ratio). Furthermore, some of the results published indicate an interaction of the effects of AD with soil properties (table 2).

From a methodological point of view it must be highlighted that most of the available studies measured N_2O emissions for a relatively short period after manure application and showed that N_2O emission was highly variable, whole year inventories are rare. Whole year inventories indicated that most soil N_2O fluxes occurred within 20-40 d of treatment application [16] [17] [18]. For an assessment of system change related effects whole year inventories are mandatory. Some studies compared AD treated materials with the raw undigested feedstock but they also introduced further variations into the experimental design (e.g. addition of further feedstocks to the manure for AD, separation before or after AD, etc.), which did not allow for the assessment of the effect of AD itself.

Table 2: Overview of the experiments about the effects of AD on soil N_2O emissions [14] [15] [16] [17] [18] [19] [20] [21] [22] [23]

feedstocks used for AD	further sources of variation in the experimental design	field application technique	duration of inventory	effects on N_2O emissions (%) [1)]	reference
	no	surface application	whole year	- 12.3 (n.s.)	Schauss et al., 2006;
cattle slurry	no	injection	44 days	no effect	Thomsen et al., 2010
cattle slurry	no	soil incorporation	whole year	- 18.0 (n.s.)	Schauss et al., 2006
cattle slurry	no	injection	35 days	+ 126	Möller & Stinner, 2009
cattle slurry	no	injection	21 days	- 36.0	Rubæk et al., 1996
cattle slurry	no	surface application (trail hose)	21 days	- 85.3	Rubæk et al., 1996
cattle slurry	soil water content	incubation experiments	8 days	- 60.2 (sign. Interaction with soil water content)	Clemens & Huschka, 2001
cattle slurry	no	surface application (trail shoe)	whole year	+ 4.9 (n.s.)	Clemens et al., 2006
pig slurry	no	surface application	21 days	loamy soil: -62.5 sandy soil: -51.7	Chantigny et al., 2007
pig slurry	soil type	band incorporation	whole year	clay: + 8.0 (n.s.) loam: - 21.1 (n.s.)	Chantigny et al., 2010
pig slurry	no	soil incorporation in mesocosm study	58 days	- 64.5 (n.s.)	Bertora et al., 2008
slurry from local farms and industrial waste products	reference treatment did not meet feedstocks for AD	soil incorporation	growing season	- 20.0	Petersen, 1999
pig slurry	digestate solid/liquid separation before AD	surface application	growing season	- 23.9	Vallejo et al., 2006
cattle slurry & green manures & field residues	incorporation of field residues in autumn, return of digestates mainly in late winter	surface application	whole year	- 41.3	Schauss et al., 2006
green manure crops and field residues	incorporation of green manures and field residues in autumn, return of digestates mainly in late winter and spring	soil incorporation/ surface application	whole year, entire crop rotation	- 37.6	Möller & Stinner, 2009
green manure crops	harvesting/mulching of green manures in summer, return of digestates in spring	not described	whole year	- 21.9 (n.s.)	Nadeem et al., 2012
cattle slurry	no	soil incorporation/ surface application	growing season	- 26.2	Collins et al., 2011
cattle slurry & urban biowastes	reference treatments did not meet feedstocks for AD	trail hose application	42 days	arable land: n.s. grassland: + 91	Wulf et al., 2002b
pig slurry	no	surface application	whole year	- 35.1 to - 49.9 [1)]	Lemke et al., 2012
silage maize	reference treatment (cattle slurry) did not meet feedstocks for AD	trail hose	growing season	+ 11.1 (n.s.)	Senbayram et al., 2009
cattle slurry and industrial waste products	reference treatments did not meet feedstocks for AD, and solid-liquid separation after AD	soil incubation	29 days	+ 440	Saunders et al., 2012

Conclusions

Increased NH_4^+-N content in digested slurries compared to undigested slurries and increased pH values do not necessarily lead to higher ammonia emissions. The pattern of ammonia losses however is different, indicating higher loss rates after spreading compared to slurries. Since the losses often exceed 30 % of the applied ammonium-N, generally emission abatement measures has to be taken in to account. Below ground injected digestates show lower ammonia, but increased denitrification losses. The extent of N_2O-losses is variable and needs further to be analysed by research work.

References

[1] Döhler, H.; Haring, F. (1989): Ammoniakverluste nach der Gülleausbringung in Abhängigkeit von Boden und Ausbringungstermin. *Poster DBG-Tagung September 1989.*

[2] Döhler, H; Horlacher D.: 2011. Ammoniakverluste nach der Ausbringung organischer Dünger. In: Emissionen landwirtschaftlich genutzter Böden; KTBL-Schrift 483.

[3] Meßner, H. (1988): Düngewirkung anaerob fermentierter und unbehandelter Gülle. Dissertation, TU München.

[4] Wulf, S., Maeting, M., Clemens, J., 2002. Application Technique and Slurry Co-Fermentation Effects on Ammonia, Nitrous Oxide, and Methane Emissions after Spreading: II. Greenhouse Gas Emissions. J. Environ. Qual. 31, 1795–1801.

[5] Ni, K., Pacholski, A., Kage, H., 2012. Analysis of ammonia losses after field application of biogas slurries by an empirical model. J. Plant Nutr. Soil Sci. 175, 253-264.

[6] Gericke, D., Bornemann, L., Kage, H., Pacholski, A., 2012. Modelling Ammonia Losses After Field Application of Biogas Slurry in Energy Crop Rotations. Water Air Soil Pollut 223, 29–47.

[7] Möller, K., Müller, T., 2012. Effects of anaerobic digestion on digestate nutrient availability and crop growth: a review. Engineering in Life Sciences 12, 1-16.

[8] Chantigny, M.H., Rochette, P., Angers, D.A., Massé, D., Côte, D. 2004. D., Ammonia volatilization and selected soil characteristics following application of anaerobically digested pig slurry. Soil Sci Soc Am J 68, 306–312.

[9] Chantigny, M.H., Angers, D.A., Rochette, P., Belanger, G., Massé, D.I., Côté, D., 2007. Gaseous nitrogen emissions and forage nitrogen uptake on soils fertilized with raw and treated swine manure. J. Environ. Qual. 36, 1864–1872.

[10] Chantigny, M.H., MacDonald, J.D., Beaupré, C., Rochette, Ph., Angers, D.A., Massé, D., Parent, L.E.,2009. Ammonia volatilization following surface application of raw and treated liquid swine manure. Nutr Cycl Agroecosyst 85, 275–286.

[11] Möller, K., Stinner, W. 2009. Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and on gaseous nitrogen losses (ammonia, nitrous oxides). European Journal of Agronomy 30, 1-16.

[12] Pain, B.F., Misselbrook, T.H., Clarkson, C.R., Rees, Y.J., 1990. Odour and Ammonia Emissions Following the Spreading of Anaerobically-Digested Pig Slurry on Grassland. Agric. Wastes 34, 259-267.

[13] Rubæk, G.H., Henriksen, K., Petersen, J., Rasmussen, B., Sommer, S., 1996. Effects of application technique and anaerobic digestion on gaseous loss from animal slurry applied to ryegrass (*Lolium perenne*). J. Agric. Sci., Camb. 126, 481-492.

[14] Petersen, S.O., Lind, A.-M., Sommer, S.G., 1998. Nitrogen and organic matter losses during storage of cattle and pig manure. J. Agric. Sci. 130, 69–79.

[15] Miller, M.N., Zebarth, B.J., Dandie, C.E., Burton, D.L., Goyer, C., Trevors, J.T., 2009. Influence of Liquid Manure on Soil Denitrifier Abundance, Denitrification, and Nitrous Oxide Emissions. Soil Sci. Soc. Am. J. 73, 760-768.

[16] Thomsen, I.K., Pedersen A.R., Nyord, T., Petersen., S.O., 2010. Effects of slurry pre-treatment and application technique on short-term N2O emissions as determined by a new non-linear approach.

[17] Schauss, K., Ratering, S., Stinner, W., Deuker, A., Möller, K., Schnell, S., 2006. Auswirkungen auf die bodenbürtigen Distickstoffoxid- und Methanemissionen. In: Möller, K. et al. (eds.) Auswirkung der Fermentation biogener Rückstände in Biogasanlagen auf Flächenproduktivität und Umweltverträglichkeit im Ökologischen Landbau. Final report, available at: http://orgprints.org/10970/, pp. 169- 240.

[18] Chantigny, M.H., Rochette, P., Angers, D.A., Bittman, S., Buckley, K., Massé, D., Belanger, G., Eriksen-Hamel, N., Gasser, M.O., (2010): Soil nitrous oxide emissions following bandincorporation of fertilizer nitrogen and swine manure. J. Environ. Qual. 39, 1545-1553.

[19] Clemens, J., Trimborn, M., Weiland, P. and Amon, B., 2006. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. Agriculture, Ecosystems & Environment 112, 171-

[20] Bertora, C., Alluvione, F.,, Zavattaro, L., van Groenigen, J.W., Velthof, G., Grignani, C., 2008. Pig slurry treatment modifies slurry composition, N2O, and CO2 emissions after soil incorporation. Soil Biology & Biochemistry 40, 1999–2006.

[21] Petersen, S.O., 1999. Nitrous oxide emissions from manure and inorganic fertilizers applied to spring barley. J. Environ. Qual. 28, 1610–1618.

[22] Vallejo, A., Skiba, U., García-Torres, L., Arce, A., López-Fernández, S., Sánchez-Martín, L., 2006. Nitrogen oxides emission from soils bearing a potato crop as influenced by fertilization with treated pig slurries and composts. Soil Biol. Biochem. 38, 2782–2793.

[23] Collins, H.P., Alva, A.K., Streubel, J.D., Fransen, S.F., Frear, C., Chen, S., Kruger, C., Granatstein, D., 2011. Greenhouse gas emissions from an irrigated silt loam soil amended with anaerobically digested dairy manure. Soil Sci Soc Am J 75, 2206-2216.

[24] Lemke, R.L., Malhi, S.S., Selles, F., Stumborg, M., 2012. Relative effects of anaerobically-digested and conventional liquid swine manure, and N fertilizer on crop yield and greenhouse gas emissions. Agricultural Sciences 3, 799-805.