

Ammonia emissions during post treatment of anaerobic fermented biomass

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Introduction

Due to the upcoming energy crises, production of bioenergy from different biomass sources gains more and more importance. Anaerobic treatment is one possibility for bioenergy generation. In Germany, the numbers of anaerobic treatment plants are increasing these years. These plants mainly treat agricultural residues, but also energy crops and partly municipal (mixed or organic) residues. This development has been encouraged by the German governmental, supporting energy production from renewable resources (EEG, 2004).

Problems resulting from waste nitrogen (N) during or subsequent to anaerobic treatment were reported e.g. by Fricke et al. 2007. In this paper the ammonia emissions (NH_3), which occurred during composting of the anaerobic treated biomass were investigated. The paper focuses on the fate of $\text{NH}_3\text{-N}$ during post-treatment of digestion residues by composting, because NH_3 can cause environmental problems.

Environmental Impacts of Ammonia

NH_3 develops predominantly as a consequence of intensive animal husbandry and of fertiliser application. Industrial NH_3 -emissions mainly result from the manufacture of NH_3 , N-containing fertiliser and soda, as well as from brown coal coking. Further sources are combustion processes in industry, in transportation and in households (UBA, 1994; Starmans and Van der Hoek, 2007). But NH_3 can also be generated during biological treatment of agricultural, municipal and industrial waste.

NH_3 may lead to several negative environmental impacts, which are caused by the odorous and toxic properties of NH_3 . Odours cause strong nuisance in the surrounding of the emission source. Furthermore, from the NH_3 derived NH_4^+ can lead to acidity in soil. This can lead to plant damage and assist in the leaching of cations (Bahadir *et al.*, 1995). In water, NH_4^+ can lead to the disruption of the biological equilibrium and contribute, among other things, to the death of plants, animals and microorganisms, or force the development of alien organisms. Direct organism damage can be caused through the toxicity potential of NH_3 (Schuurkes *et al.*, 1985; Fabry *et al.*, 1990).

Since NH_3 can act as a nutrient, it may also lead to water pollution and over-fertilisation. In water it can provoke eutrophication. Eutrophication may result in oxygen depletion, so that oxygen-reliant creatures such as fish are deprived of their basic needs for life. In general eutrophication may be leading to a biodiversity loss (Fabry *et al.*, 1990, Bahadir *et al.*, 1995, Martinez *et al.*, 2007). Besides direct effects, ammonia may transform in the environment easily to other N-compounds. An example is nitrate (NO_3^-). NO_3^- can become problematic if it reaches drinking waters (Conrad, 1992). An other example is N_2O , which may be generated as intermediate product of denitrification. This can contribute to the climate change (UBA, 1994; Körner, 2008).

The ammonia issue is also addressed by political measures on air pollution. At international level, the UNECE "Protocol to Abate Acidification, Eutrophication and Ground-level Ozone"

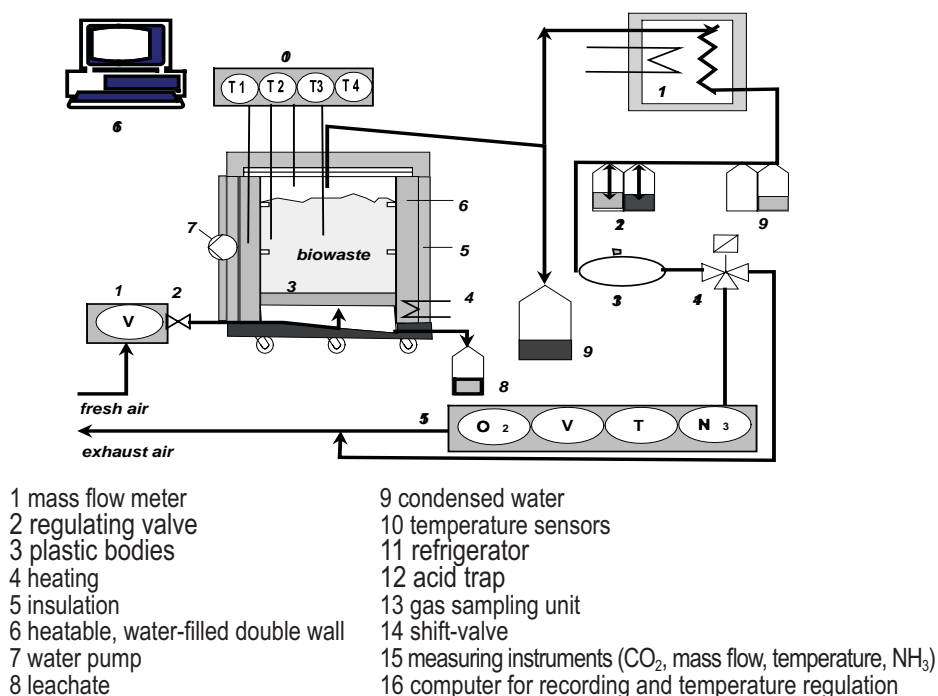
(also known as Gothenburg Protocol) entered in force in 2005. The main signatories are the European Community, the European countries, the United States of America and the Russian Federation (the last one having not ratified the protocol yet). The protocol fixes national annual emissions targets for different gases including NH_3 to be reached by 2010. On this basis, the 2001 NEC-directive (directive 2001/81/EC of the European Parliament and of the Council) also fixes national emissions ceilings to be reached by 2010. The target values are at the same level as documented in the Gothenburg Protocol (except for Portugal). The NEC-directive is currently in the process of implementation (Martinez *et al.*, 2007).

Material and Methods

The emissions of NH_3 during composting which took place immediately after anaerobic digestion (Exp. 1 a, b) were studied in comparison to sole composting of similar model substrates (Exp. 2 a, b). Furthermore a digestate from an anaerobic fermentation plant was composted (Exp. 3 a, b). The NH_3 emissions were studied in the context of the overall N-balance. 6 series of N balances were established (Figure 2 a-g). These included NH_3 exports, N leaching as well as the different proportions of N compounds in the substrate. The investigations were carried out in pilot plant scale in 100 litre reactors. The following approaches were studied:

- Exp. 1 a,b) N dynamics during a mesophilic and a thermophilic anaerobic fermentation stage with subsequent treatment through composting; substrate: model waste which simulated separately collected kitchen waste.
- Exp. 2 a,b) N dynamics during sole composting; substrate: model waste which simulated separately collected kitchen waste.
- Exp. 3 a,b) N dynamics during post-treatment by composting; substrate: digestates from an anaerobic dry-fermentation plant.

Figure 1. Set-up of composting unit: Bioreactor with periphery equipment



A well equipped technical scale biological treatment unit with 100 L reactors was used. Figure 1 shows the schematic for the unit, which allowed the simulation of aerobic and anaerobic processes with operating controls common to those in a real scale facilities: anaerobic digestion - temperature regulation, water recirculation; composting - aeration, moistening, turning. The system is described in more detail in Körner (2008).

The exhaust air was drawn off and led into tubes. It was cooled by ambient temperature and by a refrigerator (11). The condensed water was collected. The air stream was subsequent conducted through bottles with the scrubbing solution 0.5 n H₂SO₄ (12) to remove the remaining ammonia from the exhaust air.

In Exp. 1 a,b and 2 a,b,c quite similar, well defined model waste (consisting of following components: apples, potatoes, turnips, wheat, peas, meat and bone meal, wood, sand, lime) were applied. They had a very similar composition. To introduce methanotrophic organisms in Exp. 1 a,b additionally a digestate from an anaerobic fermentation plant was added. The same digestate was used in Exp. 3 for composting as a single substrate (Exp. 3 a) or with addition of wood chips for structure improvement (Exp. 3 b). The initial composition of the substrates is documented in Table 1.

Table 1: Composition of the waste used in the experiments

Experiment	Apple	Potato	Turnip	Wheat	Pie	Meat meal	Wood	Sand	Lime	Di-gestate
	% dm (dry matter)									
1 a b	6.1	4.6	3.4	34.1	12.6	1.4	11.0	12.0	7.3	7.5
2 a b c	6.8	5.1	3.2	43.4	16.3	1.9	14.7	0	8.6	0
3 a	0	0	0	0	0	0	0	0	0	100.0
3 b	0	0	0	0	0	0	18.0	0	0	82.0

Samples of the substrate were taken at the begin and the end of the anaerobic phases (Exp. 1 a,b). Furthermore sampling took place during turning in the composting phases (all experiments). The sampling day can be recognized in Fig. 2 by a bend in the devolution of the graphs. For turning that purpose the reactor was emptied by means of a toppling unit and refilled with the substrate previously mixed. Absolute mass losses of substrate during the different treatment phases were determined by a balance used for the whole reactor.

Table 2: Process conditions used in the experiments

Experiment	1a	1b	2a	2b	2c	3a	3b
<i>Anaerobic Phase</i>							
Treatment Time (d)	21	21	0	0	0	~210	~210
Temperature	35	55	-	-	-	~350	~350
<i>Composting Phase</i>							
Composting time (d)	155	155	168	168	168	77	77
Aeration rate (L/h)	100-150 ¹	150 ²	80	150	280	150 ³	150 ⁴
	0	0				30	30

0 - approximate treatment time and temperature of the waste in the anaerobic plant, where the digestate was delivered from;

¹ - till composting day 57; ² - till composting day 100;

³ - till composting day 21; ⁴ - till composting day 35.

Table 2 shows the spectrum of implemented process parameters for all experiments. In Exp. 1 a, b the biological treatment started with an anaerobic phase, which was mesophilic in Exp. 1 a and thermophilic in Exp. 1 b. For that purpose, reactors were airtight closed and

biogas collected in gasbags. In Exp. 2 a, b and c composting started from the begin, using variable aeration rates in the three experiments. In Exp. 1 a, b a subsequent aeration was used after finalizing the anaerobic phase to start post-composting. The used aeration rate was comparable to aeration rates in Exp. 2 b. The process control in Exp. 3 a and b varied as far as substrate structure is concerned. There the anaerobic phase was carried out in a technical scale facility (dry fermentation system). In the lab scale facility (Figure 1) only the post-composting of the digestate was carried out.

Substrate samples were analysed with respect to organic N, $\text{NH}_4^+/\text{NH}_3$, NO_3^- , NO_2^- , pH, water content, content on volatile solids. The liquid samples (condensate, acidic scrubbing solutions, leachate) were also analysed with respect to their N-compounds. The results from the condensate and acidic scrubbing solutions analytics were used to calculate NH_3 -emissions.

Temperature profiles, water contents, CO_2 -development and pH values before, during and at the end of the treatment were measured, but not used in this publication.

The experimental set-up of the pilot plant with its 100 l-bioreactors, the measurement technique and the chemical analysis methods used as well as the calculations to determine the NH_3 emissions and the N balances were described in more detail in Körner (2008).

Results und Discussion

The NH_3 emissions were significantly higher in the cases with anaerobic treatment and post-composting (Exp. 1a, b: 69, 85 % of the initial N) than during sole composting (Exp. 2a, b: 40-54 % of the initial N). During anaerobic fermentation proteins are converted into $\text{NH}_4^+/\text{NH}_3$ through ammonification. The $\text{NH}_4^+/\text{NH}_3$ accumulated in the substrate was stripped from digestate with the beginning of post-treatment by composting. During ongoing composting, further NH_3 was stripped. This was delivered from waste-proteins which were further ammonified. Ammonification proceeded in parallel with further substrate degradation.

When comparing the mesophilic (Exp. 1a) and the thermophilic anaerobic fermentation stage (Exp. 1b), the thermophilic variant showed higher emissions. The reason for this observation can be found in the fact that at the beginning of post-treatment by composting, the pH value of the substrate increased rapidly. After 2 weeks of composting it was 7.1 in Exp. 1a and 8.1 in Exp. 1b. The high pH shifted the equilibrium between NH_4^+ and NH_3 more into the direction exportable NH_3 . Furthermore, a noticeable influence of the temperature could be ascertained. Up to the 5th week of composting, the average temperature in the Exp. 1a was 50°C, in Exp. 1b 61°C.

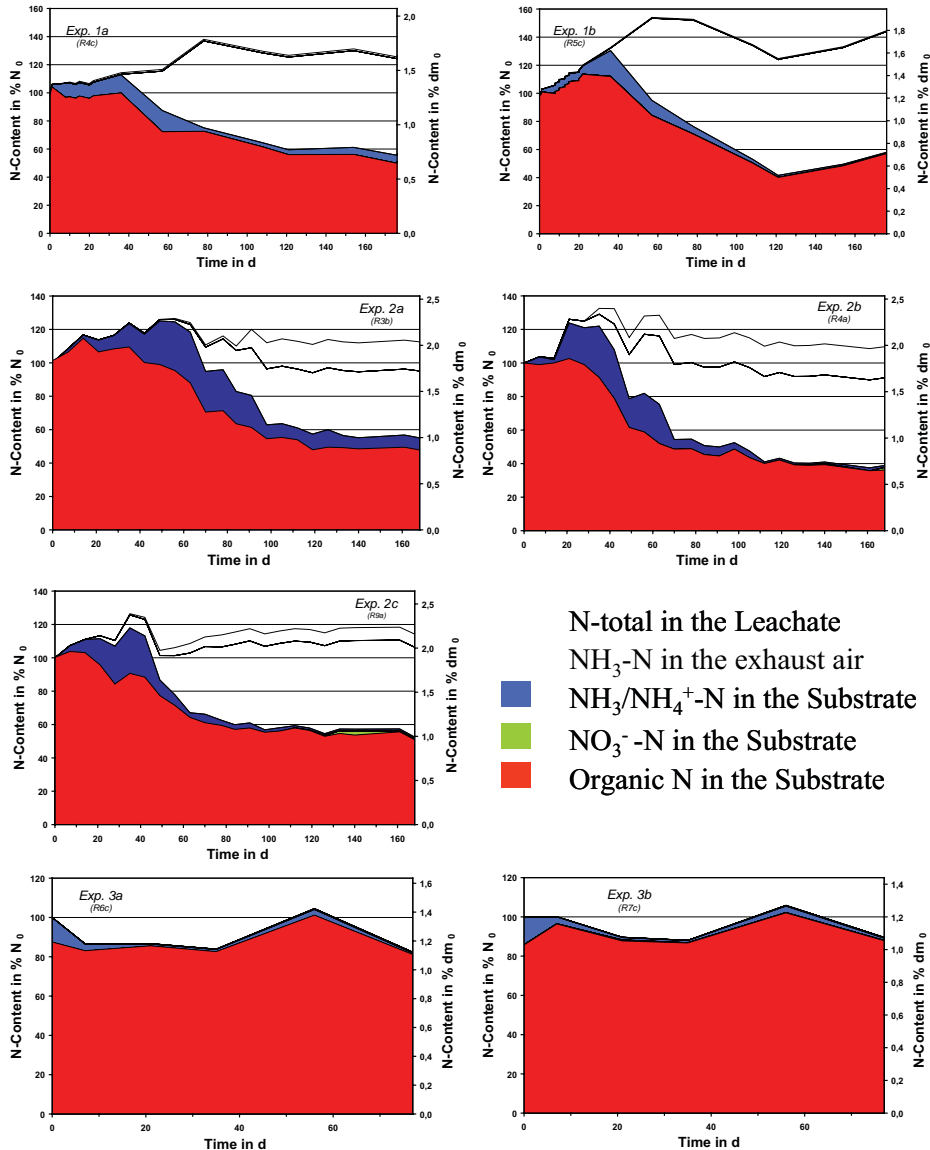
In the composting experiments 2 a,b,c the highest NH_3 -emission was detected for the aeration rate of 150 L/h (Exp. 2b). In the other experiments it was lower due to following reasons: In the composting experiment with the low emission rate (Exp. 2 a) the average temperature and pH was lower than in Exp. 2b due to a oxygen deficit.

The mean values for temperatures and pH during the thermophilic phase were as follows: Exp. 2a – 59°C, 7.6; Exp. 2b - 64°C, 7.8 All 3 factors were responsible for the reduced NH_3 -emissions (NH_3 -emission model: Körner, 2008). In the composting experiment with the high emission rate (Exp. 2 c) developed dry zones which inhibited microbial degradation and therefore the delivery of NH_3 from the proteins. The mean water contents during the experimental phases were 62 % vs. 47 %.

During the Exp. 3 a,b no NH_3 -emissions could be detected during post-composting. The reason was, that the $\text{NH}_4^+/\text{NH}_3$ was already lost as NH_3 during a storage step. Before the

digested material was introduced into the reactor, it was stored at the site of the digestion facility in a pile. During storage probably some NH_3 did get lost. In the digestate the $\text{NH}_4^+/\text{NH}_3$ content was above 10 % of the total N. The N-immobilization can be ascribed to the development of aerobic microorganisms with the beginning aeration (incorporation into microbial biomass). With the begin of composting, this content was reduced due to N-immobilization into the organic substance. The digestate was biologically degraded quite effectively during the anaerobic phase. This can be stated, since no significant mass loss occurred during composting and since self-heating not took place. Also the waste proteins were extensively ammonified already during anaerobic phase, since no further decrease of organic N occurred in the N-balance.

Figure 2: N-Balances of the biological treatment experiments



Conclusions

The behaviour of NH_3 emissions after anaerobic treatment depending on factors such as efficiency of anaerobic degradation and storage of digestate before post-treatment. Compared to a sole composting process, the overall NH_3 -emissions can be expected to be higher when the waste is firstly treated anaerobically, secondly become post-composted. During anaerobic treatment $\text{NH}_4^+/\text{NH}_3$ accumulates in the substrate. After the anaerobic phase is finished, it may become set free in large amounts. A frame condition is, that the pH increase over 7.5 (Körner, 2008), which is usually the case, if the digestate is composted.

To avoid environmental impacts and the loss of Nitrogen as a fertilizing element following procedure is suggested: 1) Effective degradation during anaerobic phase; 2) Avoidance of storage; 3) Optimum post-composting conditions for efficient and quick NH_3 -removal; 4) Recovery from NH_3 with scrubbers; 5) Transformation of the scrubber solution into a mineral fertilizer.

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