

## Nitrogen Transformation Processes Taking Place During the Intensive Phase of Composting

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The study of the N cycle during composting is of great importance for the calculation of the nutrient supplying capacity of compost (KÖRNER, 1997). In the course of compost formation the proteins found in organic wastes are converted into inorganic N compounds (ammonium, nitrite, nitrate) or into other organic compounds (microbial biomass, humus). In the course of compost formation the decomposition of the main carbon sources, the carbohydrates (cellulose, hemicellulose, lignin) takes longer than that of the N sources, so a considerable quantity of  $\text{NH}_3\text{-N}$  may be lost during the first, thermophilic phase of composting (OTT, 1980; MADRID et al., 2002). High temperature and moisture content reduce the activity of the cellulose decomposing microorganisms, which are chiefly thermophilic fungi with a heat optimum of 50 °C. At temperatures above 55 °C the decomposition of cellulose declines sharply and the ammonium loss increases considerably (MEYER, 1979). Substantially less protein can be demonstrated at 60–75 °C than at 50 °C. It can be concluded from this that microbial activity is greatly reduced and that in this temperature range the mineralization of proteins is still intensive, while the decomposition of carbohydrates is considerably reduced (MEYER, 1979). As the result of high temperature and alkalinity dominant in the thermophilic phase, the  $\text{NH}_3+\text{H}_2\text{O} \rightleftharpoons \text{NH}_4^++\text{OH}^-$  equilibrium arising in the course of ammonification shifts towards the formation of ammonium, a large proportion of which leaves the system in gaseous form (WITTER, 1986; GOTTSCHALL, 1990). Ammonium emission occurring during the compost formation process was reduced by 45% in an experimental reactor when the system was cooled and the oxygen content was maintained at 10% (VEEKEN et al., 2001). The N loss can be calculated easily from the  $\text{NH}_3$  gas formed during the intensive phase of composting and the N forms dissolved in leakage water (KÖRNER, 1997), so these forms were measured in the present studies. Bioreactors can be divided into two groups, depending on whether they

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involve adiabatic or isothermic systems. Isothermic bioreactors model composting systems to which material is added continuously and in which the temperature of the composted material remains relatively constant. However, isothermic systems, unlike adiabatic ones, do not allow an analysis to be made of the changes occurring in the microbe population composition as the result of changes in the temperature, moisture content and available nutrients (NAKASAKI et al., 1985; SIKORA & ENKIRI, 2000). In adiabatic systems the conservation of heat can be achieved by insulating the system or by placing it in a water bath. Adiabatic systems are more suitable for the tracing of N transformation processes than isothermic ones (CSEHI, 1997; KÖRNER, 1997), so an adiabatic bioreactor constructed by authors was used for present N transformation studies.

The aims of the research were: a) the construction of an adiabatic composting bioreactor for tracing N transformation processes; b) measurement and description of N transformation processes occurring during the intensive phase of composting; c) manipulation of the process to reduce negative components such as NH<sub>3</sub> loss.

### Materials and Methods

#### *Raw materials (Tables 1 and 2)*

*Horse manure*: horse manure containing straw litter is favourable for compost formation studies, as its moisture content, nutrient composition and structured nature facilitate intensive composting without the addition of additives. *Sewage sludge*: dehydrated sludge arising from the cleansing of communal sewage. *Straw*: cereal straw used as structure material and carbon source during composting. *Bentonite*: ground clay with high adsorption capacity (T value: 120 meq/100g), containing three-layered clay minerals of the montmorillonite type, used as an additive to improve the adsorption capacity of the compost. *Biowaste*: kitchen waste and vegetable remains from households and institutions. A representative sample of various types of biowaste was compiled for the studies.

Table 1  
Raw materials used in the composting experiments

Sample code	Composition
HM	Horse manure
SLUDGE I	Sewage sludge (70 vol%), straw (30 vol%)
SLUDGE II	Sewage sludge (30 vol%), straw (70 vol%)
SLUDGE III	Sewage sludge (30 vol%), straw (65 vol%), bentonite (5 vol%)
BIO	Potato and apple peelings (15 vol%), paprika waste (10 vol%), crushed egg shells (5 vol%), peach waste (5 vol%), grass cuttings (30 vol%), chopped wood (25 vol%), shredded paper (10 vol%)

Table 2  
Properties of the raw materials used in the experiment

Sample	Dry matter	Organic matter	pH (KCl)	Total N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	C/N ratio
	%						
SLUDGE I	40.3	72.65	7.65	19750	2073.6	37.6	21.02
SLUDGE II	50.4	76.5	7.32	11235	586.4	23.2	38.91
SLUDGE III	57.4	65.3	7.11	9340	340.7	21.4	39.95
BIO	43.2	64.26	7.07	16570	840.7	40.2	22.16
HM	57.3	83.54	7.15	8800	649.1	55.9	54.25

### Methods

*Adiabatic bioreactor:* The experiments were carried out in a 330-litre adiabatic drum composting bioreactor which ensured satisfactory conditions for process control. The heat retaining effect of the compost was modelled in the bioreactor by heat insulation. The oxygen supply was adjusted to 10 l/kg(dry matter)/hour, based on literature data, using a compressor to provide continuous air flow (CSEHI, 1997; KÖRNER, 1997). To ensure the perfect homogenization of raw materials the bioreactor was in constant vertical and horizontal movement (no. of revolutions = 5/day, angle of inclination =  $\pm 30^\circ$ .) The composting process was extremely intensive in the bioreactor: in all samples the thermophilic phase was completed within 21 days. The temperature of the maturing compost was measured using a thermometer made of platinum-iridium amalgam, placed in the centre of the reactor. In addition to compost temperature, the temperature of the laboratory atmosphere and of the air emitted from the reactor were also recorded. The air emitted from the compost was cooled and samples were taken daily from the condensation water. The ammonium arising in the course of composting was collected daily in absorption vessels containing sulphuric acid, the concentration of which was 0.1 M in the first vessel and 0.01 M in the second. The quantity of ammonium in the condensation water and collected in the absorption vessels was determined using a Parnass-Wagner steam distillation apparatus. The leakage water arising during composting was drained off every other day through a tap at the bottom of the simulator. The total quantity was measured and samples were collected every three days to determine NH<sub>3</sub> and NO<sub>3</sub> contents by means of steam distillation. The moisture content was determined in a drying cabinet by drying the samples to constant weight at 105 °C. The total organic matter content was calculated from the combustion loss (at 700 °C for 5 hours). The pH was measured by the direct potentiometric method. After the necessary calibration a suspension prepared from 4 g sample and 12.5 cm<sup>3</sup> 1 M KCl was used for the measurements. The total N content of the samples was determined after digestion with sulphuric

acid using a Parnass–Wagner steam distillation apparatus. The readily available N compounds were determined after digestion with 1% KCl (Parnass–Wagner apparatus). The C/N ratio was calculated from the total N content and the organic matter content using the following equation (VKS, 2001): Organic matter content (dry matter) /  $1.725 \times$  nitrogen content (dry matter).

## Results and Discussion

The temperature of the system was continuously measured in order to determine the length of the intensive, high temperature phase of composting. It was found that a 21-day treatment was sufficient for the completion of the thermophilic phase of composting. This phase began in all raw materials after only a few hours and thermophilic temperatures were measured in all treatments the day after composting began. Temperature curves were similar for all raw materials, with a gradual reduction in the temperature of the compost from the 11–13<sup>th</sup> day on. After the 21<sup>st</sup> day compost temperature was the same as the ambient temperature. The maximum temperature (72.5 °C) was measured on the 3<sup>rd</sup> day for the BIO sample, which could be attributed to the optimum C/N ratio, nutrient and moisture contents. No correlation was observed between the ambient (laboratory) and compost temperatures, indicating that the insulation of the system was satisfactory. The temperature of the air emitted from the bioreactor exhibited a curve similar to that of compost temperature.

In all samples the pH values rose in the early stages of composting due to the ammonification occurring as the result of the decomposition of organic matter. In later stages the pH exhibited a declining tendency and was neutral in all treatments by the 21<sup>st</sup> day. The highest pH was recorded, as expected, in the case of HM, where the pH > 7.5 even at the end of the composting process.

N transformation processes are depicted on a model, all the parameters of which were measured during the experiments (Figure 1).

Changes in the carbon content of the compost were measured in samples collected during the intensive phase of composting. A function was fitted to the data, after which the rate constants were determined. A linear correlation was observed between time and carbon content, and it was found that the samples' carbon content decreased gradually during composting as the result of biodegradation. The steepness of the decrease in carbon content was the greatest in the case of HM ( $k_2 = -6935.8$ ). This could be attributed to the joint presence of the highest initial carbon content and the most favourable conditions for biodegradation (texture, moisture content). The slowest rate of decrease was obtained for biowaste, due to its smallest initial carbon content.

Similarly to the carbon content, the total N contents of the samples were also measured. On the basis of curve fitting, the changes in N content also exhibited a linear correlation over time. The total N content and organic N content of the

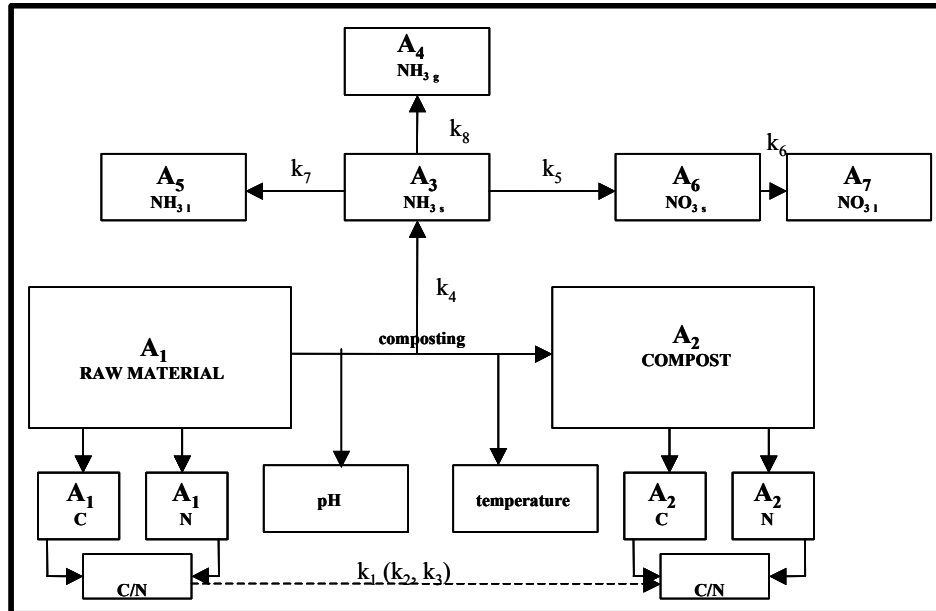


Figure 1

The composting process and the parameters measured

$k_1$ : rate constant for changes in the carbon content of the compost;  $k_2$ : rate constant for changes in the nitrogen content of the compost;  $k_3$ : rate constant for changes in the C/N ratio of the compost;  $k_4$ : rate constant for changes in the  $\text{NH}_3$  content of the compost;  $k_5$ : rate constant for changes in the  $\text{NO}_3$  content of the compost;  $k_6$ : rate constant for changes in the  $\text{NO}_3$  content of the leakage water;  $k_7$ : rate constant for changes in the  $\text{NH}_4$  content of the leakage water;  $k_8$ : rate constant for the formation of gaseous  $\text{NH}_3$

samples grew during composting due to the reduction in organic matter, so there was a relative accumulation of N in the composts. The rate of increase in N content was the greatest in the HM treatment ( $k_3 = 250.12$ ) due to the intensive reduction in organic matter (carbon) content. The C/N ratio was calculated from the carbon and N contents of samples. This ratio is extremely important not only for the regulation of the process and the measurement of N losses, but also for the determination of the maturity of the composts. In the course of composting the C/N ratios of samples declined gradually due to the reduction in organic matter content (Table 3). The rate of decrease differed, chiefly as a function of the initial C/N ratio and the solubility of the carbon and N sources.

The greatest rate of decrease in the C/N ratio was observed when composting HM (the ratio declined by 1.38 units a day), due to the wide initial C/N ratio and the optimum conditions available for composting. In the case of sludge samples, the addition of structural materials, which also represented a source of carbon, led to an increase in the C/N ratio (from 21.32 to 40.53) (Table 3).

Table 3  
Changes in C/N ratio during the composting of various raw materials

Days	SLUDGE I	SLUDGE II	SLUDGE III	BIO	HM
0	21.32	39.47	40.53	22.48	55.03
3	20.22	36.54	38.49	20.92	51.14
6	18.15	33.14	36.64	18.41	47.00
9	16.16	31.86	35.30	16.33	44.48
12	13.95	28.59	33.23	15.30	39.05
15	13.16	27.76	30.62	15.01	33.87
18	12.78	26.63	26.94	13.92	29.64
21	12.37	25.12	25.93	13.28	26.94

For raw materials: see Table 1

*Readily available nitrogen content of the composts (A3, A6)* – The readily available N content of the composts could be traced well in the course of composting. As a result of ammonification the  $\text{NH}_4$  ion concentration increased in the early stages (days 6 to 9), but later decreased due to immobilization and nitrification. The ammonium ion quantities measured differed in the various samples as a function of the initial N content and C/N ratio. The highest  $\text{NH}_4$  ion concentration was recorded for SLUDGE I and the lowest for SLUDGE III.

The nitrification process began in the samples from the 3<sup>rd</sup> day and can be attributed to the rise in the quantity of ammonium ions and the decrease in temperature, which result in the development of conditions optimum for nitrifying bacteria. The most intensive nitrification process was observed during the composting of horse manure (HM), where the quantity of nitrate exceeded that of ammonium by the 11<sup>th</sup> day, while at the end of the process, on the 21<sup>st</sup> day, a total of 2177 ppm nitrate was recorded.

*Loss of  $\text{NH}_3$  from the system (A3)*. – Among the N transformation processes occurring during composting, the study of the formation of  $\text{NH}_3$  gas and the factors influencing it is the most important, as the greatest N losses arising during composting are due to the escape of  $\text{NH}_3$  during the thermophilic phase (VOGTMANN, 1980; WITTER, 1986; KÖRNER, 1997). The quantity of  $\text{NH}_3$  leaving the system was measured during the intensive phase of composting, a function was fitted to the data and the rate constants were calculated. Significant differences were observed between the quantitative data of ammonium liberation from various raw materials. The greatest ammonium formation was recorded for SLUDGE I, which had the highest initial total N and  $\text{NH}_4$  contents and the smallest quantity of additives providing texture and carbon sources. The volatilization of  $\text{NH}_3$  ran the same course in all samples: due to the initial rapid ammonification, and the high temperature and pH values the formation of  $\text{NH}_3$  first exhibited an increase, followed by a decrease after reaching a maximum.

The curves recorded for biowaste and horse manure were similar; in the sludge sample containing more structural material (SLUDGE II) ammonium formation commenced earlier than in the BIO and HM samples, but began to decline after the 6<sup>th</sup> day, while very little ammonium formation was observed after the 12<sup>th</sup> day. The lowest N losses (0.49%) were measured in the sample which contained

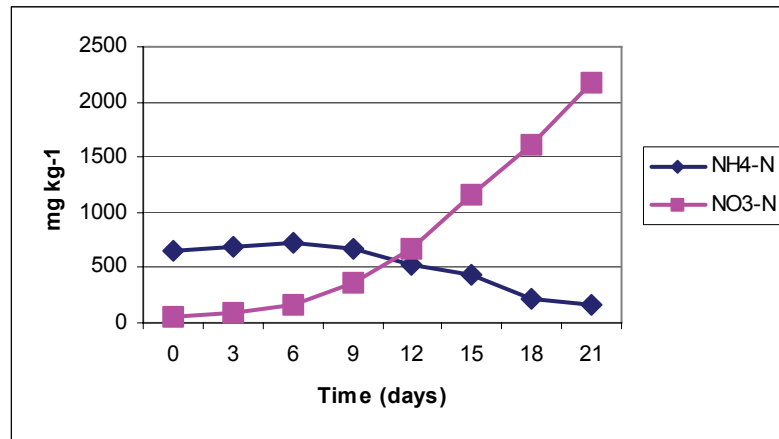


Figure 2

Changes in the NH<sub>4</sub> and NO<sub>3</sub> contents of horse manure (HM) compost

not only a large quantity of structural material but also bentonite (SLUDGE III), demonstrating the favourable effect of additives with high adsorption capacity.

As can be seen from Table 4, N losses in the form of ammonium were very high for the SLUDGE I sample (19.12%), which can be attributed to the high initial content of readily decomposable N and NH<sub>4</sub> and to the high temperature. The highest daily values of NH<sub>4</sub> formation from the various raw materials were recorded between days 3–8. The maximum daily amount was measured earliest on the 3<sup>rd</sup> day (SLUDGE II sample), and latest on the 8<sup>th</sup> day (HM sample). In the SLUDGE III sample the increase in the adsorption capacity due to the addition of bentonite led to a substantial reduction in the volatilization of NH<sub>4</sub> as compared to SLUDGE I and II samples. The high adsorption capacity of SLUDGE III is indicated by the fact that no NH<sub>3</sub> could be detected by the 15<sup>th</sup> day, while in SLUDGE I considerable quantities of NH<sub>3</sub> were still recorded on the 17<sup>th</sup> day. The quantity of NH<sub>4</sub> formed in the BIO and HM samples was similar to that in the SLUDGE II sample, but the NH<sub>4</sub> formation process took longer, continuing until day 19–20, respectively. Studies on the correlation between the volatilization of NH<sub>3</sub> and the temperature and pH of the compost showed that NH<sub>3</sub> formation only became significant several days after the beginning of the composting process, while the temperature reached its highest value at an earlier date (temperature and NH<sub>3</sub> formation peaks did not coincide).

Table 4  
Nitrogen losses in the form of NH<sub>3</sub> emission

Raw materials	NH <sub>3</sub> -N emission (mg)	Total N-content of the samples (mg)	N losses (in the form of NH <sub>3</sub> ) as a % of total N
HM	44.21	2444.08	1.81
BIO	55.75	1812.80	3.08
SLUDGE I	779.58	4078.38	19.12
SLUDGE II	44.93	1219.00	3.69
SLUDGE III	5.43	1109.13	0.49

For raw materials: See Table 1

The plotting of the cumulated quantities of NH<sub>3</sub>-N gives autocatalytic, logistic curves (Figure 3). Among the samples the volatilization of NH<sub>3</sub> was an order of magnitude greater in the case of SLUDGE I than in the other four samples, so the SLUDGE I sample is not included in Figure 3. An analysis of the course of the S curves shows that the steepest slope ( $k_8 = 0.76$ ), i.e. the fastest rate of NH<sub>3</sub> formation, was given by the SLUDGE II sample, the reason for which was the large quantity of readily decomposable N available. The greatest A value, i.e. the greatest quantity of NH<sub>3</sub>, was found for the BIO sample, which could be attributed not only to the high initial total N content but also to the ease with which the N compounds could be decomposed.

The point of inflection, i.e. the steepest point of the S curve, was observed between days 7 and 8 in the HM and BIO samples and between the 3<sup>rd</sup> and 5<sup>th</sup> days for the SLUDGE samples, confirming that the N sources are least stable in the sludge samples irrespective of the quantity of N, while the ammonification process is more intensive than in the HM and BIO samples. When examining the correlation between NH<sub>3</sub> loss and the C/N ratio it was found that in the SLUDGE I sample the C/N ratio was lower (21.32/1) than the optimum initial C/N ratio of 25–30/1 (KÖRNER 1997), but this in itself would not have caused such high NH<sub>3</sub> emission (19.12%), as much lower losses were recorded in the BIO sample (3.98%) which had a similar C/N ratio. It can be concluded that the C/N ratio alone is not sufficient for characterizing the composting process and the estimation of NH<sub>3</sub> emission, which also requires knowledge of the decomposability of the C and N sources.

In the case of the SLUDGE I sample, containing readily decomposable carbon sources, substantial ammonium volatilization was recorded in spite of the relatively wide C/N ratio. The pH and the temperature were well correlated with the volatilization of NH<sub>3</sub> (in the BIO sample  $r = 0.85$  and  $r = 0.92$ ).

*Analysis of the leakage water* (A5, A7) – The analytical data indicated that the ammonification and nitrification processes taking place in the course of composting could be satisfactorily traced despite the fact that, due to intensive



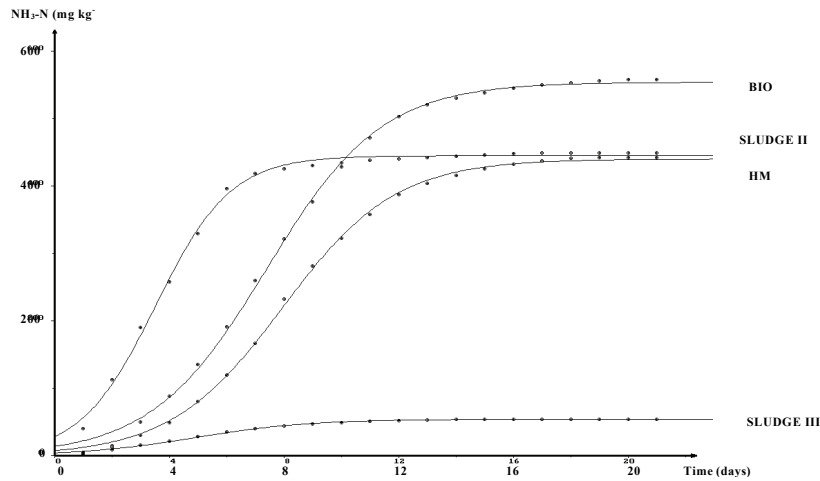


Figure 3  
Quantity of  $\text{NH}_3$  formed during the composting of four different samples

aeration, very little leakage water was formed and the quantity of N lost in this way was negligible as compared to the total N content of samples. An analysis of the leakage water indicated that in four different samples the quantity of  $\text{NH}_4$  ions increased at first due to ammonification, followed by a rapid decrease, primarily due to the intensification of nitrification. In the SLUDGE I sample  $\text{NH}_4$  ion concentration showed a declining trend right from the beginning of the composting process, probably due to the high initial  $\text{NH}_4$  content. In the HM sample almost as much  $\text{NH}_4$  was recorded in the leakage water than in SLUDGE I, despite the lower N and  $\text{NH}_4$  contents. This could have been caused by the greater  $\text{NH}_4$  volatilization and higher temperature in the SLUDGE I sample.  $\text{NO}_3$  was first detected in leakage water on day 3–5, which can be explained by the slow initiation of nitrification. The leakage water  $\text{NO}_3$  content was highest in SLUDGE I, which could be caused not only by the intensive nitrification due to high N content but also by the high moisture content ( $\text{NO}_3$  leaching). The cumulative plotting of the leakage water  $\text{NH}_4$  content gives a saturation curve, while the increase in  $\text{NO}_3$  content follows an exponential curve.

### Summary

N transformation processes taking place during the intensive phase of composting were analyzed for characteristic compost raw materials in an adiabatic composting bioreactor by analyzing composts (in various stages of maturity), emitted gases and leakage water.

Temperature exhibited a similar curve for all raw materials, with a gradual decrease in compost temperature from day 11–13 on. Measurements of  $\text{NH}_3$  indicated a significant difference between the various raw materials, sometimes amounting to an order of magnitude, in the quantitative data of  $\text{NH}_4$  volatilization. Analysis of leakage water indicated that ammonification and nitrification processes could be traced satisfactorily, but the quantity of leakage water formed in the adiabatic drum composter and the associated N losses were negligible compared to the total N cycle of compost formation. Analysis of the composts showed that the organic matter content of the samples declined during composting as the result of biodegradation.

**Key words:** composting, nitrogen transformation, adiabatic reactor, nitrogen losses reduction

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