NH_3 dynamics in composting

Assessment of the integration of composting in manure management chains

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You assume to know who accomplished this book. A look at the cover and you automatically conclude that I did it. Well … no, not really. I perhaps contributed the most to its contents and you are free to point at me for its shortcomings. Only I cannot claim sole accomplishment. For that, I owe far too much to those steering my work or the course of my life in the last years. Without them, this thesis would not be this thesis or possibly it would not be at all. So, hereby follows a brief account of those not mentioned on the cover, but who definitely have a share in the making of this book.

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ABSTRACT

Nitrogenous (N) emissions from solid manures pose a significant environmental problem. Improvement is possible to achieve, if a composting treatment is introduced into the manure management chain. As N retention of composting is a matter of debate, this thesis undertakes the investigation of the ammonia (NH_3) dynamics of the process. A complete picture of NH_3 dynamics is given, where factors of volatilization, nitrification-denitrification, and assimilation are described and analyzed in quantitative and qualitative terms. The focus is on extensive and intensive composting methods and conventional aerobic storage.

The completed assessment of available literature indicates that NH_3 volatilization is a key process in intensive composting, while nitrification proves to be central in extensive processes. It also suggests that the carbon-to-nitrogen (C/N) ratio loses relevance as an N loss indicator when higher aeration rates are applied during the composting process. Results from own trials dealing with extensive composting of a swine manure-wheat straw mixture demonstrate that monthly turning highly improves the compost bed structure. This improvement results in much higher organic matter degradation during a four-month treatment than in the undisturbed control piles. The turned piles also show low NH_3 and N_2O emissions, while the undisturbed control piles emit a considerable fraction of their N as N_2O. The results prove that wheat straw amended swine manure with very low C/N ratios can be treated directly without significant N emissions if the bed structure is optimized.

With a trial on intensive composting, the roles of key parameters in NH_3 volatilization were analyzed and modeled. A chemical model was presented and validated with experimental and literature data. The results show that pH and temperature are key factors in the aqueous equilibrium of NH_3 - NH_4^+, and that aeration rate and temperature are the key parameters in determining distribution of NH_3 in the liquid and gas phase. A comparative study of extensive and intensive composting processes was also carried out. Its objective was to investigate whether N loss from composting can be better indicated by a model derived C_{org}/N_{org} ratio parameter than with the conventional C/N ratio. This model includes the quantification of organic matter biopolymers and clarifies the role of microbiological biomass growth on organic matter turnover. The validation step reinforces that the model can properly monitor biopolymer degradation. Although completing the model would require a relevant microbial decay rate, it does give an improved insight into NH_3 dynamics and the role of microbial assimilation.

The results of this thesis provide insight in the factors controlling NH_3 dynamics and the related N emissions and losses. The evaluation of extensive and intensive composting methods shows that these can offer several advantages compared to the regularly applied aerobic storage. The main advantage of composting application turns out to be its control capacity over the extent and form of manure N emissions. While N emissions from composting can not always be prevented, application of these methods improves both the environmental and the nutrient aspects of manure management chains. The qualitative and quantitative assessment strategies described in this thesis can be used to reduce N losses and harmful emissions and thereby achieve significant improvements in composting systems.

Keywords: manure, composting, ammonia, assimilation, nitrification, volatilization

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1 GENERAL INTRODUCTION

1.1 Background

Intensive swine production systems of the Netherlands are characterized by high production rates in greatly concentrated regions. The density of swines per area in the production regions is the highest in the European Union (CBS, 2006). The production volume combined with the limited agricultural space means that most of the produced slurries and manures are in excess to local needs. As a consequence, the excreta produced in animal houses have to be managed prior to application on external agricultural lands. These manure management chains commonly contain manure storage, transport and land application steps which are designed to meet several requirements (Table 1.1) (based on Burton *et al.*, 2003; Croezen *et al.*, 2003; Cools *et al.*, 2001).

Table 1.1 Main constraints and objectives of manure management chains

Constraint	Objective
Environmental	- reduction of environmental emissions and odors
Economical	- reduction of weight and volume of the manures
Public health	- removal of pathogens and weed seeds
Resource management	- recovering nutrients or energy from the manures

Simultaneously to above objectives, two important trends have emerged in manure management in recent years. The first trend, an increasing concern for animal welfare, has resulted in the wide spread application of straw (Møller *et al.*, 2000) or similar bedding for the kept swines. At present, the management of these solid manure-bedding mixtures poses (Käck *et al.*, 1994; Verdoes *et al.*, 1992) a significant and still growing challenge (ALFAM, 2006). The second trend in manure management (Schans *et al.*, 2002) was the shifting of policies from P (phosphorus) based regulations to nitrogen (N) as a result of high manure-N losses to the atmosphere and the soil (ECETOC, 1994). Unstable manures emit N mainly in the form of ammonia (NH_3), nitrous oxide (N_2O) and nitrate (NO_3^-) and are likely to occur at each of the manure management steps. Nitrogenous emissions do not only constitute an adverse environmental load, they also reduce the efficiency of N recovery from manures. A possible option to reduce nitrogenous losses from solid manures would be the introduction of a treatment step into the management chain.

Composting - a solid-state, aerobic, biological treatment method - is a potential option. It is already widely applied for the processing of various household or green wastes. Processes for treating animal manures are also well developed. Several authors agree (Rudrum, 2005; Fukumoto *et al.*, 2003; Elwell *et al.*, 2001; Keener *et al.*, 2001; Imbeah, 1998; Tiquia and Tam, 1998; Käck *et al.*, 1994; Haug, 1993; Martins and

Dewes, 1992) that composting is a technically suitable method for the combined sanitation and stabilization of solid manure-straw bedding mixtures. During a composting treatment, both weight and volume of the manure-bedding mixture are significantly reduced, hereby assuring cheaper transportation. Pathogens and weed seeds are sanitized in the process and odors are eliminated. Next to improving transportability, stability of the manure is also increased through the composting process. The final product of a composting process is a stable, humus-like material that is useful as soil-conditioner.

Conversely, composting methods are not commonly used in manure management chains. Their practical feasibility is questioned both by scientific research (Sommer, 2001; Kirchmann and Lundvall, 1998) and by the present practice in manure management. Despite the problem that manure production constitutes in the Netherlands, only about 1 % of the produced excreta (mainly the solid manures originating from organic agriculture) is composted (based on CBS, 2006). The central reason for omitting composting from the management chain (Rudrum, 2005; Burton *et al.*, 2003) is the N retaining efficiency of the process.

Schuchardt (1990) reported that 3 to 75 % of the initial ammoniacal N content (NH_3+NH_4^+) could be volatilized as NH_3 from animal manure composting. Total nitrogen ($N_{total} = N_{Kjeldahl} + NO_2^- + NO_3^-$, where $N_{Kjeldahl}$ is based on Kjeldahl (1883)) losses from composting processes are in a similarly wide range (Bhamidimarri and Pandey, 1996; Martins and Dewes, 1992). This broad N loss array corresponds to the difference in substrates, the management of the composting process but also to the choice of composting design. Adding the complexity of composting N flows, it is not surprising that emissions can range from relatively little to the major part of N available in the substrate. It also explains that the use of composting is debated for manure treatment purposes.

In composting processes, the N flows can be best described through NH_3 dynamics. This dynamics encompasses the production, volatilization, conversion and assimilation of NH_3. To dissolve the contradictory views of the process, NH_3 dynamics in manure composting will have to be examined. Before this can be done, features of manure management chains and differences in composting methods will be described in detail. This is necessary as composting is not a stand alone process here, but an embedded part of the manure management chain. As composting is a flexible treatment method, the essential differences in methods will be given together with the functions of the main composting parameters. Only when this context is given, can composting NH_3 dynamics be meaningfully explained.

1.2 Manure management chains

Solid manure systems always produce excreta in combination with a bedding material (straw, hay etc.). The scientific data on such manure-bedding mixtures is still scarce, despite the growing use of such systems. Therefore the description of manure management chains will be based on the conventional (slurry) systems. While the differences between the two systems are acknowledged, the similarities allow for a suitable description on the applicability of composting.

Animal housing is the first step of conventional manure management chains (Figure 1.1). After excretion, the manure and urine are collected and are regularly removed from the animal houses. After housing, manures and slurries can be stored aerobically or anaerobically (ECETOC, 1994; Asman, 1992). Between treatments steps, manure is often transported. Manure transport may occur following storage and/or directly after the housing step. After transport and storage, the managed manure is finally applied on agricultural land as fertilizer. The application step involves the spreading of manures or slurries and their incorporation into the upper layers of the agricultural soils. At this step, the fraction of manure-N that is not emitted yet, will either be stored in the soil or will be taken up by plants in the growing season. It is important to note, that only the fraction that is utilized by plants can be considered recovered N from the excreted N flow.

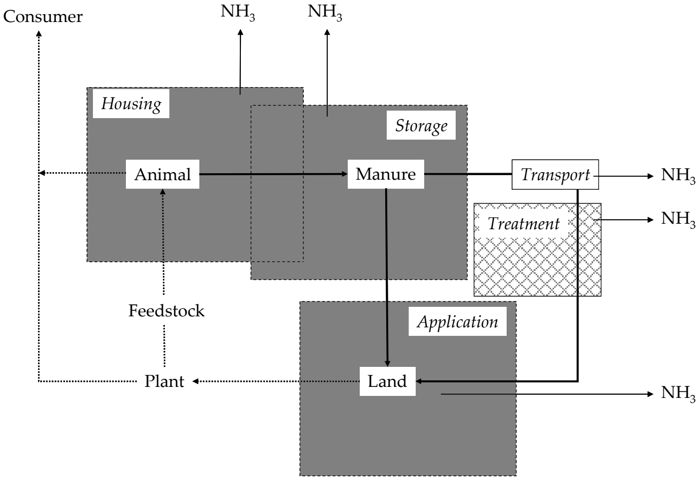

Figure 1.1 N flow and NH_3 emissions in manure management chains
Remarks: bold arrow: manure-N; dotted arrow: product-N (such as feedstock or meat, milk products), thin arrow: NH_3 emission. Note that in practice, the treatment stage is optional.

As was mentioned, management of solid manure-bedding mixtures differs somewhat from slurry systems. Whilst slurries contain most N in the form of mineral N (NH_3+NH_4^++NO_2^-+NO_3^-), the excreted solid manures rich in organic N (N_{org} = N_{total}-mineral N) are immediately mixed with the carbon (C) rich bedding. The resulting carbon-to-nitrogen (C/N) ratio enables more N assimilated into microbiological biomass thereby reducing the amount of N susceptible for emission. However, the NH_3-rich urine produced is also incorporated in this mixture and it is only partly absorbed by the straw. The solid nature of the mixture and the presence of both N_{org} and mineral N fractions make solid manure straw mixtures difficult to store without significant NH_3 emissions.

NH_3 emissions from the different steps of manure management show a wide range (Oenema *et al.*, 2000). This can be attributed to the produced animal species, the large number of housing-storage-application systems (Oenema *et al.*, 2000), and the quality of management within a category. Table 1.2 demonstrates the significance of the management steps for the main animal categories in the Netherlands.

Table1.2 NH_3 emission contributions of the different steps in manure management chains in 2004. The presented values represent the percentage of the excreted manure-N that was lost in the form of NH_3

Manure species	Housing	Storage	Application	Total NH_3 emitted
Milking cows (corn)	6.6	0.6	9.2	16.4
Milking cows (grass)	6.6	0.6	10.7	17.9
Breeding swines	19.5	0.3	12.1	32.0
Fattening swines	18.0	0.2	8.3	26.5
Laying hens	22.5	4.2	6.2	32.9
Broiler chicken	14.1	2.3	3.9	23.0

Source: MNP, 2004. Note, that transport related losses are not included in the table, as they are considered to be negligible (Croezen et al., 2003).

Table 1.2 shows that with each animal category, housing and application are the highest emitters in the chain. ECETOC (1994), Oenema *et al.* (2000) and Oudendag and Luesink (1998) agree that the contribution of storage to the total NH_3 emissions from the chain is low. Transport related emissions were found to be insignificant by the TEWI report (Croezen *et al.*, 2003).

While techniques are available to reduce NH_3 emissions from land application, Table 1.2 indicates that a significant portion of NH_3 is lost on arable land. Research of Wrage (2003) has also indicated that NH_3 emission reduced by manure incorporation into soil could cause an increase in N_2O emissions and an enhanced leaching of NO_3^-.

The high contribution of the management stage land application to NH_3 emissions indicates that the emission control over untreated manures is not effective. Treatments could possibly improve this control by handling manures prior to land application either before or succeeding the storage step. However, despite the restrictive policies, only 5.7 % of the total manure-N was treated at all in 2004, while the rest was transferred directly to arable lands (CBS, 2006). Table 1.3 shows the main manure treatment methods and their characteristics.

Table 1.3 Characteristics of the main manure treatments in the Netherlands

Treatment	Product	Advantages	Disadvantages
Incineration	Energy and ash	Energy production and volume reduction	Costly, requires gas and water treatment
Drying	Sanitized, transportable dry cake	Volume reduction	Emissions on rewetting
Wet air oxidation	P and K-rich ash	Good fertilizer alternative	Costly, requires wastewater treatment
Anaerobic digestion	Energy	Produces energy; NH_3 has fertilizing value	Wet, NH_3-rich and not-sanitized product
Composting	Compost	Sanitation, stabilization; good soil conditioner	NH_3 emissions, N loss - reduced fertilizer value

The main treatments applied in solid manure management are those (Table 1.3) that can produce either energy or easily transportable, nutrient rich fertilizers. The composting treatment steps are supported as they provide a way to recycle organic matter, nutrients and minerals to agricultural soils. In her policy for sustainability, the European Union recommended composting as one of the main treatment methods for manure management (European Commission, 2001).

1.3 Composting – a manure management option

1.3.1 Defining composting

The previous section has shown that there is disagreement on whether the extent of nitrogenous emissions should hinder composting application in manure management chains. One of the reasons that this debate exists is related to the uncertainty in the definition of composting. Composting is a flexible treatment method and the basic, natural process is known for millennia (Gotschall, 1984; Minnich and Hunt, 1979). However, its application was based on little control for most of the time. As scientific knowledge on composting improved in the last century (Haug, 1993), the treatment became more widespread in engineered installations. Although, the insight in the complex conversion processes still deepens today, the necessary science and technology to treat and stabilize organic matter is well founded (Haug, 1993).

Today, composting is a widely and frequently used process that is hard to define because of its flexibility. The generally accepted description is from Haug (1993):

> *"Composting can be defined as the biological decomposition and stabilization of organic substrates, under conditions that allow development of thermophilic temperatures as a result of biologically produced heat, to produce a final product that is stable, free of pathogens and plant seeds, and can be beneficially applied to land".*

There exists inconsistency in whether naturally occurring processes - where no engineering intervention takes place - should also be termed composting. Therefore, above definition is extended here with another important feature. It is proposed that only those solid-state, dominantly aerobic processes are to be termed composting, where the organic matter is converted by microorganisms following or under engineering intervention. Biological, at least partially aerobic, solid state processes that lack significant engineering intervention of any kind are to be titled storage. Another terminological question is the application of the term composting for anaerobic conversion processes. In the past, also anaerobic digestion processes were sometimes termed as anaerobic composting. For simplicity, composting represents exclusively the aerobic processes throughout this work. When mentioned, anaerobic conversions are termed digestion.

It was mentioned that flexibility in composting designs is likely to be one of the reasons for the wide range of nitrogenous emissions from the process. Still, basic features can be drawn that are true (although in differing relevance) to all manure composting processes. These are also the features that arise in discussions over the feasibility of composting in a manure management context. The general features are summarized in Table 1.4.

In general, the possibilities to tackle these disadvantages are common in all composting designs. Reduction or elimination of the disadvantages is possible by:

- optimization of the starting material (substrate);
- adjustment of the process through the optimization of the process parameters.

Table 1.4 General features of manure composting (based on Burton *et al.*, 2003)

Advantages	Disadvantages
Reduction of odor emissions.	Potential N loss (NH_3, NO_3^-, and N_2O).
Stabilization of nutrients against volatilization and leaching.	Compost is hard to sell, because of the difficulty to maintain constant properties.
Removal of pathogens and weed seeds.	Odor nuisance if improperly managed.
Conversion of organic matter in manures to create a balanced product for soil improvement.	Slower release of nutrients in compost elongates the growth period, making compost less suitable as fertilizer.
Reduction of weight and waste volume to improve compost handling and transport.	Costs, as the processing requires time, labor and money compared untreated manures.

The term optimization is defined here as the adjustment of a composting parameter in order to achieve either higher N retention in the compost bed or an increased control over the nitrogenous emissions in NH_3 dynamics. The main tool of substrate optimization is the addition of amendments (or bedding) to the solid manure. Adjustment of the process mainly involves control options such as the agitation of the compost bed or the controlling of air flow and temperature.

1.3.2 Classification of composting methods

The flexibility of the composting process (Haug, 1993) indicates that altering a design is likely to result in different NH_3 dynamics and an ultimate N efficiency. The next section presents a classification on the main methods of manure composting and the implications of design selection on NH_3 dynamics.

1.3.2.1 Composting vs. storage

Most solid manures are stored and/or treated prior to transport and application on land. Although the difference between storage and treatment was already briefly mentioned, a precise definition is required to sufficiently differentiate the two handling processes in the manure management context. In manure management and composting literature, storage and composting are often used with an overlap between the two processes. This is partly due to the flexibility of the composting process, as it can be adjusted to a wide range of engineering challenges. This results in large variations in technological designs. It also implies that there is a considerable confusion in the definition and the classification of composting methods.

Storage is defined here as the standard method of handling in present-day manure management chains. Storage commonly means the stocking of manures between two activities like housing and transport or transport and application. The objective of storage is often the preservation of nutrients without the alteration of manure composition. If the pile is hermetically closed the storage is termed anaerobic, otherwise we speak of aerobic storage. However, aerobic storage does show strong features of anaerobic conversion.

A frequently applied solid manure handling method of Danish organic farmers was termed composting during storage by Sommer and Møller, (2000), Sommer (2001) and Osada *et al.* (2001). Nicks *et al.* (2004) mention in-situ composting of deep litter manures at inside storage. However, both terms are debatable as their conditions are more suitable for preservation of the organic matter than for conversion. Also, this sub-optimal conversion is mainly anaerobic; thereby bringing these processes closer to anaerobic digestion. Only marginal technological intervention is applied in case of these storage compostings. Whereas the starting substrate of storages are sometimes optimized by the addition of bedding materials, the storage 'process' is almost never controlled. Composting, on the contrary, is a treatment method, and its objective is to alter the manure composition: stabilize, sanitize and concentrate the starting material through a controlled process.

It is suggested, that if a handling method is meant for preservation of manure, storage is perhaps a more fitting term to use. Even, if it means the neglecting of minor conversion (mainly anaerobic) processes. Therefore, from here on the term aerobic storage will be used for a solid manure handling method that (i) is intended for the preservation of the composition of manure matter, regardless of the extent of actual conversion and (ii) the manure bed is not hermetically closed. Latter condition differentiates aerobic storage from anaerobic storage, where no O_2 transfer between the bed and the environment is allowed.

1.3.2.2 Classification categories of composting methods

The variations in composting processes show a wide range in the required amount of investment, maintenance, and level of control over the substrate or the process. Different authors have categorized composting methods (Zhu *et al.*, 2004; Veeken *et al.*, 2002; Rynk and Richard, 2001; Møller *et al.*, 2000; Fernandes and Sartaj, 1997; Haug, 1993). An important feature of composting classification is that it may be done based on several parameters or engineering features. The main classifying matters are listed in Table 1.5.

A large number of the combinations from above classification categories can be found in composting practice. To reduce the amount of practical designs that need to be examined, it is useful to look at design classification according to the level of technological control in the optimization of the composting substrate and/or that of the process.

Table 1.5 Main classifications of composting designs (Rynk and Richard, 2001; Haug, 1993)

Classification	Categories
Aeration	O_2 diffusion / natural convection / forced aeration
Reactor	open (non-reactor) / closed (in-vessel or reactor)
Process	batch / flow (vertical, inclined, horizontal) / modular (multiple units of batch)
Scale	small (farm-scale) / industrial (central processing)
Agitation (turning, mixing)	None / periodical / (semi)continuous

1.3.3 A practical classification of composting methods

Whilst the standard classification categories are grouped according to one parameter, the following technological classification offers a simplified and more practical categorization of composting designs. The reason of creating a new classification is to simplify categorization of available composting designs for the sake of NH_3 dynamics research. This technological control approach looks at the required technology and the achievable control over substrate and process. The technological scale categorizes composting processes from a zero-level engineering intervention in the composting process (like in case of aerobic storage) to the state-of-the-art reactor composting designs with a high level of engineering involved. In such a control approach extensive and intensive composting methods can be defined. While former would contain mainly the passive aeration methods, latter is comprised of forced aeration or in-vessel designs (Table 1.6).

Table 1.6 Classification of aerobic storage, extensive composting (EC) and intensive composting (IC) methods according to engineering intervention principles

	Aerobic storage	EC	IC
Objective of the method	preservation	conversion	conversion
Optimization of (starting) substrate	no*	yes**	yes
Optimization of substrate during process	no	yes	yes
Process control	no	limited	advanced
Aeration	no	passive	forced
System/Reactor	open	open	closed
Agitation	no	optional	optional

*Remarks: * Except where amendment is already included in the manure. ** Note, that the table describes generally occurring features from which variations are possible in practice.*

Table 1.6 classifies manure composting methods and aerobic storage according to the level of engineering and control involved in the process. As composting is a replacement or subsequent treatment step to storage (and the two management steps overlap) storage is also included in this comparison.

General composting studies (Haug, 1993; Minnich and Hunt, 1979) provide sufficient information on reactor, aeration and agitation features, but the optimization of substrates and the composting process will be explained in detail in the next section.

1.3.4 Optimization of the composting treatment

1.3.4.1 Optimization of the substrate

Composting of solid manures is carried out almost exclusively with the addition of C-rich bedding amendments. This amendment is necessary as the average manure substrate is a wet, N-rich material with poor structural characteristics (Haug, 1993). If bedding material is added in the animal house, it will also function as amendment in a composting process. Because of these amendments, the composting characteristics of these manure substrates are enhanced. Next to improving animal welfare, the addition of bedding is one of the central optimization tools of the starting substrate. Amendments such as wheat straw, hay, leaves or rice hulls have the following influences on substrate parameters: (i) the improvement of physical structure, (ii) optimizing C/N (carbon-to-nitrogen) ratio and (iii) the increasing of the total solids (dry matter) and energy content of manure.

Substrate optimization for aerobic storage means optimization for the prevention of conversion. It may include the compaction, acidification and/or covering of the pile (Sommer, 2001). Mostly, the pile is then left intact until it is transported or directly applied on land. As storage is aiming to preserve manure, process related optimization is not typical.

Extensive composting methods are characterized by low labor and financial requirements, and a low level of control. As control over the process is limited, the optimization of the starting substrate is an essential option in these methods.

1.3.4.2 Optimization of the process

Substrate optimization prior to composting is a control option available equally to both extensive and intensive composting categories. However, a significant optimization of the process is attributed only to intensive designs (Table 1.6). Intensive composting processes can exercise continuous control over one or more parameters. In case of the other two methods it is not possible. As Table 1.6 showed, storage is never optimized for the process. This is logical as conversion is not an objective at storage steps. Extensive compostings are almost exclusively non-reactor processes without forced aeration. Here, the aeration is supplied via natural convection and it is enhanced via regular agitation of the compost bed. Mixing and turning of the bed or the setting of aeration pipes loosens the material and enables the air to pass through the central parts of the bed. The control over the process is limited to the effect from the adjustment of the starting material and the frequency of the mixing and turning. It has to be mentioned that the lack of high level process control generally limits the use of extensive composting to farm scale designs. As extensive compostings are open systems that require fresh air from the surrounding, emissions can not be controlled significantly.

Intensive composting processes are in-vessel designs where aeration is arranged via forced aeration allowing controlled flow rates. The cost of the reactor, the aeration and the measurement of control parameters make the design more expensive, its scale is often industrial size. Due to the high level of process control, the end product is of higher quality. Important to note is that purification or recycling of the air flow enables the entrapment of unwanted emission gases thereby reducing the environmental load of the process.

1.3.5 Main parameters of manure composting

After selecting a composting design, the next level to approach NH_3 dynamics is the understanding of the functioning of composting parameters. Composting is a microbiological method and so the optimization of its degradation rate is achieved by the optimization of the environmental conditions for the microorganisms (biomass) involved. Conditions for the reduction of NH_3 emissions may be improved through the optimization of the composting material (substrate) and through the optimization of the process parameters. The main parameters influencing the biodegradation process are the following:

Substrate parameters:

- Moisture content
- Structure of compost bed
- Composition of organic matter (C/N ratio)
- pH

Process parameters:

- O_2 concentration in compost bed
- Temperature and temperature gradient in bed

Although the basic working of above parameters is standard to each composting process, it is important to note, that their influence and working changes with (i) starting material quality, (ii) composting design and (iii) with the temporal progressing of the treatment.

1.3.5.1 *Substrate parameters*

Moisture content

Moisture is necessary for the metabolic processes of composting microorganisms. The dry matter range of organic wastes and animal manures starts at about 20 % TS (total solids content) to above 60 %, but the optimal range for processing is considered between 35 – 60 % depending on the sort of substrate (Haug, 1993; Rynk *et al.*, 1992). A too dry substrate slows or even inhibits microbiological reactions. Extremely high moisture contents lead to the reduction of free air space in the composting material. The smaller free air space causes a reduced aeration rate and a lower O_2 transport in the compost beds. The low O_2 level results in an increase of anaerobic regions in the compost bed leading to the enhanced production of odors and NH_3 emissions.

The optimal moisture content depends on the structural characteristics of manures and it is related to the porosity of the material. In general it can be said, that highly porous material can be efficiently degraded with higher moisture contents, whilst compact substrates with smaller particle sizes tend more to become anaerobic. During the composing process, water is produced at the degradation of organic matter and is depleted from the compost bed by the removal of heat in the form of vapor.

Structural parameters

Structural parameters are a group of interrelated parameters. They include particle size, porosity, free air space, permeability, and the mechanical or structural strength (the ability of the compost bed to resist compaction). An optimal structure is essential for a good composting process as it allows sufficient supply of fresh air into the compost bed, ensures aerobic conditions, and enables the removal of excess heat.

Particle size is the parameter that determines porosity and permeability; it has a direct influence on pile structure. Particle size also determines the rate of anaerobic and aerobic degradation. Even small particles are only partially penetrated with O_2 (Hamelers, 1993) and the particle core, poor in O_2, will exhibit anaerobic degradation. Because of the degrading particle surface, particle size decreases throughout the composting process. Although this increases the active aerobic surface to degrade, smaller particles reduce porosity and the structural strength of the compost bed.

Porosity is the ratio of void volume to total volume of the composting mass and, together with the distribution of particle size, influences the resistance to airflow. Free air space is similar to porosity but it excludes the water filled space in the void volume. It is an important parameter of composting as it represents the space for O_2 in the bed. Particle size and moisture content alters with the substrate conversion. As a result, porosity and free air space are also subject to change. Suess (1985) found that free air space conditions lower than 14 % are insufficient for composting and under 10 % the aerobic conversion is completely replaced by anaerobic degradation.

Permeability is the parameter that expresses the resistance that the flow of air meets in the compost bed. The influence of the parameter permeability highly depends on the homogeneity of the mixture. Ginkel *et al.* (2002) found that gas permeability decreases with wetness for raw material, whereas for composted materials they found no clear relationship. They also found that gas permeability decreased as gas velocity increased.

C/N ratio

In composting, the most important nutrients required by the microorganisms are C, N, P and K (potassium). N, P and K are also of primary importance for plants, so their concentrations influence the fertilizer value of compost as well. Microorganisms use C for both energy and growth, whilst N is essential for the protein synthesis and reproduction. According to Rynk *et al.* (1992) the optimal C/N ratio depends on the sort substrate but it is usually in the range of 25-30. A sub-optimal C/N ratio is considered to be one of the main reasons for amplified NH_3 emissions. Rynk *et al.* (1992) also reported that a balanced C/N ratio in composting material is likely to ensure a good balance of other nutrients as well.

pH

The large diversity of microorganisms in a compost bed ensures a natural buffer capacity for the process, which makes the process relatively insensitive to pH (Haug, 1993). In general, the pH of the composting materials is initially slightly acid. The production of volatile fatty acids (VFA) at the early stages of decomposition causes further acidification of the compost bed to levels of pH 4.5-5.0. The pH in the bed is the result of equilibrium between NH_3 and VFA's. Ekinci *et al.* (2000) reported that the pH has a strong influence together with the C/N ratio on the rate of NH_3 volatilization from paper waste composting. Witter and Lopez-Real (1988) observed increased NH_3 emissions already above pH 7 and at temperatures higher than 40 ^{o}C. The conversion of VFA increases the pH and temperature alike. If conditions are aerobic, the amino-acid decomposition leads to an increase of the pH between 8.7-8.9 (Andersson, 1996). Sufficient quality composting is possible to achieve in a pH range of 5.5 (6.0 at Elwell *et al.*, 2001) until 9, with an optimum range of pH 6.5-8.0 (Rynk *et al.*, 1992; Zucconi and Bertholdi, 1986). Stable compost products feature a slightly alkaline pH (7.5-8.5) at the end of the composting process.

1.3.5.2 *Process parameters*

O_2 level

As composting is basically an aerobic process, O_2 has to be available for the microorganisms to grow (Haug, 1993). It can be supplied to the compost bed by diffusion, wind, natural convection or forced aeration. The role of wind in composting has not been studied in depth yet and diffusion is not capable of sufficiently supplying the compost bed with O_2. Aeration (either via convection or forced) can ensure that the bed (and the process) remains largely aerobic. Even though successful composting experiments were reported with O_2 concentrations as low as 1 % in the airflow (Rudrum, 2005; Richard, 1997) concentrations above 5 % were found recommendable. Beneath 5 %, the low O_2 concentrations lead to an anoxic or anaerobic bed promoting NH_3 volatilization.

The O_2 requirement is the highest in the initial phase of composting as the readily degradable components are degraded then. Therefore, anaerobic conversions are also likely to take place especially during the initial decomposition. However, the overall contribution of the anaerobic processes to the whole composting process usually remains very small. The limitation of O_2 in the cores of larger particles is caused by the way of its transport to the microorganisms. The transport takes place via a water film. Concentration of O_2 in water is 32 times less than in air (Treybal, 1968) and maximal solubility decreases with increasing temperature. As transport rate through water is lower than through air, providing sufficient free air space in the compost bed is essential for restricting O_2 limitations in the bed pores (Haug, 1993).

The air flow through the bed does not only supply O_2 to the microorganisms but also removes heat, water vapor and gases. Generally, the aeration rate required to lower the moisture content is greater than the rate needed for O_2 supply and both requirements are lower than what is needed for heat removal.

Temperature

The energy produced in biological conversions is responsible for the temperature changes in the compost bed. The initial increase in the temperature of the bed occurs as a result of heat release from the biological break-down of polymer substrates to monomers by microorganisms. Heat production depends on the age of the process (concentration of the organic matter), temperature and the available O_2. Initially, the pile is soon heated to mesophilic conditions, creating a favorable environment for a range of mesophilic organisms. As more organic matter is degraded the compost bed is further heated. With the generated heat, the bed soon becomes thermophilic reaching 50-60 °C in its core. If the temperature further rises, thermal kill of most of the thermophilic bacteria occurs rapidly at the range 70-80 °C. Therefore, a high temperature does not only offer better sanitation of pathogens but it also destructs 'useful' microorganisms in a pile. Zhu *et al.* (2004) listed the different temperature optimums for sanitation (>55 °C), maximum rate of biodegradation (45-55 °C) and highest biodiversity of microorganisms (35-40 °C).

1.3.6 General NH_3 dynamics and N conversion in manure composting

The previously mentioned parameters are responsible for the control over NH_3 dynamics. Ammonification, nitrification and volatilizations of NH_3 on its turn will determine not only the extent of NH_3 lost to the environment, but will also influence the subsequent N conversions in a composting process.

With varying relevance, all composting processes show the same general N converting features regardless of method. Figure 1.2 presents a generalized version of NH_3 dynamics in the composting substrate. The following paragraphs highlight the most important features shown in Figure 1.2, and describe the related processes and products.

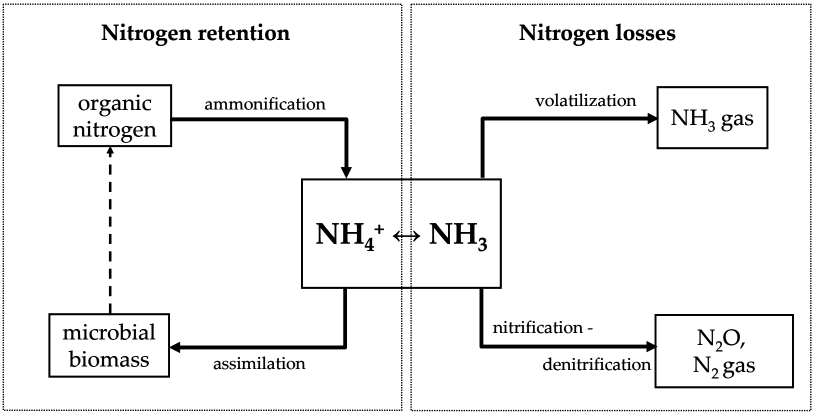

Figure 1.2 NH_3 dynamics in the compost bed (based on Veeken *et al.*, 2000)

1.3.6.1 Ammonification and NH_3 volatilization

In the original manure substrate, N is present in organic matter as protein or in urine in the form of urea. NH_3 is produced from the hydrolysis of protein in the organic matter. This process is called ammonification. If urea is the source of NH_3, it is degraded to NH_3 by the enzyme urease, which is produced by bacteria present in the feces (Aarnink and Elzing, 1998). Here, the following reaction takes place:

$$NH_2\text{-}CO\text{-}NH_2 + 3\,H_2O \rightarrow 2\,NH_4^+ + 2\,OH^- + CO_2$$

The NH_4^+ formed is in equilibrium with NH_3. This equilibrium is pH and temperature dependent. Because of the heating and acidification of composting matter in the first phase of the process, most N in this equilibrium is likely to appear in the form of NH_3-N. This NH_3 is susceptible for volatilization thereby depleting the N content of the compost matter. A fraction of the remaining NH_4^+/NH_3 is present in the liquid phase of the matrix or may be adsorbed to solid particles. However, the dominant part of NH_4^+ is either assimilated into microbial matter or nitrified to NO_3^- (Figure 1.2).

1.3.6.2 Assimilation

Assimilation is the immobilization of the ammoniacal N by incorporating it into the composting microorganisms (Figure 1.2). Microbial biomass such as bacteria, viruses and fungi require N for their cell matter, which they gain from NH_4^+ through assimilation into the cell tissue. With the growing amount of microbial life in composting matter, more N is in organic form. However, with the decay of organisms this microbial N supplies the pool of mineral-N again through ammonification. This ammonification is the same process as with the original N_{org} of the manure. Biological transformation of the N present in organic wastes like manures is strongly linked to the C content, especially to the available C content (Kayhanian and Tchobanoglous, 1992). Lemus and Lau (2002) found, that adding readily available C to organic wastes resulted in a significant decrease of NH_3 emissions and increase in assimilated N.

1.3.6.3 Nitrification-denitrification

If conditions are aerobic, the remaining NH_3 (that was not assimilated or emitted) will be nitrified. Nitrification is an aerobic process, where bacteria convert the NH_3 into NO_3^- in a two-stage process. At the first stage, the NH_3 is reduced to NO_2^- in a mostly *Nitrosomonas* and *Nitrococcus* dominated environment. In the second stage, NO_2^- is further reduced to NO_3^-. This reduction is mostly carried out by the *Nitrobacter* species.

During denitrification NO_3^- is used by facultative microorganisms as electron acceptor in the absence of O_2. The metabolic processes occurring while NO_3^- is used as electron acceptor are equal to those occurring with the presence of O_2. Consequently, it is better to characterize denitrification as an anoxic rather than an anaerobic process.

N can be lost as NO_3^-, NO_2^-, N_2 or N_2O through the process nitrification-denitrification. The most significant from these emissions is the emission of N_2O, which is a highly potent greenhouse gas and as such its formation and emission should be reduced to the minimum.

1.4 Thesis objectives

NH_3 dynamics influence degradation and emission of nitrogenous compounds, and the nutrient value of compost. In literature, there are contradicting views on the applicability of composting in manure management chains. Presumably, this contradiction exists because the available knowledge on NH_3 dynamics is inadequate. Therefore, to improve the composting process in manure management, knowledge on NH_3 dynamics during composting needs to be further investigated.

The previous paragraphs explained the influence of composting design selection, parameters on the NH_3 processes on the N flow of the process. Based on this information, this thesis set the objective to improve scientific knowledge on (i) the relation of main process and substrate parameters on NH_3 dynamics processes in composting, (ii) the level of achievable NH_3 control in extensive and intensive composting methods, (iii) the effect of NH_3 dynamics on subsequent N turnover and the N content in the end-product and finally to determine (iv) the relevance of composting in (swine) manure management chains.

Initially, the research of this thesis is set-up to investigate in-depth the available scientific knowledge on composting NH_3 dynamics. To achieve this, a critical review is given on the state-of-the-art scientific knowledge on manure composting with respect to NH_3 dynamics. The influence of starting substrate and the composting process is investigated on the extent of NH_3 emission and final N content. Next to intensive and extensive composting methods, aerobic storage (the standard management step at present) will be compared.

This is followed by experimental data collection carried out on lab- and pilot-scale on extensive and intensive composting processes on swine manure-bedding mixtures. These two methods differ primarily in aeration mode and level of engineering control. Here, exploration of NH_3 dynamics related processes are assessed such as NH_3 emission and formation, NH_3-assimilation and nitrification-denitrification. To facilitate this, the regular parameters analyzed during composting experiments (total and volatile solids content, C/N ratio, pH, O_2 concentration in the gas phase and temperature) have to be extended. Therefore, structural parameters (particle size, porosity, and permeability), concentration of significant N forms (N_{org}, NH_3/NH_4^+, NO_2^-/NO_3^-,) and nitrogenous emissions (NH_3, N_2O) are also measured and calculated. Hereby, complete N balances of the composting processes can be drawn. This serves more purposes. First, the significance of NH_3 volatilizations can be determined compared to other nitrogenous losses. Secondly, the influence of NH_3 dynamics on subsequent N conversion becomes visible. Finally, as the feasibility of composting is assessed in an agricultural context, the process can not be evaluated in isolation. The combined process – end-product approach will have as consequence that not only

NH_3 related processes are taken into account but also the subsequent N conversion influenced by the NH_3 dynamics. In this way the intended use of the end-product is also integrated in the evaluation.

The findings are intended to deepen scientific and practical knowledge on manure composting NH_3 dynamics. The outcome should be applicable for tackling problems in technological designs of composting processes and estimating significance of NH_3 formation and emission. The insight given on N turnover of the process should be possible to apply in practice for the evaluation of composting feasibility in manure management chains.

1.5 Outline of the thesis

In the following, a short description is given on the chapter-content of this thesis.

Chapter 1 introduces the problems related to excess manures in intensive animal production. The chapter offers information on the present manure management practice and the potential of composting therein. The main composing parameters related to NH_3 dynamics are described and an evaluation approach is presented. The chapter concludes with the thesis objectives and outline.

Chapter 2 reviews the available literature on ammonification and NH_3 emissions from aerobic storage, extensive and intensive composting methods. The review provides detailed knowledge on the N flow of the process and an in-depth description of NH_3 dynamics in the selected methods. It investigates the influence of substrate optimization and level of process control. Finally, it presents extent of NH_3 emissions and final N content in the compost as found in literature.

Chapter 3 presents NH_3 conversion during extensive composting of a straw-rich swine manure mixture. This chapter evaluates mass balance and N turnover from extensive composting methods. It also evaluates effect of monthly turning on organic matter degradation, temporal changes of structural parameters and main nitrogenous emissions. Influence of initial C/N ratio and structural parameters on the nitrification-denitrification processes are discussed.

Chapter 4 assesses NH_3 volatilization from intensive composting methods. The process of NH_3 volatilization is described through a chemical model. Validation of the model with experimental and literature data is provided.

Chapter 5 contains a study on N assimilation from an extensive and an intensive composting process. In this chapter, protein conversion is quantified together with turnover rates of other organic substances. The conversion calculations are prepared with consideration to the microbial biomass yield of the composting process.

Chapter 6 and 7 give the summaries and general conclusions of this thesis in two languages (English and Dutch). These chapters list the assessment of manure composting with respect to the dynamics of NH_3. The importance of NH_3 emission and nitrification-denitrification on the N efficiency are also discussed. Composting is viewed in the context of the whole manure management chain. Practical use and innovativeness of the research is evaluated, and recommendations are given for future research.

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2 NH_3 DYNAMICS IN MANURE COMPOSTING: A CRITICAL REVIEW

Abstract

Composting is a frequently applied method for the treatment of several types of organic wastes. It is a highly flexible process, where mineral nitrogen is assimilated into microbial matter and becomes stabilized as organic nitrogen. Still it is an uncommon choice in manure management because of the wide range of ammonia (NH_3) emissions (5.0-24.0 % of the total initial nitrogen (N)) and the related total nitrogen loss (3.5-72.2 % of the total initial N) during the process. In this critical literature review, analysis on the feasibility of solid manure composting is carried out. The focus is given on C/N ratio in the starting substrate and aeration rate during the composting process. The following treatment methods are evaluated: aerobic storage, extensive and intensive composting.

This analysis points out that the estimating strength of the parameter C/N ratio towards NH_3 emissions increases with the lowering of aeration rate during a composting process. C/N ratio optimization of the starting material also tends to have more influence on NH_3 losses from low aeration rate using processes as storage and extensive composting. Most of the intensive composting studies indicate that the (NH_3 emission reducing) influence of substrate or process optimization decreases with increasing aeration rate. Higher aeration rates are likely to hinder further conversion of NH_3 and facilitate its volatilization.

Process selection appears to considerably influence NH_3 and total N losses from composting treatments. The review shows that NH_3 volatilization from intensive manure composting processes is possible to reduce with 5-11 % through optimization of the compost bed. The application of designs offering high-level control over the substrate or the process can also improve N retaining efficiency in composting, provided that the aeration rates are low. This review also suggests that a deeper insight on N assimilation could help improving N immobilization in composting matter.

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2.1 Introduction

Composting is a biological, aerobic, solid-state treatment method frequently applied for organic household and green wastes (Li, 1998; Fernandes and Sartaj, 1997; Bhamidimarri and Pandey, 1996; Gloueke and Diaz, 1996; Rynk *et al.*, 1992; Sartaj *et al.*, 1997; Haug, 1993). However, the concerns related to high nitrogen (N) losses of the process (Burton *et al.*, 2003; Sommer, 2001; Kirchmann and Lundvall, 1998), make it a rarely applied treatment in manure management. Organic animal production is the only agricultural sector where composting is frequently applied for manure treatment.

2.1.1 Composting of animal manures

There is an increasing relevance for the investigation of composting feasibility for manure management purposes because of the growing amount of biological animal production farms and conventional solid or semi-solid manure systems (ALFAM, 2006; Sommer, 2001; Lehmann *et al.*, 1993). At present, these manure management chains handle surplus manures by storing them prior to transport and utilization on agricultural land (Burton *et al.*, 2003). Apart from a logistical concern, manures also cause environmental problems mainly in the form of NH_3 and nitrous oxide (N_2O) emissions (Oenema, 2000; Olivier *et al.*, 1998; Sommer and Hutchings, 1995). These emissions may appear from the moment of manure excretion in the animal houses until the manure-N uptake by plants. Reduction of these emissions is complex because measures taken to reduce one nitrogenous loss might trigger the emission of another N compound. For example, land application techniques exist to minimize NH_3 volatilization by incorporation of manure into the soil, but the reduced NH_3 loss is likely to be compensated by higher N_2O emission and nitrate (NO_3^-) leach out (Wrage, 2003).

Composting animal manures could be an option to control the N flow in manure management chains. It is a highly flexible process that is adjustable to a wide range of technological challenges. During this process, mineral N (NH_3, NH_4^+, NO_2^- and NO_3^-) is assimilated into microbial matter and becomes stabilized as organic nitrogen (N_{org}) (Hümbelin *et al.*, 1980). Ripe composts contain mainly N_{org} which is less susceptible to leaching out or nitrogenous emissions. The diverse dead and living organisms as bacteria, actinomycetes or fungi were reported to comprise as much as 25 % in composts (Satriana, 1974). Researchers (Imbeah, 1998) and environmental policy-makers (European Commission, 2001) indicate the suitability of composting in manure management chains. However, the N management and NH_3 dynamics (formation, conversion and emission of NH_3) of the process make its use debatable (Martins and Dewes, 1992).

2.1.2 Emissions during manure composting

Composting processes show variable nitrogenous losses. The losses occurring during microbial conversion are mainly in the form of NH_3, N_2O and nitrogen gas (N_2) (Garrison *et al.*, 2001; Haug, 1993; Rynk *et al.*, 1992). These emissions can add up to 40 % of the N_{total} (total ($N_{Kjeldahl}$+NO_2^-+NO_3^-) nitrogen, where $N_{Kjeldahl}$ is based on Kjeldahl (1883)); initially present in the manure (Lemus and Lau, 2002 based on Møller *et al.*, 2000; Pel *et al.*, 1997; Kuroda *et al.*, 1996).

Emissions of NH_3 from composting processes of solid animal manures show a wide range and are emitted especially at the initial phase of the process and at agitation of the compost bed (Lemus and Lau, 2002, Osada *et al.*, 2001; Tanaka and Yakushido, 2001). N_2O emissions occur mainly from denitrification processes and despite their significance were not often reported from composting processes until recently. Other significant gaseous nitrogenous losses from the process nitrate (NO_3^-) and nitrite (NO_2^-) emissions have been reported, but are considered less significant (Martins and Dewes, 1992; Körner *et al.*, 1999). These emissions do not only pose an environmental problem, but also decrease the agronomic value of compost (Hao and Chang, 2001, Sommer, 2001; Fraser and Lau, 2000; Kirchmann and Lundvall, 1998).

This chapter attempts to identify the reasons behind the differing views on manure composting by analyzing the NH_3 dynamics of the process. It is believed, that the attained knowledge on composting NH_3 dynamics can provide an improved background for feasibility studies.

2.2 Review methodology

2.2.1 Methodological background

Unlike most composting assessments, present chapter compares NH_3 emissions and losses of (total) N on the basis of the complete N balance calculated with absolute N weights in a compost bed. Also, a life cycle analysis (LCA) approach is used where process related N emissions are viewed parallel to the N content of the compost product. This approach and the N calculations based on absolute weight (kg) allow observation of otherwise unseen shifting or swapping of (nitrogenous) emissions (Sommer, 2001).

This review is concerned about two main factors in manure composting experiments. These are the influence of starting material and that of the process control on NH_3 dynamics. Influence of the C/N ratio was examined in the starting substrates for their influence on NH_3 emissions, and effect of the aeration rate was investigated in the composting processes. For the selection of relevant process designs, a novel approach was used. Here, composting processes were grouped according to the level of control they can exercise on the dynamics of NH_3. This means, that an increasing level of control contains the possibility of optimization of either the composting substrate or the process for the reduction of emissions. The following classes can be identified (i) aerobic storage (AS) experiments, where aeration is led by diffusion; (ii) extensive composting (EC) experiments, where natural convection introduces the fresh air into the compost bed and (iii) intensive composting (IC) experiments which make use of forced aeration. These groups are devised as they profoundly differ in aeration features and required technological assets, whilst their NH_3 dynamics are considerably documented.

2.2.2 Aerobic storage

The method hardest to define is aerobic storage. In scientific literature, there are seemingly opposing views to be found on what storage is. In this chapter, aerobic storage will be defined as a conservation method for solid manure and amendment mixtures. This method represents the storage stage in solid manure management of conventional animal production systems. As the stored manure is not closed hermetically at this method, it is comparable to a static composting pile method without agitation. Although the process objective is conservation of the manure instead of conversion, aerobic storage can be looked at as a composting method where only starting substrate optimization may be considered and no significant process optimization takes place. The level of control over NH_3 and other nitrogenous emissions is very low. Due to the minimal intervention, the initial warming up of the bed is followed by limited conversion of the organic matter. The temperature is usually sufficient for some degradation but the limited oxygen (O_2) availability slows the aerobic process.

2.2.3 Extensive composting

EC is similar to AS methods with the difference that it is possible to optimize the compost bed not only for the substrate, but also for the process. In practice, it mainly includes agitation and mixing of the bed to ensure the occurrence of natural convection. Here the degradation induced warming facilitates the convection of O_2 rich air into the bed maintaining an aerobic environment for the microorganisms.

2.2.4 Intensive composting

IC methods include composting designs with active aeration using blowers. Process control is often based on either temperature of the bed or aeration rate. It is assumed, that gaseous N emissions from the composing reactors can be trapped and treated only in this scenario. It was also assumed, that entrapment and treatment of the off gas is carried out in a way that it meets relevant environmental regulations.

Finally it is important to note that this review only investigated solid manure and amendment (straw, rice hull etc.) mixtures. At some of the researches, these amendments were already added as the bedding of the animals, kept according to deep-litter 'principles' or organic agriculture regulations. In case of experiments on phase-separated manures, the carbon (C) containing amendment was added prior to the composting treatment as no bedding material was present in the animal houses. This difference in amendment addition was assumed to be negligible for the NH_3 emissions and was not reported. The manure and the amendment were assumed to be well mixed sufficiently to achieve semi-homogenous conditions. Further differences in manure characteristics are considered in the interpretation of the reviewed data later in this paper.

2.3 Theoretical NH_3 dynamics of composting processes

NH_3 dynamics has been defined and summarized in Chapter 1 as the collecting name for NH_3 related conversion processes. These processes supply or deplete ammoniacal N to or from the NH_3-NH_4^+ pool in the compost bed. Manure composting NH_3 dynamics are embedded in a complex organic matter degradation matrix, where processes occurring on micro- and macro-scale mutually influence each other. In the following paragraphs, the NH_3 routes listed in Table 2.1 are explained and discussed based on the composting particle kinetics (CPK) model of Hamelers (1993).

Table 2.1 Overview of NH_3 dynamics related conversion processes in composting

Route	Process	Organism	Substrate	Product	Environment
Ammonification	Proteolysis (hydrolysis)	Bacteria/Fungi	Pr	AA	Aerobic/ anaerobic
	Ammonification	Bacteria/Fungi	AA, U	NH_4^+	Anaerobic
	NO_3^- - ammonification	Bacteria	NO_3^-	NH_4^+	Anoxic
Assimilation	Protein synthesis	All organisms	AA	Pr	Anaerobic
	Amino acid synthesis	Bacteria	NH_4^+	AA	Anaerobic
	N fixation	Bacteria	N_2	Pr	Anaerobic
Nitrification-Denitrification	Nitrification	*Nitrosomonas* *Nitrobacter*	NH_4^+ NO_2^-	NO_2^- NO_3^-	Aerobic Aerobic
	Denitrification	Bacteria	NO_3^-	N_2	Anoxic/ anaerobic
	Nitrifier denitrification	*Nitrosomonas*	NO_2^-	N_2O, N_2	Anoxic

Remarks: AA: amino acids; U: urea; Pr: protein

2.3.1 The CPK model

The compost bed is considered to be a packed bed of irregular shaped particles (Figure 2.1) according to the CPK model. On a micro-scale, these particles are comprised of solid, fluid, and gas phases. The solid phases of the particles are built up of insoluble organic matter and insoluble inorganic compounds. These compounds form the solid matrix of the particle, which contains micro-pores holding the fluid-phase and gases. Organic and inorganic matter is dissolved in the fluid-phase (Figure 2.1). On a macro scale, the aeration of the compost bed is ensured through the gas filled spaces among these particles.

Biological activity may take place at two locations on a micro-scale: in the fluid phase and at the interface of the fluid phase with the solid and gas phase. Within the particle only diffusional mass transport occurs in the fluid and gas phase. Diffusion is assumed to be negligible in the solid phase. According to calculations of Hamelers (1993), particles with a diameter above the range of 30-180 μm are anaerobic due to the small rate of O_2 diffusion into the particle. Most composting aggregates are considerably larger than that range, indicating that anaerobic conversion is also present in compost beds.

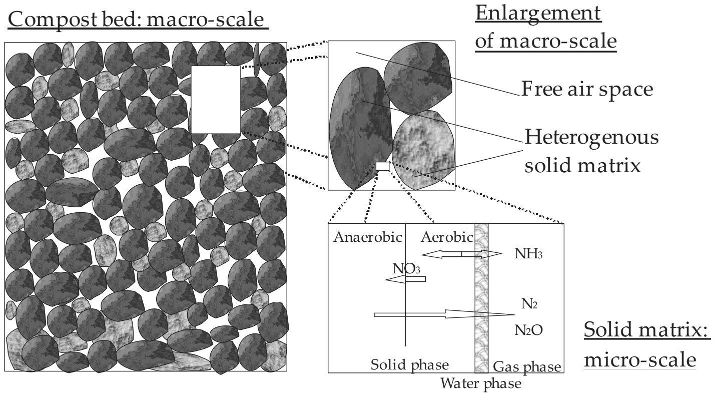

Figure 2.1 Composting of a manure-amendment mixture bed at macro- and micro-scale

The main feature of the model is the implication of close coexistence of aerobic and anaerobic microorganisms (Figure 2.1). As a result, a range of complex anaerobic and aerobic conversion sequences take place on the micro-scale. Although aerobic conversion products may also be reduced in anaerobic segments, initially fermented products of anaerobic bacteria are mostly further converted by aerobic organisms on the surface film of the particles. This leaves the aerobic environment the determining factor in the composting process. The following sections present the role of NH_3 dynamics in this context.

2.3.2 Ammonification

There are three possible routes to the formation of NH_4^+ in animal manures. Urea-N may be ammonified into NH_4^+ (Table 2.1). The contact of urea with the enzyme urease (present in the feces) brings about the following proteolytic reaction (Table 2.1):

$$NH_2\text{-}CO\text{-}NH_2 + 3\ H_2O \rightarrow 2\ NH_4^+ + 2\ OH^- + CO_2 \qquad (2.1)$$

This enzymatic process is strongly temperature, pH and urea concentration dependent. This route is likely to be the main supplier of the initially present ammoniacal N in the manure.

Another hydrolytic reaction in composting is the NH_4^+ formation from the protein compounds present in the feces. The protein-N in feces is either originally in the manure in the form of the excreted organic matter or comes from the decaying microorganisms (biomass) present. Its conversion is a sequence of proteolysis and ammonification. The spatially closely allocated aerobic and anaerobic environments in the compost bed provide an optimal setting for the efficient degradation of the manure-proteins to amino acids. The first phase of this hydrolysis process, also called protein conversion or proteolysis (Table 2.1), is followed by ammonification, which is the formation of NH_4^+ through the oxidative de-amination of the produced amino acids. Finally, NH_3 can also be formed from NO_3^- via the NO_3^- ammonification route. However, this process is not considered significant in manure composting.

2.3.3 NH_3 volatilization

NH_3 volatilization depends on the balance of NH_4^+ and NH_3 in the in the compost bed. The ammoniacal equilibrium determines the concentration or partial pressure of NH_3 in the liquid phase of the particles. It is a crucial point in NH_3 dynamics of manure composting methods because of the susceptibility of NH_3 to evaporate to the gas phase and emit in a gaseous form.

In the starting phase of the process the initially available total ammoniacal N ($TAN=NH_4^++NH_3$) determines the amount of available NH_3 in the compost bed. At this early stage, the compost bed is slightly acidic. Microbial conversions increase bed temperature which results in higher conversion rates. The production of VFA at the early stages of hydrolytic decomposition causes further acidification of the bed to levels of pH 4.5-5.0 as a result of NH_3 and volatile fatty acids (VFA) equilibrium. The pH increases and the temperature rises as the VFA are further converted. If conditions are aerobic, ammonification may result in an increase of pH 8.7 to 8.9 (Andersson, 1996). While most aqueous ammoniacal N is in the form of NH_4^+ at lower temperature and pH, with the increase of the two parameters the equilibrium shifts to NH_3 (Emerson *et al.*, 1975; Martins and Dewes, 1992). The amount of NH_4^+ and NH_3 change depending on pH and temperature is

$$NH_4^+{}_{(aq.)} \leftrightarrow NH_{3\,(aq.)} + H^+ \leftrightarrow NH_{3\,(gas)} + H^+ \qquad (2.2);$$

giving an equilibrium constant (K_{eq})

$$K_{eq} = [NH_3]*[H_3O^+] / [NH_4^+] \qquad (2.3),$$

where all units are in moles per volume. On a macro-scale the produced gaseous NH_3 is transported from the compost bed by aeration caused by either natural convection or a forced aeration flow.

2.3.4 Assimilation of ammoniacal N

Part of the NH_3 that is not emitted from the compost bed may assimilate to form microorganisms (biomass). Assimilation of ammoniacal N is the consecutive amino acid and protein synthesis of NH_3 into microbial biomass (Table 2.1). N is required as it is the main constituent of protoplasm in microorganisms. As proteins are the only compounds in organic matter that supply N to the NH_3 pool, it seems logical that protein degradation plays a central role in NH_3 dynamics. Unfortunately, little research information was found in scientific literature on this matter.

Although the microbiologically synthesized N (N_{org}) is not susceptible for emissions, the decay of microorganisms brings about ammonification of the microbial protein. The amount of N_{org} is likely to become constant after some time because the simultaneous synthesis and decay of microorganisms reaches stability. As a consequence, re-release of NH_3 occurs via the ammonification of the decaying microorganisms. As N assimilation provides N_{org} that is less susceptible to nitrogenous emissions, the re-introduction of N into the NH_3 pool through decaying bacteria is an important process of NH_3 dynamics. Elwell *et al.* (2001) found a delay in NH_3 release compared to the temperature-increase in the compost bed and interpreted it as NH_3 originating not from the original organic matter but from the decaying biomass microorganisms after reaching equilibrium of ammonification and N synthesis of the biomass. Another supply route of microbial N may be the process of N fixation (Madigan *et al.*, 2000) (Table 2.1), where N_2 gas is broken up in an energy consuming reaction. However this latter transformation is not considered significant in compost processes.

Alternative routes for the conversion of NH_3 have also been investigated in recent years for wastewaters and soils (Ahn, 2006; Wrage *et al.*, 2001). The physico-chemical adsorption route is not considered significant in manure composting processes. Although processes as nitrifier denitrification or anammox were proven to exist in solid or liquid environments, none of them was been demonstrated to be significant in composting processes. Therefore these alternative processes are dealt with only marginally in this work.

2.3.5 Nitrification-denitrification

After ammonification, the produced ammoniacal N can be nitrified as long as the conditions are aerobic. The product of nitrification is nitrate (NO_3^-) (Table 2.1). This process consists of two phases. First, the NH_3 is oxidized to nitrite (NO_2^-) in the mostly *Nitrosomonas* and *Nitrococcus* dominated environment and in the second phase NO_2^- is further oxidized to NO_3^- mostly by *Nitrobacter* species (Anthonisen *et al.*, 1976). Because of the microbial diversity of composting processes, the exact nitrifying species are not investigated in most of the literature. The chemical reactions occurring in nitrification are the following:

$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2\ H^+ + H_2O$ + energy (*Nitrosomonas*) (2.4) and

$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$ + energy (*Nitrobacter*) (2.5).

The optimum pH for a complete nitrification is in the range of 7-8.5. The optimal temperature values can be found approximately at 33 °C with a higher limit of 40 °C (Myers, 1975). Although a large number of substances are known to inhibit nitrification (Anthonisen *et al.*, 1976), only the inhibiting feature of free NH_3 (in high concentrations) is suggested to be relevant in manure composting.

The process of nitrification is followed by partial or complete denitrification of NO_3^- (Table 2.1). During denitrification, nitrate is applied as an electron-acceptor in the absence of O_2. The bacteria responsible for the degradation are facultative. Since the metabolic processes occurring while NO_3^- is used as electron-acceptor are equal to those in the presence of O_2, it is better to characterize denitrification as an anoxic process instead of an anaerobic one. Denitrification can be carried out by heterotrophic species of *Pseudomonas*, *Achromobacter* or *Aerobacter* bacteria. The degradation is accompanied by more intermediate products:

$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$.

The optimal pH condition for denitrification is around 7-8, but it can be carried out up to pH 11 in a temperature range of between 50-65 °C. N_2O is also produced during nitrification, but emission of this nitrogenous greenhouse gas is mainly due to denitrification (He *et al.*, 2000). As a potent greenhouse gas, emission of N_2O should be minimized. That it is possible, was shown by Tam *et al.* (1996), who found that highly wet manures provided a favorable environment for denitrifiers and to convert N_2O to N_2.

2.4 Influence of the starting material on NH_3 dynamics

The quality of the composting substrate at the start of the process is an important 'parameter' that influences NH_3 dynamics. Having or setting the main substrate parameters (see section 1.3.5) in their optimal range is likely to improve the microbial environment in the compost bed thereby contributing to an increased (bacterial) growth rate and a faster process. Although more parameters can influence growth of microbial organisms in composting processes, carbon-to-nitrogen (C/N) ratio of the initial solid manure and amendment mixture is considered a central parameter in controlling NH_3 emissions (He *et al.*, 2000). Tam and Tiquia (1999) found that the C/N ratio in the starting material was the most important factor for changes of N_{total} and N_{org} concentrations of the end product, in which pH was the most important chemical factor affecting changes in mineral N forms. Burton *et al.* (2003) and Rynk *et al.* (1992) also reported the C/N ratio to be a central parameter determining ammoniacal emissions.

The C/N ratio is found to be a useful guide when mixing manures with amendments. However, Kayhanian and Tchobanoglous (1992) and Lopez-Real and Batista (1996) recognized that not the total amount of C, but only the biodegradable fraction is the right component to consider at the C/N ratio. That C is not always present in an available form is because the carbonic compounds in woody materials are largely bound by lignin. Lignins are organic compounds highly resistant to biological degradation. As a significant portion of C originates from the added amendment; it increases the importance of bedding materials in solid manure systems (Andersson, 1996). Mathur *et al.* (1990) demonstrated that manure co-composted with a C-rich peat amendment of good structural characteristics significantly decreased NH_3 volatilization from the process. The most frequently used amendments are wheat straw, rice hulls, leaves or wooden by-products.

According to Rynk *et al.* (1992) an optimal C/N ratio is substrate dependant, but in general is in the range of 25-30. Generally, a C/N ratio beneath 20 leads to significant NH_3 emissions. C/N ratio's above 40 cause slower conversion of organic material because of the limiting amount of N for the bacteria. The C/N ratio changes continuously during the composting process because of emissions and differing microbial degradability of C- and N-containing compounds in the composting organic matter. For example, microorganisms can rapidly utilize sugars and starches, while (hemi)-celluloses undergo partial and slower decomposition.

The assessed experiments exhibited a large diversity in general composting designs, scientific approach and the published parameters. Therefore, present review simplified this part of the investigation to the analysis of optimized and not-optimized C/N ratio groups. Experiments where the starting substrate showed C/N ratio's of 25 or higher comprised the group of optimized experiments. The other group was comprised of manure and amendment mixtures with sub-optimal C/N ratios. It is acknowledged here, that the weight of the researches in Table 2.2 might differ because of differences in quality of experimental design, number of repetitions or substrate quality. Acknowledging this fact, this review limits its scope to the providing of suggestions based on the investigated phenomena, instead of a numerical analysis.

Despite the extended literature search, only a few articles have been found to publish a complete N balance for the executed composting experiments. Only swine and cattle manure experiments were found in both optimized and not optimized designs. Table 2.2 also shows an uneven distribution of optimized experiments towards the intensive designs. While no optimized research was found for aerobic storage experiments, almost all forced aeration experiments feature an optimized starting substrate.

The TAN content of the starting materials differs largely, but in general it is higher for swine manures than for cattle or poultry. This is likely to be the result of the differences in the supplied feedstock and the digestive differences of the animal species examined. The amount of N lost during the composting processes is also higher for swine manures than for cattle. Although the only 'N_{total} lost' data for poultry in Table 2.2 suggests even greater nitrogenous emissions, data in Table 2.4 may suggest that poultry emissions are in general lower.

In swine manure composting, starting materials optimized for C/N ratio appeared to reduce both the N emissions from the treatments and the contribution of NH_3 emissions to the total nitrogenous emissions. While Fukumoto *et al.* (2003) published total N emissions of only 39-42 % of initial N_{total}; Tiquia *et al.* (2002) showed that their range of not-optimized experiments resulted in an emission range of 37-59 % of initial N_{total}.

No difference could be presented on the duration of NH_3 emissions of manure compostings. Where it was published, durations ranged from the start of the process until the end of the first 1-2 weeks and eventually re-occurred with the turnings or mixings of the compost beds. Elwell *et al.* (2001) showed a correlation on the extent of aeration and NH_3 volatilization. Table 2.2 data suggests that regardless of the high NH_3 emissions, initially available TAN does not have an important influence on the final N loss from the composting process.

Table 2.2 Initial NH_3 content, NH_3 emission, total N loss and emission duration from composting processes

Animal	**Method**	**C/N**	**$TAN_{initial}$**	**N emissions**			**Source**
species				**N_{total}**	**NH_3**	**Duration**	
		[initial]	[g N*kg TS^{-1}]	[% $N_{initial}$]	[% $N_{initial}$]	[-]	[author, year]
Swine	IC	25		3.5-25.0	8.2-18.3	~ 10 days	Elwell *et al.*, 2001*
Swine	IC	25		2.9-15.7	6.4-10.6	when aerated	Idem
Swine	IC	25	14.3	39.9			Veeken *et al.*, 1999
Swine	EC	>25	3.9	39.5	11.28	when turned	Fukumoto *et al.*, 2003
Swine	EC	>25	3.9	42.5	12.74	Idem	Idem
Swine	EC	11	15.3	37-59			Tiquia *et al.*, 2002
Swine	AS	11	13.7	40-60			Idem
Swine	AS	12	5.3	48	23	about 14 days	Petersen *et al.*, 1998
Swine	AS	10	21.2	57	24	about 14 days	Idem
Cattle	IC	27	1.9	5.9			Dewes, 1999
Cattle	IC	13	2.3	10.8			Idem
Cattle	EC	14	3.9				Amon *et al.*, 2001
Cattle	EC	14	2.9				Idem
Cattle	AS	17	2.6	16.8	23	~ 5 days	Osada *et al.*, 2001**
Cattle	AS	18	8.5	18	14.9	~ 7-10 days	Sommer, 2001
Cattle	AS	22	4.5	11.6	7.2	~ 7-10 days	Idem
Cattle	AS	20	6.4	15.4	16.7	~ 7-10 days	Idem
Cattle	AS	10	9.6	22	5	~ 14 days	Petersen *et al.*, 1998
Poultry	IC	15	10.9	72.2			Tiquia & Tam,2000**
Poultry	EC	14	3.8				Brodie *et al.*, 2000
Poultry	AS	15	3.5				Idem

*Remarks: * only a selection of runs considered; ** an estimation based on ash balance;* N_{total}*: total (*$N_{Kjeldahl}+NO_2^- +NO_3^-$*) nitrogen, where* $N_{Kjeldahl}$ *is based on Kjeldahl (1883);* $TAN_{initial}$*: total ammoniacal nitrogen (*$NH_3+NH_4^+$*) at the start of the experiment; TS: total solids; empty field: no data was available.* $N_{initial}$*:* N_{total} *values attained at the start of the experiments. AS, EC, IC are aerobic storage, extensive composting and intensive composting methods, respectively.*

2.5 Influence of process selection on NH_3 dynamics

2.5.1 Aerobic storage experiments

Aerobic storage methods are a convenient and cheap way to store animal excreta until further treatment or application on land (Sommer, 2001; Lopez-Real and Baptista, 1996). Although the bed is not agitated or controlled, some aerobic conversion takes place in the stored manure. Fernandes and Sartaj (1997) defined aerobic manure storage as a process without active or passive aeration where only diffusion plays a role in the O_2 transfer to the bed. In practice, it means that the core of the bed is partly or fully anaerobic.

As the process is rarely optimized in AS systems, the quality of the starting material is the main influencing factor of nitrogenous losses. It is generally accepted that solid manure storage systems in animal housing emit more NH_3 than liquid manure systems. However, Dewes (1999) found that stored solid manure emitted less NH_3 on a longer term than liquid manure, provided the C/N ratio was optimized. Liquid systems without available biodegradable C were reported by him to emit high level of NH_3-N. Dewes also reported that the high NH_3 emissions from solid manure with bedding were only found at the beginning of microbial degradation. Amon *et al.* (2001) found that anaerobic storage methods tend to have higher greenhouse gas emissions (N_2O, CH_4) compared to composting, latter often showed higher NH_3 emissions.

Table 2.3 NH_3 and total N characteristics of AS processes

Animal	**C/N** [initial]	**$N_{initial}$** [g*kg TS^{-1}]	**N_{total} lost** [% $N_{initial}$]	**NH_3 lost** [% N_{lost}]	**Source** [author, year]
Swine	11	37.3	40-60		Tiquia *et al.*, 2002*
Swine	8	46.7	48	48	Petersen *et al.*, 1998
Swine	9	49.4	57	42	Idem
Cattle	17	23.4	16.8		Osada *et al.*, 2001**
Cattle	18	23.3	18	82.8	Sommer, 2001
Cattle	22	19.3	11.6	62.1	Idem
Cattle	20	21.8	15.4	108.4	Idem
Cattle	18	24.2	27.7		Idem
Cattle	10	37.6	22	23	Petersen *et al.*, 1998
Poultry	22	20			Fernandes & Sartaj,
Poultry	15	18.9			Brodie *et al.*, 2000

*Remarks: * starting material was optimized for structure; ** an estimation based on ash balance;* N_{total}*: total* ($N_{Kjeldahl}$+NO_2^-+NO_3^-) *nitrogen, where* $N_{Kjeldahl}$ *is based on Kjeldahl (1883); TS: total solids; empty field: no data was available.* $N_{initial}$*:* N_{total} *values attained at the start of the experiments.* N_{lost}*: total N lost during the process.*

Table 2.3 shows that AS processes are in general not optimized and C/N ratio is sub-optimal for significant aerobic degradation. This is partly because of the objective of AS: the containment of manure until field application on land. The experimental end-products in Table 2.3 showed that the N content of the end product was above 1 % VS (data not presented), consequently sufficient for the composts to be termed fertilizers (Barker, 1997). In case of swine manure compostings, the N emissions are relatively high, and the cattle experiments show low N losses. However, where the N indicators are advantageous, it is not due to the advanced process features. The durations of the processes are relatively short which is indicated by the high contribution of NH_3 emissions (occurring particularly in the beginning of the process) in the total N lost. Petersen *et al.* (1998) carried out experiments which had a longer process time that shows lower NH_3 emission contribution and high total N lost. So it is likely that at the lower N emission experiments, predominantly the easily degradable fraction of the organic matter was converted and the initially available NH_3 was emitted from the beds. It is also likely that the rest of the organic matter was converted only to a little extent. Due to the little conversion, the end-product is suggested to exhibit NH_3 dynamics features similar to untreated manure on the field. This condition seems likely to result in relatively high N_2O emissions and leach out of NO_3^-.

2.5.2 Extensive composting experiments

EC methods are characterized by low costs and easy-to-operate designs. Their disadvantages are considered to be the longer process times compared to forced aeration methods and the relatively little control over composting parameters. However, EC treatment of poultry manure-amendment mixture was shown to reduce the required process time to a 100 days, while similar substrates composted with AS conditions took over 300 days to complete (Brodie *et al.*, 2000) (Table 2.4). Passive aeration of EC is ensured either via pipes (Fernandes and Sartaj, 1997) or via regular agitation (mixing and turning) of the manure (Haug, 1993). A considerable amount of research has been done on the allocation and arrangement of aeration pipes (Keener *et al.*, 1997), and the influence of the frequency of turning (Keener *et al.*, 1996).

Agitation by turning and mixing was shown to have an advantageous central role of passively aerated composting by Illmer and Schinner (1997). As EC processes make use of natural convection for air supply, turning offers two more advantages to the composting process. The loosened material temporarily gives a better structure by eliminating or reducing the effect of previous bed compaction. Turning the compost material also mixes and homogenizes the bed. Disadvantages of turned windrows were considered to be the labor intensiveness and relatively high NH_3 volatilization from the process (Rynk *et al.*, 1992). De Bertoldi *et al.* (1983) found that with similar composting substrates, turning resulted in higher N_{total} loss than forced aeration (18 % vs. 5 % $N_{initial}$, respectively). Tiquia and Tam (1998) also confirmed that turned and intensive composting of swine manure resulted in similar N efficiency and maturity of the compost product. Tiquia *et al.*, (1997) determined that turning positively influences more composting parameters, among others temperature, pH and NH_4^+ concentration.

Although literature suggests that EC processes do not show advantageous N balances, it is still remarkable that only a few papers could be found where N emissions were central in the research. These papers do not present complete N balances over the processes which resulted in relatively poor data availability (Table 2.4). The N losses indicate that the optimized design resulted in a higher N % remaining in the end-product. Tiquia *et al.* (2002) also found that while turning gave the most important difference on N losses from an operational point of view, the optimal initial C/N ratio was the most important factor in determining N losses from a swine manure-cornstalks mixture.

Table 2.4 NH_3 and total N characteristics of extensive composting processes

Animal	**C/N** [initial]	**#$N_{initial}$** [g*kg TS^{-1}]	**N_{total} lost** [% $N_{initial}$]	**NH_3 lost** [% N_{lost}]	**Author/year**
Swine	25		39.5	28.4	Fukumoto *et al.*, 2003
Swine	25		42.5	29.8	Idem
Swine	11	36.0	37-59		Tiquia *et al.*, 2002***
Cattle	14	23.3			Amon *et al.*, 2001
Cattle	16	30.3			Idem
Poultry	22	20			Fernandes and Sartaj,
Poultry	14	20.1			Brodie *et al.*, 2000

*Remarks: *** starting material was optimized for structure; N_{total}: total ($N_{Kjeldahl}$+NO_2^-+NO_3^-) nitrogen, where $N_{Kjeldahl}$ is based on Kjeldahl (1883); TS: total solids; empty field: no data was available. $N_{initial}$: N_{total} values attained at the start of the experiments. N_{lost}: total N lost during the process.*

The contributions of NH_3 emission to the total N lost are low in the Fukumoto *et al.* (2003) experiments. This indicates that most NH_3 is converted within the compost bed and emitted as N_2 gas or N_2O. Part of the NH_3 was reported to be adsorbed in the colder, outer layers of the compost bed (based on Groeneveld, 1995). The adsorbed NH_3 is again available for further conversion resulting in higher total N emissions. The N concentrations that could be calculated from the available data are not high, but they are still above 1 % (data not presented).

2.5.3 Intensive composting experiments

IC systems offer an improved control over the whole composting process. At this scenario, NH_3 emissions can be trapped and treated, and organic matter conversions are in general faster. Aerobic conditions of the compost bed may be maintained with more composting methods (like AS or EC), but only IC processes can assure sufficient concentration of O_2 combined with temperature control (Finstein and Hogan, 1993). Disadvantages of intensive composting methods are the higher investment and operational costs. Literature suggests that two main features of forced aeration compostings can influence extent of NH_3 emissions from animal manures, i. e.:

- mode of control (O_2 and/or temperature; intermittent vs. continuous aeration (Fraser and Lau, 2000))
- treatment of emissions, if applicable (no treatment vs. air-scrubber (with trapped NH_3 in condensate) vs. biofilter)

Table 2.5 NH_3 and N_{total} characteristics of intensive composting processes

Animal species	**Aeration**	**C/N**	**$N_{initial}$**	**N_{total} lost**	**NH_3 lost**	**Author/year**
		[initial]	[g*kg TS^{-1}]	[% $N_{initial}$]	[% N_{lost}]	
Swine	CA	25		3.5-25.0		Elwell *et al.*, 2001*
Swine	IA	25		2.9-15.7		Idem
Swine	CA	25	38.0	39.9		Veeken *et al.*, 1999
Swine	CA	22	18.6	28.4	26.5	Hong *et al.*, 1998
Swine	CA	24	17.7	30.6	13.5	Idem
Swine	IA	27	16.3	20.3	18.2	Idem
Swine	IA	22	19.2	29.7	13.7	Idem
Swine		19	28.1			Tam and Tiquia,1999
Swine	CA	18	25.1	30.1	37.6	Hong *et al.*, 1998
Swine	CA	19	23.6			Idem
Swine	IA	19	24	24.2	8.3	Idem
Swine	IA	17	25.4	17.8	17.1	Idem
Cattle	IA	27	5.19	5.9		Dewes, 1999
Cattle	IA	13	5.38	10.8		Idem
Poultry	IA	22	20			Fernandes and Sartaj, 1997
Poultry		15	33.9	72.2		Tiquia and Tam, 2000**

*Remarks: *only a selection of runs was considered; ** an estimation based on ash balance; Remarks:* N_{total}*: total (*$N_{Kjeldahl}+NO_2^-+NO_3^-$*) nitrogen, where* $N_{Kjeldahl}$ *is based on Kjeldahl (1883); TS: total solids; empty field: no data was available.* $N_{initial}$*:* N_{total} *values attained at the start of the experiments; empty field: no data was available; CA (continuous aeration); IA (intermittent aeration).* N_{lost}*: total N lost during the process.*

The susceptibility of swine and poultry manures to high nitrogenous emissions is visible compared to those of cattle manure (Table 2.5). However, insufficient data were available to determine N concentrations of the compost for cattle experiments.

The reviewed literature indicates that intermittent aeration experiments resulted in somewhat lower nitrogenous emissions, and that the contribution of NH_3 emission to that of the total N lost was also smaller. Finstein and Hogan (1993) proposed that aeration modes may also inflict significant influence on compost bed temperature and organic matter converting efficiency. Elwell *et al.* (2001) found that increase in the aeration rate rather than aeration mode (continuous vs. intermittent) correlated well with the rate of NH_3 emission. Hong *et al.* (1998) found that intermittent aeration did reduce the rate of NH_3 volatilization compared to continuous aeration of swine manure with no significant differences in conversion rate.

Although the emitted N results in lower N concentrations in the end-product, the form of emissions is equally important. Resulting from the faster conversion due to the intensive aeration, most NH_3 is likely to be emitted from the compost bed instead of being assimilated into new biomass matter. Optimization of the process does not result in clear divisions between the N losses of EC and IC methods. Not-optimized systems show a similar range in N_{total} lost indicating that the C/N ratio has a limited influence if the aeration rate is high in the compost bed. This agrees with findings of Fraser and Lau (2000), who found that feedstock composition was important in relation to N emissions, and emphasized importance of an optimal C/N ratio. Beck *et al.* (1997) have shown that an optimal C/N ratio could result in low NH_3 emissions at forced aeration experiments, provided air supply was kept close to the demand of microorganisms. The Hong *et al.* (1998) and Dewes (1999) experiments show that optimization (i.e. optimal C/N ratio) increases retaining of N at intermittent aeration. Here, the lower aeration rate corresponds to higher N losses if conditions are optimized, but it is the result of the higher overall conversion of organic matter. On average, the NH_3 emission share from total N losses is smaller (13-26 %) from optimized experiments than from not optimized ones (8-37 %). Still, the final N content reflected in the fertilizer value shows a small difference in favor of the not optimized values (data not presented).

An important feature of the intensive composting systems is the possibility of off-gas entrapment or treatment. If gas treatment is available in the system, it will ensure that the NH_3 is caught in a scrubber or its concentration is reduced by a biofilter in the outgoing gas.

2.6 Discussion

2.6.1 Approach and data availability in scientific literature

Based upon the data and information attained, the presented 'absolute N' approach and the composting method classification appear to provide a practical framework for the analysis of NH_3 dynamics in manure composting. The methodological approach leads to the investigation of the complete N balance of the composting process. Hereby the main control points can be easier identified to reduce NH_3 emissions if necessary. The main achievement of the composting method classification is that it results in a practical (low tech vs. high tech) division of composting processes. At the same time, the classification covers the technological flexibility range of the composting process through three distinctively different aeration mechanisms. Together, the approach and classification support an improved evaluation on the relevance of composting in the manure management chain.

Scientific literature on manure composting NH_3 dynamics appears to be very diverse, hindering the drawing of conclusions and often allowing indications only. It also appears that presentation of the complete N balance is scarce in literature. It may be because of space limitations for articles, but lack of measurements seems often more likely. Investigating and presenting of complete N balances would be advantageous as (i) it could improve comparison/assessment of composting, (ii) could help identifying significant emissions in the process and (iii) could indicate significance of N related emissions in subsequent manure management steps. These improvements could support advanced identification of technological measures to reduce N losses in manure management.

The findings also indicate that the role and significance of amendments is not studied sufficiently. Although total solids content and C/N ratio influence of amendments after mixing is well documented in papers, the structural influence of straw, leaves and other bulking agents are neglected in research. There is a lack of reports on the measurement of porosity and permeability which is especially important if natural convection is expected to be the driving force of aeration. The third area where little information could be obtained was the knowledge on alternative N conversion to nitrification and denitrification. While this area has considerably progressed in wastewater and soil research in recent years, little is known on whether nitrifier denitrification or similar conversion processes are of significance during the composting process. A deeper knowledge of this topic could help identifying the influence of NH_3 dynamics on subsequent N conversions and the bottlenecks of N_2O emission in the latter phase of the composting process.

2.6.2 Influence of the starting material on composting NH_3 dynamics

The results indicate that the extent of NH_3 emissions take up a very wide range. The related N conversion is shown to vary mainly due to quality of starting material and process control. The main parameters in starting material optimization include C/N ratio, total solids content and bed structure features. NH_3 emissions show a much smaller spread where experimental conditions were optimized. Especially the C/N ratio can be considered as the main possibility to control N loss.

It was found that the influence of the optimalized C/N ratios to reduce NH_3 emissions decreased with an increasing level of control in the process. C/N ratio optimization of the starting material tends to have more influence on NH_3 losses from AS and EC. Most IC studies indicate that the positive influence of optimization decreases as the aeration rate increases. Higher aeration rates are likely to have a flushing effect on NH_3 and thereby prevent its subsequent N conversion.

At IC processes, optimization of the starting material has a stronger influence on NH_3 loss if intermittent or a lower aeration rate is applied. The analyzed literature showed only slightly higher NH_3 and total N emissions for optimized designs at a higher percentage of organic matter conversion. The optimization appeared to result in less improvement in N retention at continuous aeration designs. This indicates that the influence of starting material optimization for C/N ratio decreases with increasing aeration rate in the compost bed.

Initially available TAN is likely to be the main reason behind the high NH_3 losses at the starting phase of composting processes. However, the analyzed experiments have shown comparable ultimate N losses from different initial ammoniacal N values. This implies that composting processes can only immobilize N on a larger scale by assimilation. If that is true, the role of biodegradable C-rich amendment is crucial in the conversion process.

2.6.3 Influence of process control on composting NH_3 dynamics

The reviewed literature shows that the standard manure handling method, aerobic storage, is based on little process control leading to a largely anaerobic bed. The mainly diffusion driven aeration leads to incomplete stabilization of the organic matter, coupled with high NH_3 and greenhouse gas (N_2O, CH_4) emissions. The high percentage of NH_3 emissions compared to total N loss indicate that only a limited amount of NH_3 is converted further through a nitrification-denitrification process (Table 2.6). Most NH_3 is likely to remain in the stored bed making the compost susceptible to further emissions upon agitation or transport.

The air supply in EC methods is facilitated by the natural convection principle. These processes are capable of producing compost of satisfactory quality, but offer a narrow range of process control tools. Often, reduction of NH_3 emissions can not be guaranteed. However, the improved bed structure compared to AS and the lower contribution of NH_3 in N emissions in case of lower aeration rates indicate the presence of nitrification and denitrification (Table 2.6). This is the only one from the examined three composting scenarios, where – probably because of the lower aeration flux – NH_3 is assimilated and nitrified instead of being emitted or accumulated. While it would seem obvious to further reduce NH_3 emissions by adjusting pH and temperature in EC and IC processes, the reduction of these parameters would significantly reduce process quality. Adjustment of pH to lower levels would increase process costs, and a lower process temperature would hamper pathogen removal efficiency in the compost bed.

Forced aeration (IC) composting methods can offer high process and emission control and result in adequate organic matter degradation, according to the assessed literature. The process related N loss reduction of IC methods may not appear to be better than that of extensive methods, but the emitted NH_3 can be trapped and treated resulting in a minimal adversary environmental impact of the process. An important feature of IC processes is the high rate of NH_3 emissions likely to originate from the high aeration rates. These aeration rates are also likely to prevent gaseous NH_3 to re-enter the N cycle in the composting matter by flushing out the gaseous molecules (Table 2.6).

Table 2.6 Occurrence of N conversion processes in the investigated methods

Process	Aerobic Storage	Extensive composting	Intensive composting
Hydrolysis	++	++	++
Ammonification	++	++	++
$NH_{3,aqueous} \rightarrow NH_{3,gas}$	++	++	++
$NH_{3,gas} \rightarrow NH_{3,aqueous}$	+	++	-
Nitrification	+	++	+
Denitrification	+	++	+
Assimilation	++	++	++

Remarks: ++: occurs to a great extent; +: occurs to a small extent; -: occurrence is not significant

As Table 2.6 also indicates, the ammonification and assimilation routes are important features in all three of the investigated methods. However, the nitrification-denitrification route is most significant in EC processes and the least important in IC. It is suggested, that EC processes are more suitable for low NH_3 emission composting. However, the limited availability of control tools can guarantee neither low nitrogenous emissions, nor a good quality end product. EC was also the least researched method in the literature. It is advisable to further investigate emission control tools for this method, as only this can offer a complete N conversion to the environmentally inert N_2.

IC processes are likely to emit a large fraction of N as NH_3. Still, the possible control tools like off gas treatment or recirculation may still make this method attractive if avoiding of NH_3 emissions is necessary.

2.6.4 Final remarks

The review indicates that adversary features of aerobic storage processes can be reduced with little effort by optimizing not only the starting mixture but by also applying process control tools of extensive composting. Next to optimization of the starting material and process, it is the rate of aeration that appears to be a key parameter in NH_3 dynamics. Its influence can only be partially controlled by the adjustment of other parameters such as C/N ratio.

The review indicates that NH_3 volatilization from manure composting processes can be reduced through optimization of the compost bed and the application of designs offering high-level process control. Although C/N ratio was found to be the central parameter in determining NH_3 dynamics and emissions, it still must be pointed out that the link is rather indirect. The studied literature showed inadequate knowledge on the features of N assimilation into microbial protein. It seems likely that a deeper insight into this section of NH_3 dynamics could improve the knowledge on NH_3 emissions control.

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3 NITRIFICATION AND DENITRIFICATION DURING EXTENSIVE COMPOSTING OF STRAW AMENDED SWINE MANURE

Abstract

The extensive composting experiment took place using straw amended swine manure from organic swine farming systems. The manure amendment mixture was composted in passively aerated static piles to estimate the effect of monthly turning on organic matter degradation and NH_3, N_2O and CH_4 emissions. Turning enhanced the rate of drying and degradation. The four-month treatment degraded 57±3 % of the initial organic matter in the turned piles, while only 40±5 % in the static piles. The turned piles showed low NH_3 and N_2O emissions, 3.9±0.2% and 2.5±0.1% of total initial nitrogen, respectively. Static piles gave low NH_3 (2.4±0.1% $N_{initial}$), but high (9.9±0.5% $N_{initial}$) N_2O emissions. Prevalence of anaerobic regions in the static system was supported by the higher CH_4 emissions, 12.6±0.6% $VS_{degraded}$ for the static vs. 0.4±0.0% $VS_{degraded}$ for the turned system. It was shown, that straw amended swine manure with very low C/N ratios could be composted directly without significant nitrogenous emissions if turned on a monthly basis.

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3.1 Introduction

Modern livestock activities may result in large emissions of ammonia (NH_3), nitrous oxide (N_2O) and odors from buildings, manure storage and following application of manure to land (Burton *et al.*, 1997). These emissions lead to a large number of environmental problems (El-Ahraf and Willis, 1996). Animal manures are also a valuable resource as they can be used to recycle nutrients and organic matter to soil, thus reducing the use of artificial fertilizers and peat (Richard and Choi, 1999). Manure management is increasingly viewed as a mechanism for reducing the negative environmental impacts associated with livestock production, and a wide range of technologies are being developed and evaluated for that purpose (Burton *et al.*, 1997).

Composting is among the most promising techniques for treating the solid fraction of animal manures, as it is inexpensive and can produce a valuable end product (Lopez-Real and Baptista, 1996). The composting process results in breakdown and stabilization of organic matter, mass and volume reduction through CO_2 evolution and H_2O evaporation and destruction of pathogens and weed seeds. Correctly managed, the resulting compost can be used as an organic fertilizer in agriculture without negative impacts on plant growth and the environment (Epstein, 1997).

Commonly applied composting strategies of forced aeration and windrow turning, so-called intensive composting systems, result in short composting times but will also lead to high NH_3 emissions (Mahimairaja *et al.*, 1994; Witter and Lopez-Real, 1988). Composting of animal manures in passively aerated static piles, which are the most frequently applied extensive composting methods, gives a significant reduction in NH_3 emissions (Lopez-Real and Baptista, 1996). Although these reduced NH_3 emissions might be assumed to result in a greater conservation of N in the final product, research indicates that substantial quantities of N can instead be lost as nitrogen gas (N_2) or nitrous oxide (N_2O) via nitrification and denitrification (Veeken *et al.*, 2002; Czepiel *et al.* 1996). Compaction of the compost bed in time results in decreased air permeabilities of the structure, consequently it reduces natural convection (Das and Keener, 1996). Therefore compaction reduces aerobic degradation and may lead to increased presence of anaerobic regions, promoting emissions of methane (CH_4) and N_2O, both harmful greenhouse gases (Hellmann *et al.*, 1997; Czepiel *et al.*, 1996). Rynk *et al.* (1992) recommend periodic turning of the compost pile to restore the structure and porosity of the pile. In this way the composting process is accelerated and the removal of pathogens is improved.

This study examines the hypothesis that periodic turning might also reduce the emissions of greenhouse gases, N_2O and CH_4. Straw amended swine manure from an organic farming system was subjected to passively aerated composting for 4 months.

Two piles were not disturbed (static system) and two piles were monthly turned (turned system). The composting process was evaluated with respect to drying, organic matter degradation, and the quality of composition changes.

3.2 Experimental section

3.2.1 Composting reactor

Each of the four composting reactors had a volume of 2 m^3 with a height of 2 m and a square bottom of 1x1 m^2 as described by Veeken *et al.* (2002). At 0.2 m from the bottom a metal grid with 2x2 cm^2 holes was fixed which supported the composting bed and facilitated the inflow of ambient air from the bottom. The sidewalls of the reactor were made of sandwich insulating panels to minimize heat losses to the surroundings. Two swing-doors of 1 m in height made of sandwich insulation panels were fitted in the front side of the reactor to facilitate the filling and emptying of the reactor. A slit between the swing-doors allowed placing of polyethylene (PE) tubes (16 mm x 1.8 mm) over the height of the compost bed for temperature sensors and collection of gas samples. The experiments were operated outdoors. At 0.4 m above the compost bed, a roof was constructed which prevented rainfall from moistening the compost. The reactor design allowed air to enter at the bottom and leave at the top, thus resulting in a gradient in only one dimension. The chosen design gave a realistic simulation of a practical window composting process, and the one-dimensional profile facilitated the interpretation of the composting process while simplifying sampling and analysis.

3.2.2 Reactor operation and sampling of compost bed

Straw amended swine manure of 0 to 2 weeks old was taken from a storage pile at an organic swine farm (Uden, The Netherlands). Four reactors were run simultaneously during 4 months from July until November 1999. Two reactors were turned monthly: Turned 1 and Turned 2, and two reactors were left static for the four month period: Static 1 and Static 2. The reactors were filled manually through the front with a four-pronged fork. PE tubes were placed in the compost bed during construction of the piles (see next paragraph). At each turning of the piles (for Turned 1 and Turned 2) and at the end of the composting process (all reactors) the compost bed was manually dug out from top to bottom with a fork. The content of each reactor was divided in three equal sections in height (top, middle and bottom) each representing 1/3 of the total bed height. Both the total weight of the compost bed and the weight of each section were determined to allow density and porosity calculations per section. Three samples of 1.5-2 kg were taken from each section (9 samples for each reactor). For the monthly turned system, the complete compost mass was manually mixed with a fork before refilling the reactor. The samples were chopped and homogenized in a 5 liter stainless-steel commercial food chopper (EMS) and used for determination of total solids (TS), volatile solids (VS), Kjeldahl nitrogen (N_{kj}, based on Kjeldahl (1883)), ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), volatile fatty acids (VFA) and pH. The total weight of the compost bed was determined at the start, after each turning (for Turned 1 and Turned 2) and after the completion of composting.

3.2.3 PE tubes for temperature and gas sampling

Temperature sensors (PT-100) were fitted in PE tubes (diameter 16 mm; thickness 1.8 mm) and placed at regular intervals of approximately 0.3 m over the height of the compost bed. The temperature sensors were connected to a multi-channel automatic data logging systems (Data logger DT100, Data Electronics Ltd., Australia) and temperatures were recorded at 1-hour time intervals. Gas samples of 5 liters were collected from the PE tubes with a membrane pump (Miniport N73, KNF, Germany) in 5 liter gasbags (Teseraux, Tecobag, PETP/AL/PE 12/12/75). One PE tube was placed on top of the compost bed and was assumed to represent the air leaving the compost bed. The gas was analyzed for O_2, N_2, CO_2, CH_4 and N_2O. The NH_3 in the air leaving the compost bed was measured by sampling the air adjacent to the top of the compost bed manually with detection tubes (Draeger, 1996). The velocity of natural convection was measured online by a thermal anemometer (Testo 415, Testo, The Netherlands) placed on top of the compost bed (only for Turned 1 and Static 1). As the lower detection limit of the thermal anemometer is insufficient for the natural convection velocities which are normally expected, a Venturi tube accelerated the air leaving the compost bed. This method is described by Veeken *et al.* (2002).

3.2.4 Analysis of compost bed and air samples

Total solids (TS) and volatile solids (VS), of the samples were determined according to standard methods for compost (TMECC, 2002). Total nitrogen (N_{total}) was determined based on a Kjeldahl nitrogen analysis (Kjeldahl, 1883) that included NO_2^- and NO_3^- content. This is an adapted method of TMECC (2002) where salicylic acid ($C_7H_6O_3$) and hydrogen-peroxide (H_2O_2) are added (Vertregt and Verhagen, 1976). For analysis of NH_4^+, NO_3^-, NO_2^-, VFA (C_2-C_6) and pH, the samples were shaken with water at a sample-water ratio of 1:5 (w/w) for 0.5 hour and the filtrate was analyzed according to standard methods for compost (TMECC, 2002).

Gas samples were analyzed for O_2, N_2, CO_2 and CH_4 as described by Brummeler *et al.* (1991) and N_2O was measured according to Weiss (1981), using Hewlett Packard 5890 gas chromatographs. The NH_3 concentration in the air adjacent to the top of the compost bed was measured manually with Draeger gas detection tubes and bellow pump according to the manufacturer's directions (Draeger, 1996).

3.2.5 Calculations and statistical analysis

The amount of organic nitrogen (N_{org}) was calculated as:

$$N_{org} = N_{total} - NH_4^+ - NO_3^- - NO_2^- \qquad (3.1)$$

Loss of water during composting was calculated on basis of the total weight and change in TS. Degradation of VS was calculated on basis of the total weight, average TS and average VS of the compost bed (Veeken *et al.*, 2002). Density was calculated based on weight and volume per section. Porosity was calculated based on bulk density results according to Richard *et al.* (2004).

The content of nitrogenous compounds on a TS basis does not give information about the absolute changes of the various nitrogenous compounds during composting as organic matter (major part of TS) is also degraded. Changes in absolute amounts of N (in kg) can only be evaluated on basis of changes in absolute amount of the various N compounds. The absolute amounts of the various N compounds were calculated on basis of the total weight of the compost bed, its average TS content and average content of the various N compounds. The emission concentrations of NH_3, N_2O and CH_4 were averaged for two-week periods.

The concentrations of NH_3, N_2O and CH_4 in the air leaving the compost were represented by NH_3 in the air adjacent to the top of the compost bed and CH_4 and N_2O measured in the top of the compost bed. The airflow rate was calculated from the measured velocity of natural convection (m s^{-1}) and the surface area of the compost bed (1 m^2).

Mean and standard deviation values were calculated from the data obtained from the compost sample analyses for the total- and volatile solid contents, for the nitrogenous components and for the CO_2 and CH_4 emissions. ANOVA I based Tukey's HSD and LSD post hoc tests were used to examine whether there was a significant difference between the treatments. Tukey's tests were applied to check whether there were gradients among the three sections (top, middle and bottom) in the compost beds.

3.3 Results

3.3.1 Reproducibility of the composting experiments

The reproducibility and differences between the two treatments were tested on basis of the temporal and spatial variance in TS and VS using Tukey's method (Schloss *et al.*, 2000). Table 3.1 provides the TS and VS results in the three sections of the compost bed for all four reactors at different periods.

Visual interpretation of the temperature curves of the experiment confirmed the similarity among the four reactors in the first month of the treatment, and later between the two-two reactors within the same treatment.

Table 3.1 Profile of Total and Volatile Solids over the reactor height, extracted for statistical analysis

	Turned system						**Static system**					
	Turned 1			Turned 2			Static 1			Static 2		
Days	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom	Top	Middle	Bottom
TS (%FW)												
0	27.9±2.1[#]	28.1±1.1	28.6±0.8	28.3±3.6	27.3±0.2	28.6±0.7	35.9±12.9	33.9±5.6	28.4±0.2	29.6±1.4	26.2±1.1	26.4±3.5
30	45.8±1.0	31.8±0.1	31.5±0.7	33.7±0.7	28.6±2.1	28.0±1.8						
63	40.9±0.9	38.8±0.0	32.9±0.5	39.6±7.1	36.1±0.3	48.7±11.2						
91	46.2±9.2	43.1±2.7	38.8±0.0	46.0±6.7	37.9±1.6	43.0±5.6						
118	44.6±6.1[e]	41.1±1.7[e]	46.1±5.4[e]	44.0±3.3[e]	40.9±2.8[e]	45.9±4.8[e]	46.6±8.1[ac]	34.8±8.9[a]	28.1±0.0[c]	69.5±10.6[ac]	36.0±5.8[a]	29.9±8.1[c]
VS (%TS)												
0	74.1±2.6	68.2±3.6	70.9±0.3	70.1±0.5	71.0±1.4	73.2±1.6	73.9±1.1	69.8±2.5	70.7±0.3	71.0±4.1	72.0±1.6	71.3±5.5
30	62.1±2.0	58.3±1.8	56.4±2.0	63.9±2.9	66.7±3.2	66.1±5.5						
63	55.4±1.5	57.7±6.4	51.1±1.5	56.1±5.6	52.8±4.3	55.1±2.7						
91	54.6±6.8	49.8±4.5	52.0±1.8	48.1±7.1	49.4±2.7	50.2±3.5						
118	56.0±5.6[e]	46.6±3.4[e]	45.3±4.8[e]	47.4±6.5[e]	47.8±5.0[e]	48.8±0.8[e]	58.1±7.1	61.3±6.4[b]	69.2±8.9[b]	52.8±6.0	56.1±5.2[b]	69.4±4.2[b]

TS: total solids

FW: fresh (wet) weight

VS: volatile solids

[#] *mean ± SD (n=3)*

[a] *Significant difference between top & middle section at the end of the experiment at P=0.05, according to Tukey's HSD test*

[b] *Significant difference between middle & bottom section at P=0.05, according to Tukey's HSD test*

[c] *Significant difference between top & bottom section at P=0.05, according to Tukey's HSD test*

[d] *Significant difference between reactors within the same treatment (turned or static) at P=0.05, according to the LSD test*

[e] *Significant difference between the two treatments (turned and static) at P=0.05, according to the LSD test*

Table 3.2 Profile of TS, VS, different nitrogen species, pH and VFA over the reactor height

		Turned			**Static**		
	Time (d)	Top	Middle	Bottom	Top	Middle	Bottom
TS (g kg^{-1} FW)	0	28 ± 2[#]	28 ± 1	29 ± 1	33 ± 4	30 ± 3	27 ± 2
	30	40 ± 1	30 ± 1	30 ± 1	-[*]	-	-
	63	40 ± 4	37 ± 1	41 ± 6	-	-	-
	91	46 ± 6	41 ± 2	41 ± 3	-	-	-
	118	45 ± 3	41 ± 2	46 ± 4	58 ± 7	35 ± 5	29 ± 4
VS (g kg^{-1} TS)	0	72 ± 1	70 ± 2	72 ± 1	72 ± 2	71 ± 2	71 ± 3
	30	63 ± 1	62 ± 2	61 ± 3	-	-	-
	63	56 ± 3	55 ± 4	53 ± 2	-	-	-
	91	51 ± 5	50 ± 3	51 ± 2	-	-	-
	118	52 ± 4	47 ± 3	47 ± 2	55 ± 5	59 ± 4	69 ± 5
N_{org} (g kg^{-1} TS)	0	13.8 ± 1.7	20.1±1.2	16.6±8.0	12.2±4.6	15.4±3.0	16.7±0.9
	30	19.7±15.5	14.1±3.2	18.1±3.8	-	-	-
	63	14.0±0.9	12.7±9.1	12.3±0.1	-	-	-
	91	16.4±1.1	15.7±6.1	20.4±0.3	-	-	-
	118	13.0±5.4	15.9±4.4	15.2±0.7	14.2±1.4	13.0±3.7	16.1±5.8
NH_4 (g kg^{-1} TS)	0	11 ± 2.0	9 ± 1.0	11 ± 30.0	11.6 ± 0.5	9.0 ± 0.4	8.4 ± 0.4
	30	6.1 ± 0.4	3.6 ± 0.2	1.4 ± 0.7	-	-	-
	63	2.2 ± 0.5	4.3 ± 0.5	2 ± 1	-	-	-
	91	1.0 ± 0.4	1.0 ± 0.7	0.6 ± 0.1	-	-	-
	118	0.5 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.8 ± 0.2	3 ± 3	7 ± 4
NO_3^- (g kg^{-1} TS)	0	0.1 ± 0.1	0.0 ± 0.1	0.0 ± 0.1	0.0 ± 0.1	0.1 ± 0.1	0.0 ± 0.1
	30	0.1 ± 0.1	0.05 ±0.1	0.1± 0.1	-	-	-
	63	0.3 ± 0.2	0.1 ± 0.1	0.1 ± 0.1	-	-	-
	91	0.4 ± 0.1	0.1 ± 0.2	0.5 ± 0.1	-	-	-
	118	0.6 ± 0.1	0.8 ± 0.2	1.0 ± 0.3	1.5 ± 0.5	0.7 ± 0.5	0.5 ± 0.4
NO_2^- (g kg^{-1} TS)	0	0.1 ± 0.1	0.0 ± 0.1	0.0 ± 0.1	0.0 ± 0.1	0.3 ± 0.1	0.0 ± 0.1
	30	0.0 ± 0.1	0.0 ± 0.1	0.1 ± 0.1	-	-	-
	63	0.4 ± 0.3	0.1 ± 0.1	0.0 ± 0.1	-	-	-
	91	1.2 ± 0.5	0.1 ± 0.1	0.3 ± 0.1	-	-	-
	118	0.0 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.0 ± 0.1
pH (-)	0	8.5 ± 0.3	8.5 ± 0.1	8.3 ± 0.1	8.4 ± 0.2	8.4 ± 0.1	8.4 ± 0.1
	30	8.6 ± 0.1	8.9 ± 0.1	8.6 ± 0.1	-	-	-
	63	8.4 ± 0.2	8.7 ± 0.2	8.6 ± 0.1	-	-	-
	91	8.3 ± 0.1	8.8 ± 0.1	8.5 ± 0.1	-	-	-
	118	8.5 ± 0.1	8.3 ± 0.1	8.3 ± 0.2	8.3 ± 0.3	8.4 ± 0.3	8.8 ± 0.1
VFA (g kg^{-1} TS)	0	62 ± 20	46 ± 5	62 ± 25	62 ± 14	58 ± 20	36 ± 25
	30	28 ± 1	45 ± 8	50 ± 2	-	-	-
	63	1 ± 1	10 ± 7	5 ± 1	-	-	-
	91	0.4 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	-	-	-
	118	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.5 ± 0.6	4 ± 5	8 ± 6

[#] *mean±SD (n=6), TS: total solids, VS: volatile solids,* N_{org}*: organic nitrogen,* NH_4^+*: ammonium,* NO_3^-*: nitrate,* NO_2^-*: nitrite, VFA: volatile fatty acids. No samples were available for the static system at 30, 63 and 91 days.*

The temperature and TS-VS results show that there was no significant difference between the two turned reactors and between the two static reactors. Therefore, they could be considered duplicates. The statistical analysis of the TS and VS values of the two treatments at the end of the experiment indicated that the two treatments gave a significantly different product. The sections top, middle and bottom showed significant differences for the static reactors but they were similar for the turned piles (Table 3.2).

As the two duplicate reactors were similar for both the turned and the static composting systems, the rest of the paper will present and discuss the mean values for the turned (Turned 1 and 2) and static system (Static 1 and 2). As the duplicate reactors were similar, the velocity of natural convection of the outgoing air measured for one reactor for each composting system (Turned 1 and Static 1) was assumed to be representative for each system.

3.3.2 Temperature development

Figure 3.1 shows the temperature profiles over the compost bed (top, middle and bottom sections) of the turned and static system together with the ambient temperature. Both systems showed a strong increase in temperature directly after the start of the experiment and both systems reached a maximum temperature of 60 °C after 7 days in the top of the compost bed. The static system showed a slowly decreasing temperature leveling off to 27 °C in the second half of the treatment. After the first turning the temperature increased to 70 °C within 5 days, after which it gradually decreased. After the second turning, the temperature again rose to 70 °C within 4 days but the subsequent drop was faster this time. After the third turning, the temperature did not rise again, indicating that rapid aerobic degradation dropped to low levels.

3.3.3 TS and VS profiles

Besides the temperature gradients, gradients in composition of the compost bed are common in static pile composting systems (Haug, 1993). Therefore, the composition of the compost bed was determined separately for the top, middle and bottom sections (Table 3.2). Table 3.3 gives the average composition of the complete compost bed for each reactor, before and after composting. For this it was assumed, that each of the three sections in the pile represented one-third of the composting mass.

TS of the turned system did not vary significantly over the height of the reactor because the bed was turned monthly, thus homogenizing the compost bed (Table 3.2). The turned system showed an average increase in TS from 28±1 to 44±3 % (Table 3.3). TS of the static system increased from 28±1 to 34±11 % in 4 months (Table 3.3) and also showed a distinct gradient over the reactor height (Table 3.1). The TS content increased from bottom to top. The absolute removal of water (in kg) for both systems is shown in Figure 3.2 as calculated by Equation 3.2. Because both the turned and static systems were identical in the first month, it was assumed that drying was equal during this period.

After one month, drying continued for the turned system (with water mass decreasing from 559 to 259 kg from day 30 to 118) while drying of the static system leveled off with the water mass decreasing from 559 to 409 kg. The amount of leachate occurring at the beginning of the treatments was negligible and was excluded from the absolute calculations of the water losses.

Table 3.3 Characteristics of the turned and static composting systems before and after composting

	Turned system		**Static system**	
	start	end	start	end
Weight (kg)	1132	449	1045	611
Height (m)	1.35	0.73	1.27	0.95
Density (kg m^{-3})	838	617	823	642
TS (% of FW)	28 ± 1[#]	44 ± 3	28 ± 1	34 ± 11
VS (% of TS)	71 ± 3	49 ± 4	72 ± 3	61 ± 7
N_{org} (g kg^{-1} TS)	17 ± 3	15 ± 2	15 ± 2	14 ± 1
NH_4^+ (g kg^{-1} TS)	11 ± 1	0.4 ± 0.1	10 ± 1	4 ± 4
NO_3^- (g kg^{-1} TS)	0.1 ± 0.1	0.8 ± 0.3	0.1 ± 0.1	0.9 ± 0.8
NO_2^- (g kg^{-1} TS)	< 0.1	0.1 ± 0.1	< 0.1	0.1 ± 0.1
C/N[*] (-)	13	14	7	10
pH (-)	8.4 ± 0.1	8.3 ± 0.1	8.4 ± 0.2	8.5 ± 0.5
VFA (g kg^{-1} TS)	70 ± 13	0.1 ± 0.1	52 ± 32	3 ± 4

[#] *mean ± SD (n=18)*

[*] *assuming 50 % of VS is C*

FW: fresh weight, TS: total solids, VS: volatile solids, VFA: volatile fatty acids, N_{org}: organic nitrogen, NH_4^+: ammonium, NO_3^-: nitrate, NO_2^-: nitrite

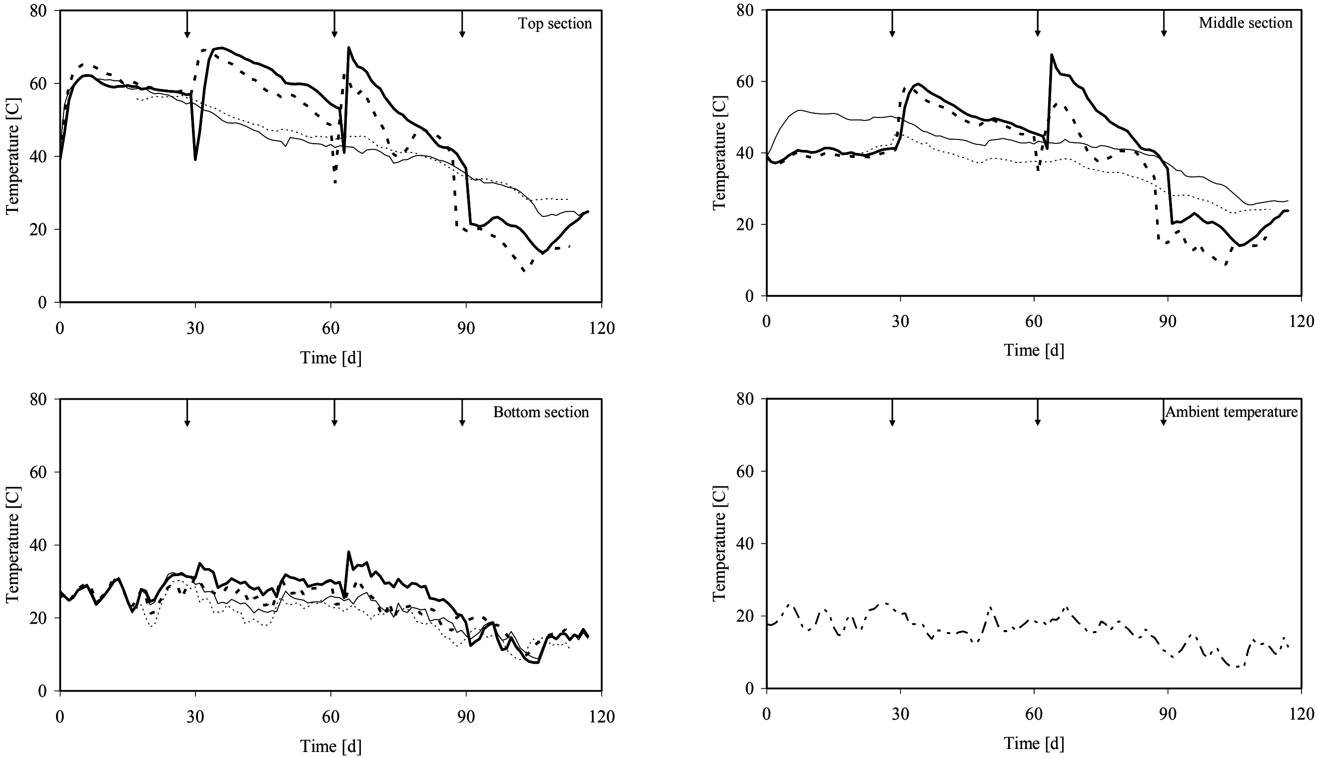

Figure 3.1 Temperature development in the top, middle and bottom sections of the turned and static reactors

Remarks: —— *Turned 1;* — — *Turned 2;* — *Static 1;* --- *Static 2;* -··- *Ambient temperature. Arrows mark times of turning. Standard deviation marks were omitted for better readability of the graphs, for values see Table 3.1.*

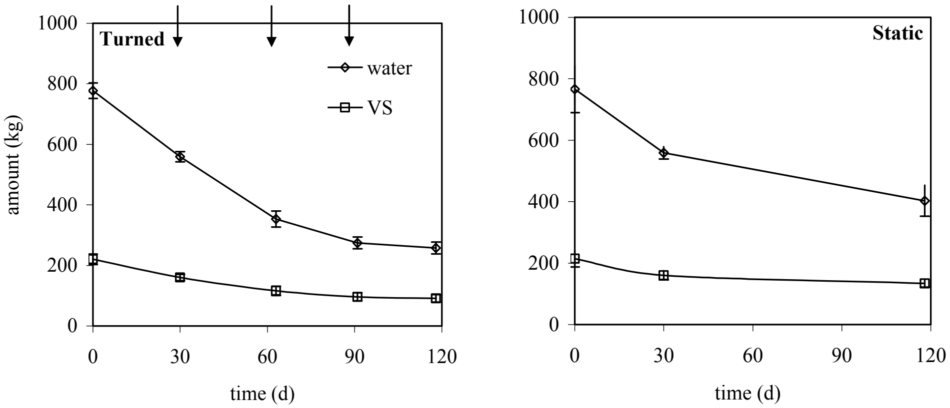

Figure 3.2 Absolute removal of water and degradation of Volatile Solids [kg] in the turned and static reactors

Note, that the arrows mark times of turning, the error bars mark extent of standard deviation (twice).

3.3.4 Velocity of natural convection

Figure 3.3 shows the velocity of natural convection as measured by the anemometers on top of the compost bed of Turned 1 and Static 2.

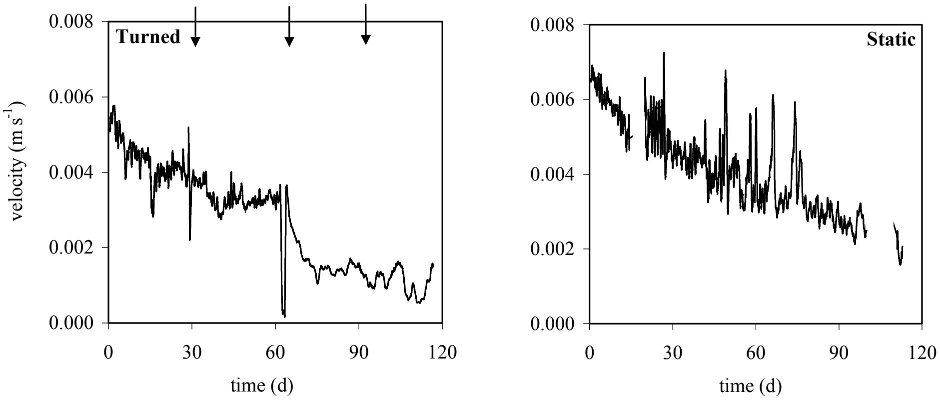

Figure 3.3 Velocities of natural convection measured on the top of the compost piles (arrows mark times of turning)

The velocity is highest at the start of composting and gradually declines. The velocity of natural convection is determined by the permeability of the compost bed and the temperature difference between the surroundings and the compost bed, as can be derived from the general Ergun equation (Beukema *et al.*, 1983):

$$v = \frac{\kappa}{\mu}\frac{g\rho}{T}\Delta T \tag{3.2}$$

where v is the velocity of natural convection (in m s^{-1}), κ the air permeability of the compost bed (m^2), μ the dynamic viscosity of air (Pa s), g the gravitational constant (9.81 m s^{-1}), ρ the bulk density of air (kg m^{-3}) and T the reference temperature. Equation 3.3 shows that permeability is on its turn mainly dependent on the particle size and the porosity characteristics of the bed (Richard et al, 2004).

$$\kappa = \frac{\varepsilon d_p^2}{K(1-\varepsilon)} * \frac{1}{150(1-\varepsilon)+1.75\,\mathrm{Re}} \tag{3.3},$$

Where ε is porosity, d_p is the particle size, K a correction factor and Re is the Reynolds number. The turned reactors showed a relatively homogeneous porosity throughout the bed during the turning events (Table 3.4). Temporally, the turned reactors have shown an increase in porosity in all three sections as the experiment progressed. The static reactors showed no change in porosity in the bottom section while towards the top section the porosity increased.

Table 3.4 Density and porosity characteristics of the turned and static composting systems at the start and end of the experiment and prior to turnings

	Density (kg m^{-3})		**Porosity**[#] (kg kg^{-1})	
Time (d)	Turned	Static	Turned	Static
Top section				
0	841	844	0.26	0.28
30	688	-	0.44	-
63	604	-	0.51	-
91	602	-	0.53	-
118	600	442	0.53	0.68
Middle section				
0	818	832	0.28	0.28
30	709	-	0.39	-
63	646	-	0.47	-
91	678	-	0.46	-
118	630	673	0.50	0.44
Bottom section				
0	856	795	0.25	0.30
30	713	-	0.38	-
63	707	-	0.43	-
91	718	-	0.42	-
118	616	810	0.52	0.29

[#] *porosities calculated according to Richard et al. (2004)*

3.3.5 Composition of gas phase and emissions

Concentrations of O_2, CO_2, CH_4 and N_2O in the air entering the compost bed (bottom), inside the compost bed (middle) and leaving the compost bed (top) are shown in Figure 3.4. The decrease in O_2 inside the bed was accompanied by an increase in CO_2. The lower O_2 level inside the compost bed of the static system indicated that this system had more anaerobic regions which were confirmed by the higher CH_4 content (Figure 3.4). For the turned system, the CH_4 content inside the compost bed was high in the first month but very low for the rest of the composting time. For the static system, the CH_4 content remained relatively high throughout the composting process. The N_2O level in the turned system generally remained very low during the course of composting (concentration in ambient air is 0.3 ppm) but in the static system the concentration dramatically increased after day 60. The NH_3 concentration in the outgoing air was between 0 to 30 ppm for both reactor systems, 0-30 ppm (Figure 3.5). These values are very low compared to intensive composting systems (forced aeration or daily turning) which can reach levels of 2000-8000 ppm of NH_3 in the gas phase (Kuroda *et al.*, 1996; Burton *et al.*, 1997).

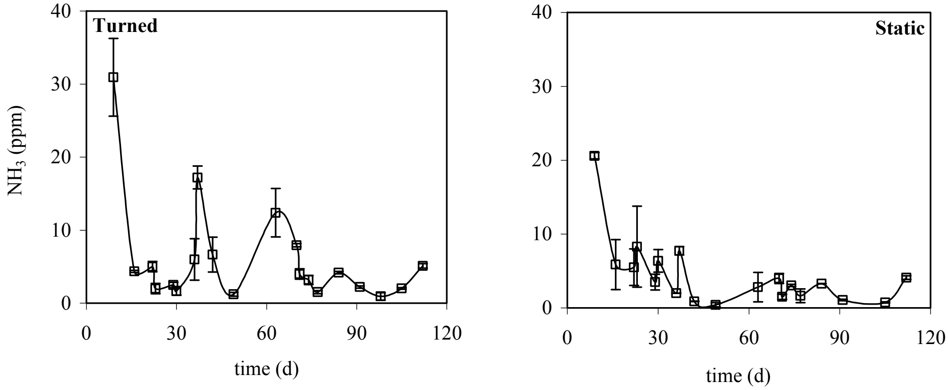

Figure 3.5 Concentration of NH_3 in the outgoing air of the turned and static reactors
Note, that the error bars mark extent of standard deviation (twice).

The emissions of NH_3, N_2O and CH_4 were calculated for 2-week periods for which the emissions were calculated from the averaged air concentrations (Figure 3.4) and averaged airflow rates (Figure 3.3). The cumulative emissions in 4 months are 165±11 g for NH_3, 335±18 g for N_2O and 1372 g for CH_4 for the turned system and 99±5 g for NH_3, 620±33 g for N_2O and 13542±645 g for CH_4 for the static system. The emissions of NH_3 and N_2O correspond to 3.9±0.2 % and 2.5±0.1 % of $N_{initial}$ for the turned system and 2.4±0.1 % and 9.9±0.5 % for the static system. Assuming 50% of VS is carbon

(Haug, 1993), the CH_4 emission corresponds to 0.4 % of the VS for the turned system and to 12.6±0.6 % of the VS in the static system.

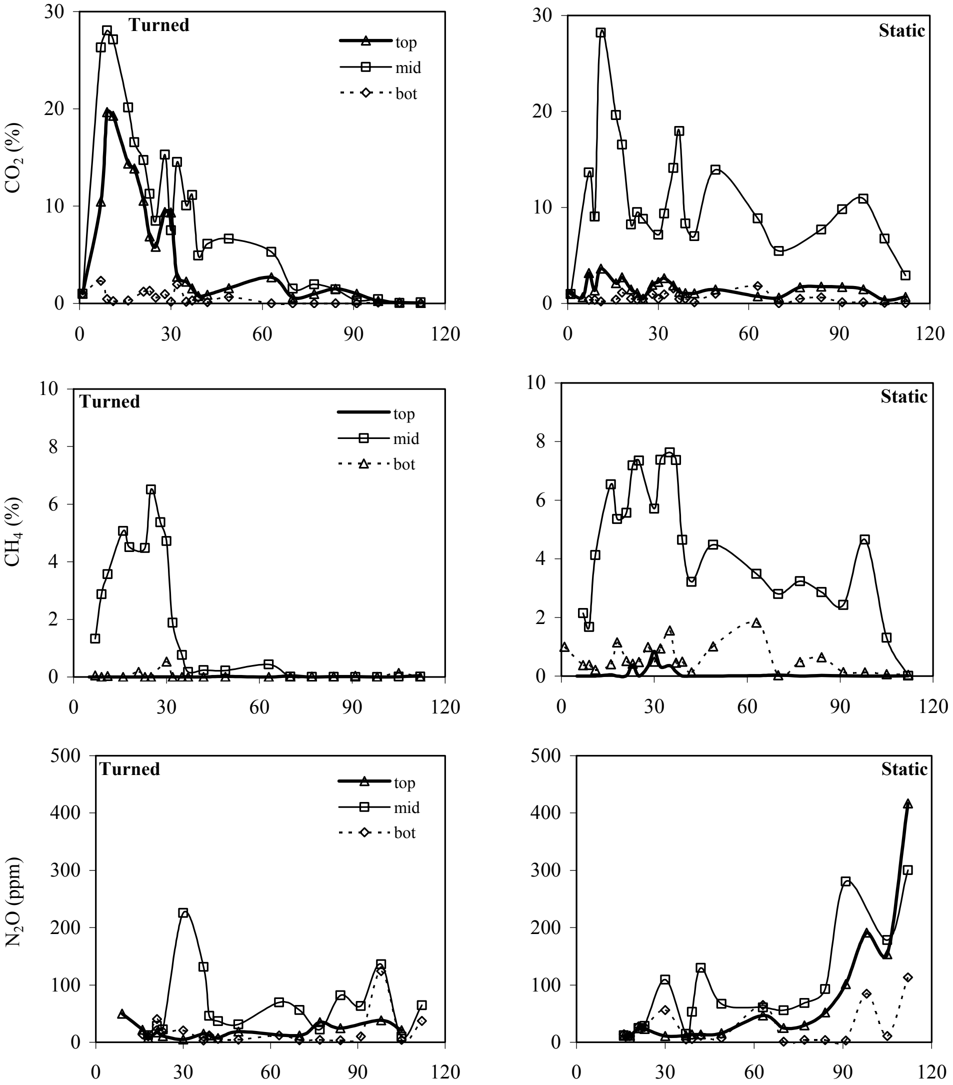

Figure 3.4 Gas concentrations of O_2, CO_2, CH_4 and N_2O in the turned and static reactors
Note, that the standard deviation marks were omitted for better readability of the graphs.

3.3.6 Nitrogen distribution in compost bed

Table 3.2 shows the N distribution (N_{org}, NH_4^+, NO_3^- and NO_2^-) in the top, middle and bottom sections of the turned and static systems. Despite thorough cutting and homogenizing of the samples, relatively high standard deviations are observed in N_{org}. This is because manure-straw mixtures are very difficult to mix thus remain relatively inhomogeneous and because wheat straw and manure have distinct differences in N_{org} (25-30 g N kg^{-1} for manure and 5-7 g N kg^{-1} TS for straw; Veeken *et al.* 1999). The extractable N compounds (NH_4^+, NO_3^- and NO_2^-) show a much smaller variation since the concentrations of water-soluble components are leveled off during composting by diffusion (Yohalem *et al.*, 1996). Due to monthly turning, the gradients in the various N compounds disappeared in the turned system. NH_4 was removed within 3 months in the turned system, but was still present after 4 months of composting in the static system (Table 3.2). As almost no NH_3 was volatilized (discussed in previous paragraph), NH_4^+ had to be converted to NO_2^- and NO_3^- by nitrification. For the turned system, NH_4^+ decreased almost equally in the three sections of the compost bed (Table 3.2) and the static system showed a significantly lower NH_4^+ conversion. NO_3^- and NO_2^- (Table 3.2) were converted by denitrifying bacteria to N_2 or N_2O. Both the turned and static systems showed a drop in N_{org} on an absolute basis, but remained relatively constant on a total solids basis. N_{org} reduction is due to the hydrolysis of N containing organic compounds, mainly proteins in swine manures (Skrede et al, 1998). VFA, a product of organic compound hydrolysis was almost completely oxidized within 2 months in the turned system but was still present in high concentrations in the lower regions of the compost bed for the static system.

3.4 Discussion

3.4.1 Development of temperature, TS and VS during composting

The temperature rise during composting is due to the heat production by aerobic degradation of organic matter. In passively aerated piles heat is predominantly removed from the piles due to water evaporation and subsequent removal of the water-saturated air by natural convection. Heat losses resulting from conduction through the surfaces of the pile are generally small (Lynch and Cherry, 1995; Haug, 1993) but can become significant when heat production rate is low or the pile volume is small (Ginkel, 1996). The velocity of natural convection depends on the air permeability of the compost bed and the temperature difference between the surroundings and the compost bed (Lynch and Cherry, 1995). Veeken *et al.* (2002) showed that the optimal density of the straw amended manure for passively aerated composting was around 700 kg m^{-3}. This study again confirmed that this density (800 kg m^{-3}; Table 3.3) provided a suitable permeability for passive aerated composting.

Investigation of temperature (Figure 3.1) and the velocity of natural convection (Figure 3.3) together show that the decline in velocity coincides with the decrease in temperature difference between ambient air and the compost bed according to Equation 3.2.

Turning homogenized the bed and disrupted the (often anaerobic) bed aggregates into smaller particles. At first, the lower velocity observed seems in contradiction with the improved, more porous structure. However, as porosity increases (Table 3.4) and TS increases (Table 3.2) more pores become present. This results in smaller effective particles that strongly decrease permeability (Equation 3.3). The smaller particle size coupled to the lower permeability can explain this drop in velocity in spite of the higher porosity. Yet, this phenomenon could not be quantified due to the lack of measurements concerning the particle size. This relation confirms that natural convection is controlling the composting process for both systems.

During the first two months, where microbial activity and organic conversions were the highest, both systems showed comparable velocities of natural convection (Figure 3.3), with the turned system expressing higher losses of VS and water (Figure 3.2). The four-month treatment showed that 57±3 % of the initial organic matter degraded in the turned piles, while only 40±5 % in the static piles. This is due to the higher aerobic character of the turned system as shown by the higher O_2 level and lower CH_4 level in the compost bed of the turned system. In the static experiments, the conglomeration of manure and straw to large aggregates results in the larger contribution of anaerobic zones to degradation. This leads to less penetration of O_2 into the core section of these aggregates. In the static system the bottom region will be compacted in time and large aggregates will be formed especially because water leaches towards the bottom. For the turned system, periodic turning disrupts the anaerobic aggregates and homogenizes the compost bed (Table 3.4). The transport of O_2 within the turned system will also be improved, as all parts of the compost bed become drier due to mixing. The anaerobic character of the middle and bottom section of the static system can also be concluded from the VFA content (Table 3.2) which is an intermediate product in anaerobic degradation (Ferguson and Eastmann, 1981). Moreover, incomplete conversion of NH_4^+ in the middle and bottom section for the static pile (Table 3.2) indicates lack of O_2. The presence of anaerobic zones may lead to uncontrolled CH_4 emissions to the environment. CH_4 emissions due to complete anaerobic degradation of organic matter to CH_4 accounted for only 0.4 % of the VS degradation in the turned system but for 12.6±0.6 % of VS degradation in the static system. The lower CH_4 emission in the turned system is promoted by the oxidation of CH_4 in aerobic regions (Figueroa, 1993).

3.4.2 The nitrification-denitrification route in extensive composting NH_3 dynamics

The weight changes of the nitrogenous compounds were calculated in absolute amounts [kg]. Table 3.5 presents the total N balance during composting (in % of $N_{initial}$) for the N compounds in the compost bed and the emitted amounts of N_2O and NH_3. Losses of nitrogenous compounds with leachate water were not considered as the amount of leachate during the process was negligible. The amount of N_{org} decreases because of the hydrolysis of proteins in swine manure (Table 3.5).

Table 3.5 Overall N-balance of the turned and static reactors

	Time (d)	**Turned**	**Static**
N_{org} (% $N_{initial}$)	0	57.6±2.1	57.6±4.8
	30	50.6±11.8	-
	63	37.8±8.6	-
	91	43.8±7.6	-
	118	37.1±5.6	42.5±0.7
NH_4^+ (% $N_{initial}$)	0	42.2±1.9	42.3±4.7
	30	16.8±5.8	-
	63	9.9±2.0	-
	91	1.8±0.4	-
	118	0.9±0.1	9.3±2.0
NO_3^- (% $N_{initial}$)	0	0.1±0.1	0.2±0.1
	30	0.2±0.1	-
	63	0.4±0.2	-
	91	0.7±0.1	-
	118	2.4±0.1	2.9±1.7
NO_2^- (% $N_{initial}$)	0	0.1±0.1	0
	30	0.2±0.1	-
	63	0.5±0.4	-
	91	0.8±0.4	-
	118	0.1±0.1	0.2±0.2
NH_3 emitted (% $N_{initial}$)	0	0	0
	30	2.5±0.1	-
	63	1.2±0.1	-
	91	0.2±0.1	-
	118	0.1±0.1	2.4±0.1
N_2O emitted (% $N_{initial}$)	0	0	0
	30	0.8±0.1	-
	63	0.6±0.1	-
	91	0.6±0.1	-
	118	0.5±0.1	9.8±0.1

The amount of NH_4^+ largely decreases due to nitrification since only a small fraction volatilizes as NH_3 gas. The oxidation of NH_4^+ in the turned system during the first two months in the top and middle part of the compost bed is very surprising, as it is commonly accepted that nitrifying bacteria are unable to thrive at thermophilic temperatures (Schlegel, 1993). However, Pel *et al.* (1997) showed that methanotrophs are capable of NH_4 oxidation under thermophilic conditions, where CH_4 is present at the O_2-limited interfaces in the manure-straw aggregates. Non-autotrophic nitrification by methanotrophs has also been observed by others (King and Schnell, 1994; Roy and Knowles, 1994). The environmental conditions for NH_4 oxidation by methanotrophs are ideal in the compost bed, as both NH_4 and CH_4 are present at the interface of aerobic and anaerobic zones. In contrast to the turned system, NH_4 still was present after 4 months in the static system. The largest amount of NH_4 was retained in the bottom of the system (Table 3.2) where anaerobic zones dominated and oxidation of NH_4 would have been less prevalent. NO_2^- and NO_3^-, both products of the nitrification, were not accumulated but were most probably converted to N_2 and N_2O by denitrifying bacteria. Conversion of NO_2^- and NO_3^- was quite likely in the anaerobic zones present of the compost bed, as NO_3^- is used as a final electron acceptor in the degradation of organic matter under anoxic conditions (Robertson and Kuenen, 1991). The turned system showed a small production of N_2O (2.5±0.1 %) and this indicates that the largest part was emitted as N_2. In the static system the contribution of 9.9±0.5 % of the N_2O is significant especially at the end of the composting process. The same trend was also observed by He *et al.* (2000) for composting of synthetic food waste; N_2O emissions become prevalent when readily available carbon becomes depleted. Under optimum conditions NO_3^- would have been completely reduced to nitrogen gas (N_2). The increased production of N_2O in the static system may also have been due to high NO_3^-, NH_3 or VFA concentrations in the anaerobic zones where N_2O can become an important end product under stressed conditions (Klemedtsson *et al.*, 1988). However, understanding of the fundamental process underlying N_2O production is still poor (Jetten *et al.*, 1997).

3.5 Conclusions

Monthly turning of the compost bed enhanced biodegradation and water removal. The improved composting process was due to the restoration of the structure and porosity of the compost bed. Although turning increased the porosity in the turned beds, the more porous structure did not bring about a higher velocity of natural convection. It is likely to be the result of the reduced particle size resulting in a lower permeability. The extensive composting process was mainly controlled by natural convection, i.e. O_2 supply and removal of heat and water were provided by convective air flows. For the static piles, compaction of the bottom part resulted in a decrease of porosity. Turning also resulted in a homogeneous product and insured that the complete compost mass experienced high temperatures, necessary for killing of pathogens and weed seeds.

Both systems showed low NH_3 emissions, but NH_4 is not retained in that form as indicated by the overall N-balance. We propose that the unaccounted N is lost via a sequence of nitrification and denitrification, which is confirmed by presence of NO_2^- and NO_3^-. NO_2^- and NO_3^- are not accumulated in the compost bed, presumably because conditions favored denitrification and conversion to N_2O and N_2.

The static system showed higher N_2O emissions, due to prevalence of anaerobic regions in combination with high NH_3 content and the absence of readily available C. Although CH_4 was present inside the compost bed for the turned system, low amounts of CH_4 were emitted (0.4 % of total VS degradation). This was due to oxidation of CH_4 in the relatively anaerobic top section. In the static system, a substantial amount of VS degradation was due to methanogenesis (12.6±0.6 %). NH_3 oxidation also took place in thermophilic regions, which was probably done by CH_4 oxidizing bacteria that can also utilize NH_4, as nitrifying bacteria are not active at higher temperatures.

Land application of animal manures may result in uncontrolled emissions of NH_3 and N_2O and leaching of NO_3^- to ground- and surface-waters. It is possible to compost animal manures with a low C/N ratio without significant emissions of NH_3 and N_2O if the conditions are optimal. Loss of N during composting is inevitable but from an environmental point of view, emissions as N_2 are favored over those of NH_3 and N_2O.

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4 CONTROLLING FACTORS IN NH_3 EMISSIONS FROM INTENSIVE MANURE COMPOSTING

Abstract

In this chapter, NH_3 volatilization was measured, modeled and validated for intensive composting of animal manures and other organic wastes. Composting literature suggests that the key parameters influencing NH_3 volatilization are pH, temperature, airflow rate and the initial total ammoniacal nitrogen (TAN) content. It is hypothesized here that next to the TAN content, NH_3 emission is directly related to the airflow rate and the gas concentration, and the latter depends on pH and temperature. To test this hypothesis, a chemical equilibrium model is presented here. It is based on the temperature dependence of pKa and K_H values of NH_3. In the second half of the chapter, the model calculations are validated with the results of experimental and literature data. The validation reinforces that temperature and pH are key factors to determine the NH_3 concentration in the liquid phase of the compost bed and that the aeration rate determines the NH_3 emission from the gas phase. This is because N incorporation in microbial biomass is much slower than NH_3 volatilization. The latter can only be reduced or prevented in intensive composting processes by (i) trapping the emitted NH_3 in acid producing a liquid fertilizer, or (ii) enhancing N assimilation by recycling the off-gas.

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4.1 Introduction

4.1.1 Intensive composting in manure management chains

Solid manures from intensive animal production systems pose a considerable environmental challenge (ALFAM, 2006). Management chains of these manures exhibit high nutrient losses. The integration of a stabilizing treatment into these chains could improve the situation (Burton *et al.*, 2003; Oenema *et al.*, 2000). A promising option is the application of an intensive or forced aeration composting treatment. Advantages of this method include a high-level process control, efficient pathogen removal, volume reduction and a fast stabilization of organic matter (Rynk and Richard, 2001; Fernandes and Sartaj, 1997). Mainly considered suitable in case of large-scale manure treatments, these composting processes allow for collection of off-gas and leachate. Latter feature also contributes to the minimization of environmental emissions. While such composting methods are considered expensive, the produced compost can be transported easier and at considerably lower costs than the untreated manures.

The main drawback of intensive composting methods is the nitrogen (N) loss of the process (Imbeah, 1998). In forced aeration processes, the main N emission is in the form of ammonia (NH_3), occurring especially in the initial stage of the process (Käck *et al.*, 1994). Other N emissions as nitrous oxide (N_2O) or nitrate/nitrite (NO_2^-/NO_3^-) are often well below 1 % (Szántó *et al.*, 2007; Kuroda *et al.*, 1996; Witter and Lopez-Real, 1988). This indicates that the other routes of NH_3 dynamics such as microbial assimilation and nitrification-denitrification are of lesser importance for intensive manure composting methods. While NH_3 emissions can be trapped and treated, the volatilized N results in low nutrient concentrations in the compost product.

This chapter concentrates on the initial phase of intensive composting processes to investigate how the process influences NH_3 volatilization and emission. The focus is on high total ammoniacal content ($TAN=NH_3+NH_4^+$) and airflow rate that result in NH_3 emissions. In the following sections, the underlying principles of this phenomenon and a related chemical model are described.

4.1.2 The main parameters influencing NH_3 volatilization

NH_3 volatilization from composting processes is a complex phenomenon. Various substrate and process parameters are known to influence its extent (see Chapter 2). In intensive composting, the most influential parameters are indicated to be airflow rate and the initially available total ammoniacal nitrogen content (Szántó *et al.*, 2007). It is hypothesized here that NH_3 emission is in direct relation to these two parameters. Through experimental results, Elwell *et al.* (2001) has already demonstrated that an increasing airflow rate has a linear relationship with increase of NH_3 emission rate.

TAN is available in high concentrations in the initial phase of the composting process of manures; therefore it is not expected to be a limiting factor in the emission process of NH_3.

It is also assumed here, that the concentration of NH_3 in the gas phase depends mainly on pH and temperature. The pH determines the liquid phase equilibrium of the ionized NH_4^+ fraction and that of the unionized NH_3 in the composting substrate. The ionized NH_4^+ fraction dominates at lower, acidic pH values, while most ammoniacal N is in the form of NH_3 with alkaline conditions. As a result, NH_3 volatilization increases strongly above pH 7 (Witter and Lopez-Real, 1988). Temperature is also a key parameter in this process, the related acid-base constant K_a and the gas-liquid equilibrium constant K_H (Henry constant) determine the ammoniacal fractions in the liquid and gas phases of the compost matrix. A high temperature is known to have a strong influence on the equilibrium shift in favor of gaseous NH_3 in this context. This ultimately leads to higher volatilization rates (Pagans *et al.*, 2006; Amon *et al.*, 1982; Emerson *et al.*, 1975). Martins and Dewes (1992) also found that higher temperatures promoted emission of NH_3 from manure composting.

In scientific literature, also other parameters were proposed to influence NH_3 volatilization. Tiquia *et al.* (2002) found that together with pH, also the C/N ratio was a central parameter in determining NH_3 loss from manure composting. Szántó *et al.* (2007) confirmed the significance of the C/N ratio for extensive manure composting methods. However, indications were found here that the relationship between C/N ratio and extent of NH_3 emissions becomes weaker with intensive composting methods. It was hypothesized to be the result of high airflow rates, which may flush out NH_3 prior to its nitrification or incorporation in biomass (Szántó *et al.*, 2007).

It is also acknowledged here, that aerobic activity may also exert influence on NH_3 emissions. A faster degradation process results in more NH_4^+ from the hydrolysis of organic matter. However, the influence of aerobic activity can only be considered significant when TAN presents limitations to the volatilization process. This normally occurs only in latter phases of composting processes; therefore it will not be treated in this chapter.

4.1.3 Objectives

If it is accepted that the airflow rate and TAN directly determine NH_3 emission from a composting process, then it is presumable that investigation of the related process parameters (pH and temperature) can provide an in–depth description to the process of NH_3 volatilization. The objective of this study is to determine whether a chemical model containing acid-base and liquid-gas equilibriums (characterized by K_a, respectively K_H) can provide relevant trends for NH_3 emission from experimental and literature data.

4.2 Materials and methods

4.2.1 Substrate characteristics

No solid manure-straw amendment mixture from a solid manure production system was available for the experiment. A comparable substrate was found in the form of phase separated swine manure that was mixed with wheat straw (see Table 4.1). The phase separation from urine was carried out by a convex conveyer belt as described in detail by Kroodsma *et al.* (1998). The manure was free of antibiotics and other by-products. Dust-free, cut-up wheat straw was used as amendment. The straw fraction amounted to 4.7 % of the total wet weight. The straw and manure was mixed by hand prior to the filling of each reactor (Veeken *et al.*, 1999).

Table 4.1 Original characteristics of manure and straw

Parameter	Unit	Manure	Straw
Total Solids	[kg.kg FW^{-1}]	0.33	0.91
Volatile Solids	[kg.kg TS^{-1}]	0.79	0.94
C/N ratio	[-]	13.3	78.1
pH	[-]	7.4	-
VFA	[g.kg TS^{-1}]	7.6	-
N_{total}	[g.kg TS^{-1}]	33	5.3
NH_4^+-N	[g.kg TS^{-1}]	15.3	0.7

Remarks: FW: fresh weight; TS: total solids, VFA: volatile fatty acids; N_{total}: total nitrogen ($N_{Kjeldahl}$+NO_2^-+NO_3^-), where $N_{Kjeldahl}$ is based on Kjeldahl (1883).

4.2.2 Reactor design and set-up

Two cylindrical shaped, stainless-steel reactors (internal height x diameter: 320 mm x 146 mm) were used for the experiment. Each reactor had an efficient volume of 4.75 L and the reactors could be controlled and run independently. Detailed explanation of the reactor design can be found in Veeken *et al.* (2004). The airflow applied in the composting process was measured by mass-flow meters (type Brooks 5850 TR) and controlled by a mass-flow controller (type Brose 5878). Prior to the sampling point of the mass flow meters, water and NH_3 of the off-gas were condensed. NH_3 was trapped in washing bottles filled with 6 M H_2SO_4. During the trial, temperature of the reactor and airflow were determined every 25 minutes. NH_3 and pH from the off gas were measured every 125 minutes. The substrate pH was measured with glass-electrodes (type Schott H63) and pH meters (type Metrohm 691 pH meter).

The two reactors (R1 and R2) were aerated for 8 days. This period was chosen, as significant NH_3 emissions during intensive composting processes are only characteristic to the initial phase of the process. Isotherm conditions were maintained in the reactors throughout the experiment. The outgoing air temperature of the reactor was fixed at 55 °C. The airflow was controlled at 1 % O_2 in the outgoing gas flow. This enabled the assessment of pH and airflow influence on NH_3 volatilization.

4.2.3 Sampling and analysis methods

Sampling for solids was done at the start and at the end of the experiment. Samples were taken for each reactor in duplicates as described in the standard methods of TMECC (2002). TS, VS, and N_{total} ($N_{Kjeldahl}$+NO_2^-+NO_3^- based on Kjeldahl (1883)); of the samples were determined according to standard methods for compost (TMECC, 2002). For analysis of NH_3, NH_4^+, VFA and pH, the samples were shaken with water at a sample-water ratio of 1:5 (w/w) for 0.5 hour and then filtered. The attained filtrate was analyzed according to TMECC methods (2002). The amount of organic nitrogen (N_{org}) was calculated as:

$$N_{org} = N_{total} - NH_3 - NH_4^+ - NO_3^- - NO_2^- \qquad (4.1).$$

The amount of NH_3 or N_{total} lost during the composting process is given in percentage of the total N content at the start of the composting process. To enable this calculation, the absolute (kg) amount of N_{total} and NH_3 in the reactor was needed. The absolute amounts of the various N compounds were calculated on basis of the total weight of the compost bed, its average TS content and average content of the various N compounds by:

$$M_N = M \cdot TS \cdot C_N \qquad (4.2),$$

where M_N is the absolute amount of a N compound (kg), M the total weight of the compost bed (kg), TS the total solids content (g.kg^{-1}), and C_N the concentration of a N compound (g.kg^{-1} TS). The C/N ratio was calculated as follows:

$$C/N = \frac{VS \cdot 0.44}{N_{total}} \qquad (4.3).$$

where, VS is the amount of organic matter in the reactor (kg) and N_{total} is the total amount of N (kg). The coefficient of 0.44 represents the average weight (kg) of C (carbon) in 1 kg organic matter containing mainly polysaccharides.

4.2.4 NH_3 equilibrium model

The model is designed to simulate the working of NH_3 volatilization in a batch composting design. It can be considered a closed system, where the total amount of NH_3 is constant (see Equation 4.4). For the equilibrium model calculations, the gas-liquid phase ratio was fixed at 1:1. It is assumed that the system is in steady-state and that NH_3 concentration is not a limiting factor. This last assumption entails that the model validity is limited to the first phase of the process, when TAN is still present in high concentrations. The following reactions are based on Stumm and Morgan (1996):

$$(NH_3)_{tot} \cong C = NH_4^+(aq) + NH_3(aq) + NH_3(g) \qquad (4.4).$$

In Equation 4.4, the system description implies that the total amount of NH_3 (in the gas and liquid phase) is considered constant (C) and is defined as the sum of the aqueous NH_3, NH_4^+ and the gaseous NH_3. Here, the denotation (aq) stands for aqueous, and (g) for gaseous. The complete NH_3 volatilization process can be described by two equilibriums and equilibrium constants (K_a and K_H):

$$NH_4^+(aq) \xleftrightarrow{K_a} NH_3(aq) \qquad (4.5) \text{ and}$$

$$NH_3(aq) \xleftrightarrow{K_H} NH_3(g) \qquad (4.6).$$

Figure 4.1 shows how the two processes are allocated within the composting matrix.

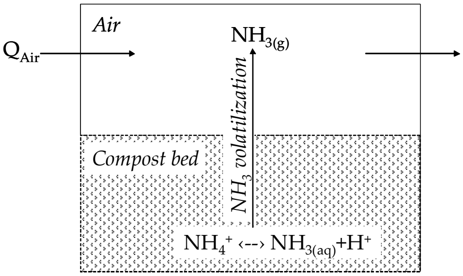


Figure 4.1 Simplified scheme for the composting NH_3 equilibriums

As illustrated, the hydrolysis product NH_4^+ is in equilibrium with the aqueous NH_3 fraction, while the latter is in balance with the gaseous NH_3 fraction. The first equilibrium is the acid-base balance of NH_4^+ and NH_3 in the liquid phase (Equation 4.7). This equilibrium depends on the temperature and the pH of the liquid. During a composting process, aerobic degradation reduces volatile fatty acid (VFA) concentrations. As a result, pH and temperature increase. Lowering the pH would reduce NH_3 emissions, but the acidic conditions would also slow down the degradation process. So considering an optimal composting process in this case, the higher pH results in the shift of equilibrium (Equation 4.7) towards an increasing fraction of NH_3:

$$NH_4^+ \longleftrightarrow NH_3(aq) + H^+ = K_a \text{ thus } K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \qquad (4.7).$$

K_a is the acid-base equilibrium constant determining the distribution of NH_3 and NH_4^+ in the aqueous phase (with a value of 9.3 at 25 °C based on Martell and Smith

(1981)). Calculation of K_a or rather pK_a (the logarithmic value of K_a) can be completed according to the following equation (based on Smith and Martell, 1983):

$$pK_{a(T2)} = pK_{a(T1)} + \Delta H * (T_2 - T_1) * (0.00246) \qquad (4.8).$$

As Equation 4.8 shows, the pK_a value is temperature dependent. T_1 and T_2 are the temperatures in Kelvin corresponding to $pK_{a(T1)}$ and $pK_{a(T2)}$ and ΔH is the enthalpy change of the liquid phase (in Joule). The result is illustrated in Figure 4.2.

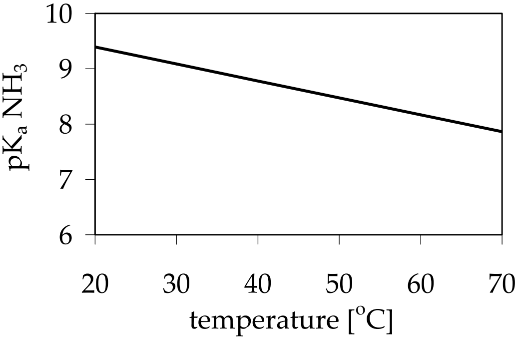


Figure 4.2 pK_a values for the NH_3 equilibrium at different temperatures

Figure 4.2 shows that a temperature increase reduces the value of pK_a. The temperature and NH_3 concentration in the liquid phase influences the balance of NH_3 between the liquid and the gas phase (see Equation 4.5). The NH_3 concentration in the liquid and gas phase depends on the Henry's law constant (Equation 4.9).

$$K_H = \frac{P_{NH_3(g)}}{C_{NH_3(aq)}} \qquad (4.9)$$

$P_{NH3(g)}$ is the NH_3 partial pressure (mol.L^{-1}) in the gas phase, $C_{NH3(aq)}$ is the concentration of NH_3 in the liquid phase. K_H is also temperature dependent and can be calculated by an Arrhenius type equation (Equation 4.10). According to Staudinger and Roberts (1996) the log value of K_H is $6.9*10^{-4}$ atm.L^{-1}.h^{-1} at 25 °C.

$$K_{H(T2)} = K_{H(T1)} \cdot \exp\left(-\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right) \qquad (4.10)$$

Here ΔH is the enthalpy change of the system, and R is the ideal gas constant 8.314 J·K^{-1}·mol^{-1}. The value of the ΔH/R quotient (T-effect) for NH_3 is -4200 K.mol, according to Sander (1999). The resulting curve is depicted in Figure 4.3.

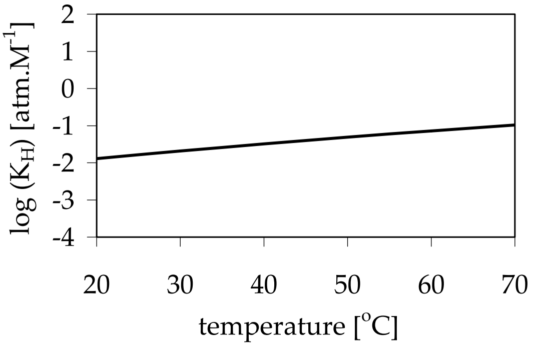


Figure 4.3 log K_H values for the NH_3 equilibrium as function of temperature

The resulting curve in Figure 4.3 confirms that the Henry constant is shifted with more than a factor of 10 in the temperature range of 20-70 °C. As a result, the concentration of NH_3 in the liquid phase decreases, and leads to higher NH_3 partial pressures in the gas phase. When the partial pressure is attained on basis of Equations 4.9 and 4.10, it can be converted to NH_3 concentration in the gas phase (Equation 4.11).

$$(NH_3)_g = \frac{P_{NH_3(g)}}{RT} \quad (4.11),$$

T is temperature in Kelvin and the gaseous concentration $(NH_3)_g$ in mol.m^{-3}. If accepted that no transport limitation of NH_3 occurs, then the NH_3 volatilization can be calculated as:

$$E_{NH_3} = C_{NH_3(g)} \cdot Q_{Air} \quad (4.12),$$

where $C_{NH3(g)}$ is the concentration (mg N.m^{-3}) of NH_3 in the gas phase, Q_{Air} is the airflow rate (m^3.h^{-1}) and E_{NH3} is the volatilization rate of NH_3 (mg N.h^{-1}).

4.3 Results

4.3.1 Model results

Based on the model calculations, the resulting partial pressures of NH_3 were obtained in relation to pH and different temperature levels. Here, we have to mention that all model calculations will be consistently given on a relative basis. In Figure 4.4, this means that the real NH_3 partial pressure at pH 3 and 20 °C was set as the value 1 (Figure 4.4). The rest of the actual values are given as the quotient between the actual real value and the real value at pH 3 at 20 °C. The relative value approach is chosen as our aim was not to quantify the volatilization of NH_3, but to prove that the volatilization trends in the model agree with the experimental emission patterns.

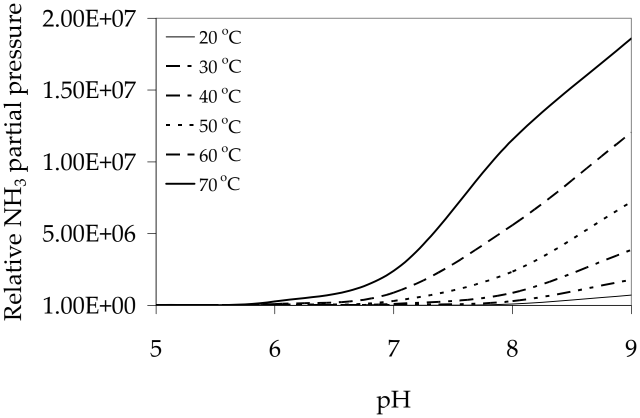


Figure 4.4 Temperature effect on the relative NH_3 partial pressure in the gas phase.
Note, that the actual values have been standardized, with pH 3 at 20 °C is set at 1.

Figure 4.4 shows that the largest increase in NH_3 partial pressure takes place between pH 7 and pH 8, and that the higher temperatures lead to significantly larger partial pressure values of NH_3. This (T and pH) range is the most common in composting processes, explaining why a significant increase in gaseous NH_3 concentrations can be seen in the initial stage of composting processes. The simultaneously increasing temperature and pH can increase the NH_3 partial pressure significantly in the mentioned ranges. A typical temperature change of 20 °C to 60-70 °C in the initial phase of a composting process is shown in Figure 4.4 to result in a 10^3-fold effect on the partial pressure of NH_3. A pH increase from pH 6 to 9 at 60 °C has a more than 10-fold increase on the partial pressure.

4.3.2 Composition of the start and end materials

Table 4.2 shows the parameter values recorded at the start and end of the composting experiment. The data from the lab-scale experiment demonstrate the total and organic solids losses from the initial 1320 g in the reactors. Reactor 1 (R1) and reactor 2 (R2) can be considered duplicates.

Table 4.2 Amounts and concentrations in the two reactors

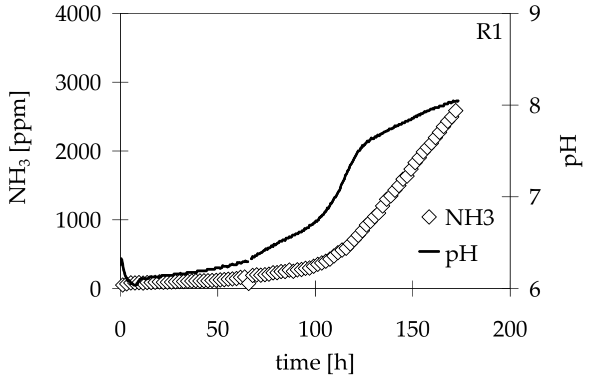
Parameter/Unit		R1 initial	R1 end	R2 initial	R2 end
Manure	[g]	1200	-	1200	-
Straw	[g]	120	-	120	-
FW	[g]	1320	1289	1320	1200
TS	[% FW]	35.9	33.1	35.9	32.5
VS	[% TS]	81.0	80.5	81.0	80.4
Lost VS	[% VS]	-	9.4	-	20.6
N_{total}	[g.kg TS^{-1}]	35.6	33.5	35.6	31.6
NH_4^+	[g.kg TS^{-1}]	11.9	12.2	11.9	12.1
N_{org}	[g.kg TS^{-1}]	23.7	21.3	23.7	19.4
C/N	[-]	10.0	10.6	10.0	11.2
pH	[-]	6.3	8.1	6.6	7.3
NH_3 lost	[g]	0	2.0	0	2.5
	[% TAN_{ini}]	0	35.7	0	44.3
	[% $N_{initial}$]	0	11.9	0	14.8
N_{total} lost	[% $N_{initial}$]	0	15.3	0	27.1

Remarks: R1 and R2: the two composting reactors; FW: fresh weight; TS: total solids content; VS: volatile solids content; TAN_{ini}: total ammoniacal content at the process start; $N_{initial}$: total nitrogen content at the process start.

These losses resulted in a slight decrease in total and volatile solids content and a relatively large reduction of TAN_{ini} and $N_{initial}$ content. Based on Table 4.2, the volatile solids loss amounted to 9.4 % for R1 and 20.6 % for R2. Also, 35.7 and 44.3 % of TAN_{ini} and 11.9 and 14.8 % $N_{initial}$ was lost from R1 and R2, respectively. The pH values increased from above pH 6 to above pH 7-8 (Table 4.2).

4.3.3 Results of the online measurements

A relatively constant airflow of 4.1-4.5 L.h^{-1} was recorded in the duplicates. The two reactors also showed a fairly similar pattern in the changing of pH and the NH_3 concentration in the gas phase (Figure 4.5). The isotherm conditions were kept successfully at 55 °C throughout the experiment.



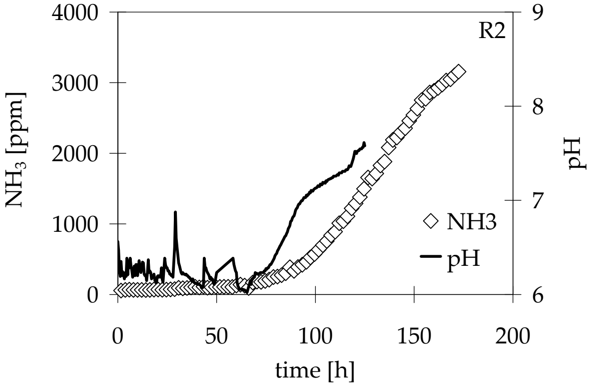


Figure 4.5 NH_3 concentrations in the outgoing airflows and the pH of the reactors during the composting experiment. The temperature was kept constant at 55 °C

The curves of Figure 4.5 illustrate that the slowly increasing NH_3 concentration accelerates in the initial three days of the experiment. At 100-110 hours, they start to show a steady and linear increase until the end of the experiment. The pH values from the experiment express less similarity: R2 shows more deviations from a steady pH increase and exhibits a break and decrease at 120 h. However, the pH reaches 7 in both reactors after 100 hours of process time. At this point, a sharper increase in NH_3 emissions can be detected which is in line with the chemical equilibrium phenomenon. The omitted pH data at R2 from 120 h is a result of unreliable measurements from the electrode.

4.3.4 NH₃ volatilization results from the experimental data

As the experiment was carried out under isotherm conditions, the relevance of pH to NH_3 volatilization could be studied. Figure 4.6 contains the correlation of the pH values and the NH_3 [ppm] concentration in the outgoing gas for the two reactors. Figure 4.6 illustrates a significant increase in NH_3 emission rate can be observed slightly above pH 7. Although R1 shows this break at a slightly higher pH, both patterns are similar.

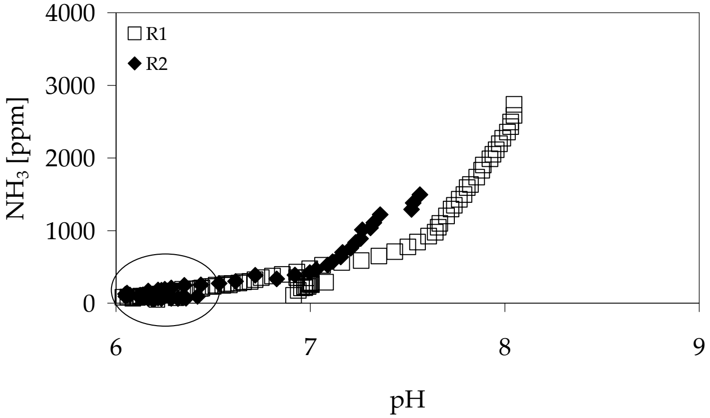


Figure 4.6 NH_3 concentrations in the outgoing airflow and pH during the swine manure-wheat straw composting experiment

Note, that the multiple NH_3 concentration values at the lower pH section are encircled.

An interesting phenomenon is the occurrence of more NH_3 volatilization values at the same pH values (see the encircled area in Figure 4.6), in the lower pH region. A possible explanation of this occurrence is given together with the model validation results in section 4.4.1.

4.3.5 NH₃ volatilization results of literature data

As the composting experiment operated with isotherm conditions, the effect of temperature on NH_3 volatilization could not be measured. For the validation of this aspect of the NH_3 model, data is used from the experiments of Käck *et al.* (1994) and Pagans *et al.* (2006) (see Figures 4.7 and 4.8).

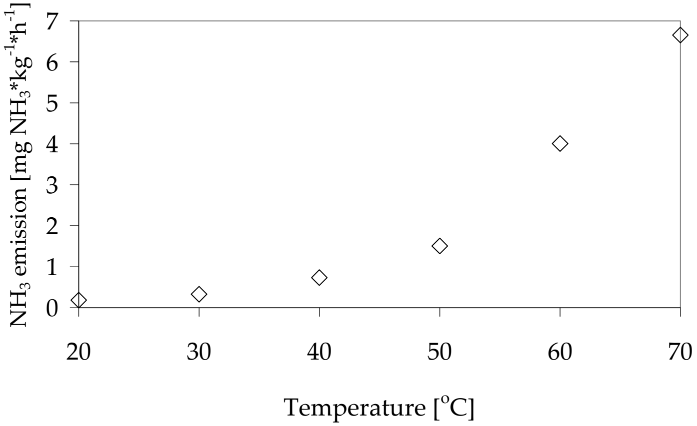


Figure 4.7 NH$_3$ emissions during the initial stage of cow manure composting as a function of temperature (Käck *et al.*, 1994)

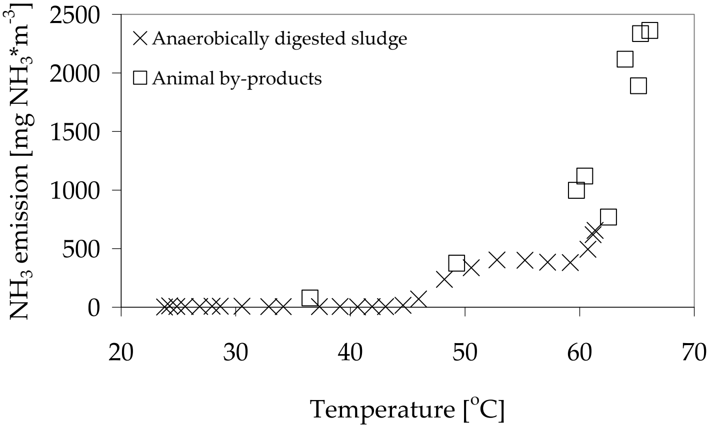


Figure 4.8 NH$_3$ emissions during the initial stage of composting processes as a function of temperature for two types of composting substrates (Pagans *et al.*, 2006)
Note, that the different composting substrates have different TAN values.

The Käck *et al.* (1994) data originate from an intensive cow manure composting experiment. The Pagans *et al.* (2006) data are based on two intensive composting experiments of two substrates i.e. anaerobically digested sewage sludge and by-products from animal processing. From the latter, it was possible to use NH$_3$ data only from the initial stage of the trials. These values ensure that TAN availability is not limiting. Therefore, the data are likely to be more in line with the model design.

4.4 Discussion

4.4.1 Validation of the pH relevance in NH_3 volatilization

In section 4.3.3, Figure 4.5 (encircled area) illustrated that more concentration values of NH_3 were attained at the same (lower) pH values. This is probably the result of the hydrolysis caused pH reduction. As a result of the decreased pH, a slower degradation occurred. This phenomenon allowed the gaseous phase to remain in equilibrium with the liquid phase NH_3. Later in the actual process, as the degradation accelerated, the pH increased at a faster rate as well. Therefore, the gas phase showed a lag phase to attain equilibrium with the liquid phase. Consequently, these NH_3 emission values from the experiment were lower than could be expected at the low pH section.

Figure 4.9 contains the comparison of the experimental results and the values derived from the NH_3 volatilization model calculations. The model calculations were carried out with the help of the PHREEQC© chemical equilibrium model (version 2.4.2). As it was mentioned earlier, the model aims to prove that the volatilization and emission trends in the model agree with the experimental emissions. The model NH_3 partial pressure values are relative values and are based on the model calculations in section 4.2.4.

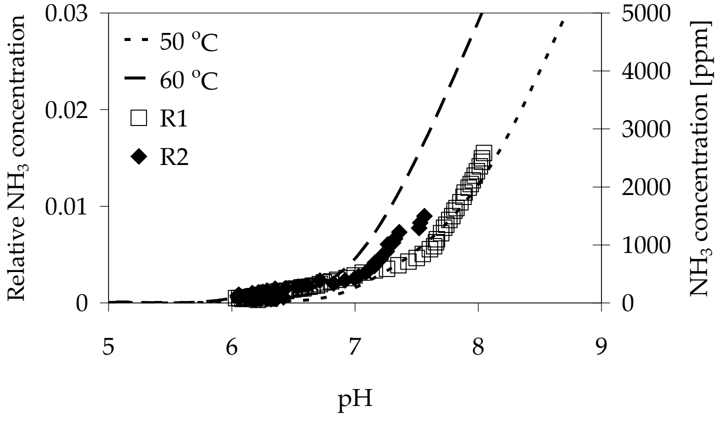


Figure 4.9 Validation curves for the NH_3 volatilization model compared to the experimental data

Note, that the left Y-axis gives the model values, while the right Y-axis relates to the experimental points of R1 and R2. The left Y-axis depict NH_3 concentration in $mg.m^{-3}$, but since we are only interested in concentration patterns, it is better to see them as dimensionless numbers.

The results of the experimental data in Figure 4.9 show a good correlation with the model calculations. In case of both reactors, the sharper increase in the NH_3 emissions starts between pH 7 and pH 7.5. While the experiment was carried out at 55 °C, the model calculations depict values at 50 °C and 60 °C. This is to allow for the better illustration of the experimental trend. Both R1 and R 2 values show a small shift at around pH 7. As higher pH values are attained normally after a few days of composting, it is possible that TAN limitation had an influence on the extent of NH_3 emitted. However, despite the slight shift, the curves follow the 50-60 °C range concentration patterns well.

4.4.2 Validation of the temperature relevance in NH_3 volatilization

Validation of the literature data was also carried out. As no pH data of the experiments were published, the equilibrium model calculations are given in the probable range of pH 6-9. Although the relative values of the equilibrium model would allow for an easy adjustment to experimental data, each of the literature data curves follows a similar pattern and each fits pH 8 curves best. This ensures that the model is not just 'fit' to the available data.

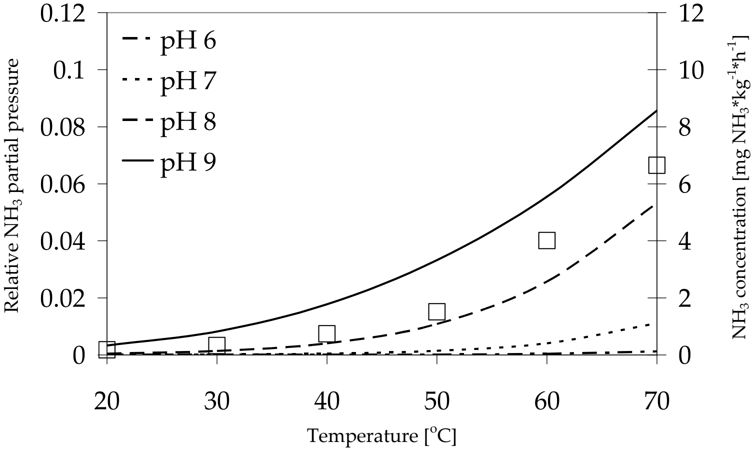


Figure 4.10 Validation for the NH_3 volatilization model compared to the Käck *et al.* data (based on Käck *et al.*, 1994)

Note, that the left Y-axis gives the model values, while the right Y-axis relates to the experimental points. The left Y-axis depict NH_3 concentration in $mg.m^{-3}$, but since we are only interested in concentration patterns, it is better to see them as dimensionless numbers.

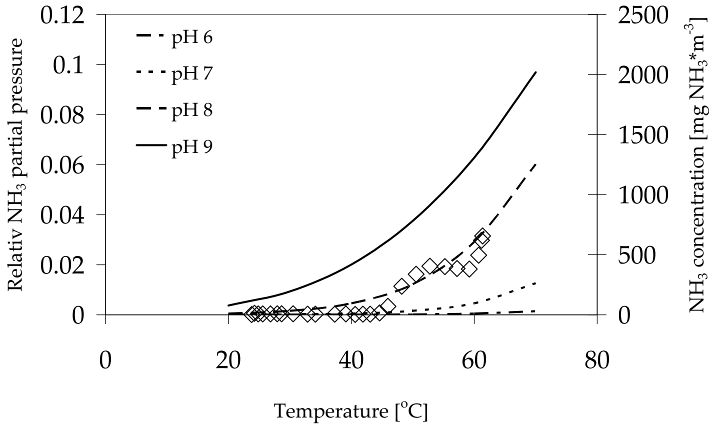


Figure 4.11 Validation of the NH_3 volatilization model with the Pagans *et al.* data on anaerobically digested sludge (initial stage) (Pagans *et al.*, 2006).

Note, that the model curves represent relative NH_3 partial pressures at pH 6-9. The left Y-axis gives the model values, while the right Y-axis relates to the experimental points. The left Y-axis depict NH_3 concentration in mg.m^{-3}, but since we are only interested in concentration patterns, it is better to see them as dimensionless numbers.

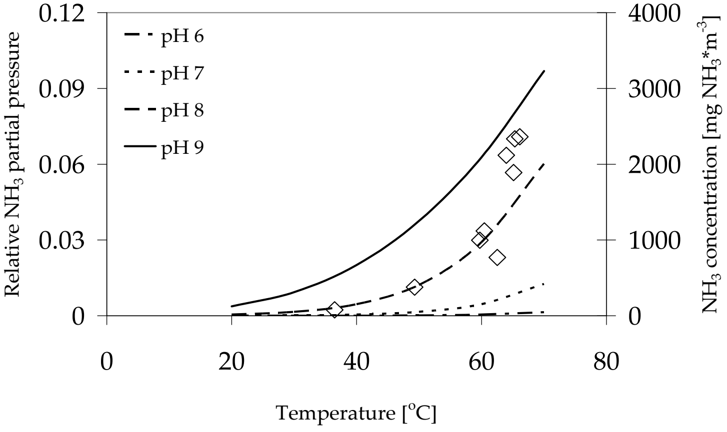


Figure 4.12 Validation of the NH_3 volatilization model with the Pagans *et al.* data on animal by-products (initial stage) (Pagans *et al.*, 2006).

Note, that the model curves represent relative NH_3 partial pressures at pH 6-9. The left Y-axis gives the model values, while the right Y-axis relates to the experimental points. The left Y-axis depict NH_3 concentration in mg.m^{-3}, but since we are only interested in concentration patterns, it is better to see them as dimensionless numbers.

The Käck *et al.* data shows a remarkable correlation with the model results. The increasing concentration values closely follow the increase calculated by the equilibrium calculations. The data of Pagans *et al.* (in Figures 4.11-12, show less agreement with the model curves. Still, the literature values in Figure 4.11 reasonably follow the curves of pH 7 and pH 8. As anaerobically digested sludges usually contain less NH_3, it is possible that the assumption of TAN not being a limiting factor might have to be adjusted in this case.

The observable concentration trend in Figure 4.12 again illustrates the validity of the NH_3 volatilization model. The literature data fits well the trend of pH 8 between 30-60 ^oC while they show somewhat higher values above that temperature range. Fig 4.10-12 show model trends that fit literature concentration data well. While the relative data do not allow exact comparisons, the similar trends ensure the temperature relevance of the NH_3 volatilization model in composting processes. Together with the successful validation of the experimental data of this study, the volatilization model is believed to give an accurate picture of the underlying processes that lead to the emission of NH_3 in the initial stages of composting processes.

It is to be acknowledged, that actual composting processes would feature much more complex NH_3 dynamics. Alterations in pH, possible mass transfer and a changing substrate composition could influence emission concentrations. However, despite this complexity, the model is believed to give a good quality description of the NH_3 emission pattern with changing pH and temperature.

4.5 Conclusions

The central problem of intensive manure composting methods was investigated in this chapter. NH_3 volatilization of a forced aeration process was measured, modeled and validated with the help of literature data and a lab-scale experiment on a swine manure-wheat straw mixture. The model handled the acid-base and the liquid-gas equilibriums of NH_3 and it described the role of pH, temperature and airflow on the gas concentration and the volatilization. The isotherm set-up of the composting experiment enabled the validation of the pH influence in the model.

The results from the validating experiment reinforced the model expectations. NH_3 emissions appeared to correlate well with the pH of the liquid phase. The good relationship between pH and NH_3 removal from the reactors proves the role of high airflow in the volatilization of NH_3. This correlation is also a strong indication that high rate aeration hinders the efficiency of other NH_3 dynamics routes like microbial assimilation or nitrification-denitrification. The model appears to simulate well NH_3 volatilization characteristics. The successful validations underline that pH, temperature and airflow are together responsible to the extent of NH_3 emissions from manure composting processes.

Unfortunately, these parameters are difficult to alter. In composting, organic conversion will evidently lead to an increase in temperature and pH. Consequently, the NH_3 gas concentration and ultimately emission will also increase. Volatilization of NH_3 can be reduced through either reduction of NH_3 in the reactor gas phase or the entrapment of NH_3 from the off gas. The reduction of NH_3 in the gas phase is possible through (i) temperature reduction, (ii) pH buffering and (iii) N assimilation. The reduction through a lower process temperature is not feasible, as it slows down the process and inhibits the sanitizing feature of composting. The reduction of pH is possible with the help of buffering agents, but it is expensive and often inefficient. The enhancement of the N assimilation process requires the addition of sufficient C-source (possibly through a carbonaceous amendment). But even with sufficient C available, this process is still expected to be slow so its efficiency remains questionable.

When opting for the reduction of NH_3 emissions from the off-gas, it can be achieved either through its capturing in an acid solution or through the recycling of the gas. The entrapped NH_3 can be used as liquid fertilizer. The recycling of gas (and the contained NH_3) can provide an opportunity for the occurrence of N assimilation. However, it still requires the optimization of the C/N ratio through the addition of a C source.

4.6 References

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5 THE ROLE OF BIOPOLYMER TURNOVER AND MICROBIAL YIELD IN THE ESTIMATION OF NITROGENOUS LOSSES DURING MANURE COMPOSTING

Abstract

Composting methods are often excluded from solid manure management chains because of concerns for high nitrogenous losses. Conventionally, the C/N ratio is measured to estimate such losses, but it is an indirect and imprecise parameter. This work investigates whether an improved alternative is available in the form of a combined model. This model approaches nitrogenous losses through organic matter turnover at the biopolymer level. Biopolymers are the constituents of organic matter that exhibit differing turnover patterns. There are four biopolymer groups: aliphatics, proteins, polysaccharides and lignins. This work introduces a combined, two-step model that allows the calculation of an organic C/N ratio parameter (C_{org}/N_{org}) of these four biopolymers. The first step includes the biopolymer model described by Veeken *et al.* (2001). This approach was proven to sufficiently monitor the degradation of the four biopolymers during manure composting. However, the resulting biopolymer degradation did not follow expected first order kinetics. It is hypothesized here, that the cyclical growth and decay of microorganisms was the reason of this discrepancy. Therefore, a second step is added to extend that model. This second step includes the modeling of microbial yield role on the degraded biopolymers. The validation of the combined model is based on the results attained at two different swine manure composting processes. The analytical characterization is provided by the 13-carbon cross polarization magic angle spinning nuclear magnetic resonance (^{13}C CPMAS NMR) method. Although the absence of a relevant decay rate did not allow quantification of the microbiologically bound C and N compounds, the presented approach appeared to be suitable to describe organic matter degradation at the biopolymer level. In addition, it managed to provide improved insight in the relationship between N loss and biopolymer degradation during composting. The model is expected to provide a good basis to the estimation of N losses from manure composting without the application of time consuming experiments.

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5.1 Introduction

5.1.1 The conventional approach to manure composting related N loss estimation

Composting methods are often excluded from solid manure management chains. It is mainly because of concerns for high nitrogenous (N) losses in the form of ammonia (NH_3), nitrate (NO_3^-) and nitrous oxide (N_2O) (Sommer, 2001; Kirchmann and Duvall, 1998; Haug, 1993). These losses may occur during the whole course of the process when protein- and NH_3-rich substrate is composted. The extent of the losses from the whole process is hard to estimate, and values attained from experiments show large variations depending on the substrate and the applied method (Szanto *et al.*, 2007a).

Almost all composting parameters may influence N loss to some extent. Conventionally, N loss estimations are mainly based on the parameters of initial mineral or ammoniacal N (TAN: NH_3 + ammonium (NH_4^+)), and the carbon-to-nitrogen (C/N) ratio of the substrate. The initial amount of ammoniacal N in the substrate allows estimation of NH_3 lost in the starting phase of the composting process. It was shown (Szanto *et al.*, 2007a), that in case of high aeration rates most of the initially available NH_3 would be emitted. However, it is the C/N ratio that allows an indication of likely N loss from the whole composting process (Burton *et al.*, 2003; Tam and Tiquia, 1999; Rynk *et al.*, 1992).

The rationale behind the C/N ratio as the main indication for N loss is that these two elements are amongst the main constituents of organic matter. This applies to both the free (i.e. originally available, non-microbial) and the microbial (i.e. microbiologically bound) organic matter. The C/N ratio of organic matter can suggest whether the amounts of C and N are in balance for microbial biomass production. If N is only available to a limited extent, the microbial yield will be limited and the aerobic conversion will remain low. In the event of N surplus i.e. a low C/N ratio, the excess N from the free organic matter will not be immobilized in the microbial biomass matter. In that case, the probable result is N loss either during the composting process (Poincelot, 1975) or at a latter stage of compost application (ECETOC, 1994). The optimal C/N ratio in manures prior to a composting process is reported to be around 25-30 (Rynk *et al.*, 1992). Significant N losses are likely to occur beneath a ratio of 20 (Rynk *et a*l., 1992; Haug, 1993), and N limitation is expected to result in a significantly lower composting efficiency above a C/N range of 40.

Unfortunately, the predictive power of C/N ratio is often suboptimal (Szanto *et al.*, 2007a). This is because not all C and N in free organic matter are available for microbial organisms. Both organic N (N_{org}) and the mineral (ammoniacal) N fraction in organic matter were found to be available for conversion during composting.

However, only the fraction of C in organic bindings (C_{org}) was biodegradable (Kayhanian and Tchobanoglous, 1992). This indicates that if the initial amount of ammoniacal N is quantified, an additional C_{org}/N_{org} parameter could give a more precise indication on the likely N loss. However, there is another problem that still complicates N loss estimation through a C_{org}/N_{org} ratio. The different constituents of organic matter exhibit differing degradation rates (Poincelot, 1975). For example, sugars are known to show higher degradation rates than proteins or lipids (aliphatics), and lignin is characterized by slow and limited degradation. Therefore, it stands to reason that organic matters with similar C/N or C_{org}/N_{org} ratio's but differing compositions should exhibit different N loss patterns.

5.1.2 N loss estimation through a biopolymer approach

There is a considerable need to improve the conventional approach to total N loss estimation from composting. This improvement could be best achieved if the underlying organic matter degradation is better understood first.

Recent progress in soil analytical methods allowed Veeken *et al.* (2001) to demonstrate organic matter degradation during composting on a sub-organic matter level. Their model describes degradation through the turnover (i.e. % degraded) of the four biopolymer groups that build up organic matter. These biopolymer groups are proteins (also containing peptides and amino acids), aliphatic compounds (mainly including lipids), polysaccharides (mainly cellulose and hemicellulose), and lignin (Wilson, 1987; Kögel-Knabner, 1997; Nelson and Baldock, 2005; Kelleher and Simpson, 2006). It is important to acknowledge here, that a scientific debate exists on the definition of biopolymers. It is questioned whether humic substances also comprise a distinctly different biopolymer group (Jodidi, 1914; Hayes *et al.*, 1989; Orlov, 1990). But while humic substances are operationally defined fractions, biopolymers are distinct chemical categories in organic matter (Lagen and Jager, 2003). Also, Nelson and Baldock (2005) successfully demonstrated for 46 different soil and plant organic matter samples that their biopolymer compositions could be explained in terms of only aliphatics, proteins, polysaccharides and lignin. Therefore this work considers organic matter to contain only the mentioned four groups.

This biopolymer approach is based on the known average (organic) C- and N-concentrations of the four biopolymer groups. As the biopolymer fractions were quantifiable during the research of Veeken *et al.* (2001), their model (Veeken *et al.*, 2001) could be used to determine the C_{org}/N_{org} parameter first for the four biopolymer fractions, and then for the total organic matter. The quantification of biopolymer fractions was also repeated over time, to enable the set up of degradation rate or turnover of the composting organic matter (Veeken *et al.*, 2001). Surprisingly, the determination of biopolymer turnovers did not result in the expected first order degradation rates. Eventual increases in the absolute amounts (kg) of biopolymers during the composting process were observed.

As microbial degradation of free biopolymers is the driving force behind composting, it is hypothesized here, that this discrepancy is caused by microbial biomass.

5.1.3 Coupling microbial biomass yield to the biopolymer approach

Microbial organic matter consists of the same aliphatics, proteins and polysaccharides as free organic matter; the only biopolymer absent in microbial biomass is lignin. It is hypothesized here, that a proper biopolymer level degradation model has to include the role of microbial biomass in the quantification of biopolymer turnover. This notion is supported by the microbial utilization of free biopolymers, where only a fraction is mineralized to gain energy (dissimilation), a significant part is used for synthesis of new microbial tissue (assimilation). The aerobic yield of biomass on simple substrates such as glucose can be as high as 0.6 (Heijnen, 1999). The hypothesized role of microbial assimilation in the link between total N loss and biopolymer degradation can be best described through composting NH_3 dynamics and the related protein conversion (Figure 5.1).

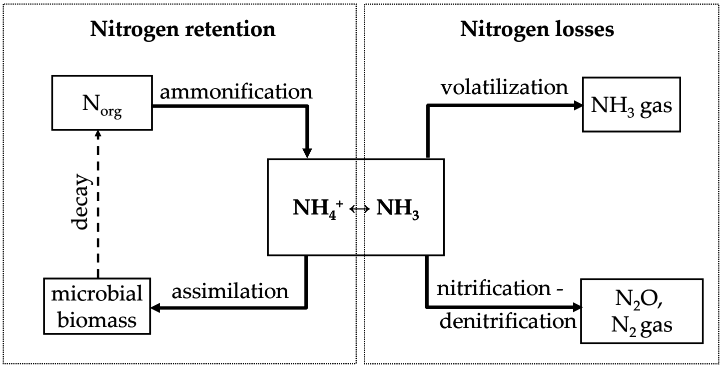

Figure 5.1 NH_3 dynamics in composting organic matter

N_{org} (as contained in protein) is an immobilized form of N. NH_3 is produced from N_{org} through the process of ammonification. Ammoniacal N can then either be assimilated into microbial biomass as protein (N_{org}), or be lost through either NH_3 volatilization or through the nitrification-denitrification route. If microbial N_{org} is produced, it is immobilized in microbial biomass until the decay of the organism. Then the process starts again and N is either available for emission or will be (repeatedly) recycled in the 'Nitrogen retention' cycle as shown in Figure 5.1. As a consequence, microbial biomass reduces the amount of a free biopolymer through assimilation and increases it through decay. As microbial biopolymers cannot be distinguished from free biopolymers through laboratory analysis, the degradation rate of free organic matter attained experimentally is misleading. This empirical degradation rate only shows the amount of degradation minus microbial production. A true or intrinsic degradation rate of free biopolymers would show the actual turnover of free biopolymers without the interference. As a result, it is likely that higher turnover rates would be calculated. The reason is that components containing C_{org} and N_{org} particles in the substrate would be repeatedly assimilated and again made available through decay into free biopolymers.

It is important to note, that the combined biopolymer and microbial yield model can offer only an indirect estimation on N loss from the composting process. The first reason is that it approaches N loss estimation through the quantification of C_{org} and N_{org} retained through assimilation in biomass. By this, the amount of N left susceptible for emissions can be quantified. The second reason is that the N retention cycle with the cyclic growth and decay of biomass has to be quantified. This quantification requires a likely yield rate and a decay rate. As no relevant decay rate is available from scientific literature so far, only the yield of microbial biomass could be quantified.

5.1.4 Determining the biopolymer composition and microbial yield

The central tool in quantifying biopolymer level degradation is the analytical background. For long, biopolymer degradation was a neglected research field in composting. The reason behind this was the lack of suitable technology to quantify the concentration of biopolymers in organic matter. In the past, degradation of biopolymers was mainly studied by wet-chemical extraction methods, so-called proximate analysis (Ryan *et al.*, 1989). Proximate analysis did not allow adequately precise separation between biopolymer fractions as the chemical extractions suffered from losses during the chemical degradation procedure, secondary reactions, and incomplete release of degradation products (Leary *et al.*, 1986; Kögel-Knabner, 1997).

The application of solid state 13-carbon cross polarisation magic angle spinning nuclear magnetic resonance (^{13}C CPMAS NMR) techniques in soil science improved the possibilities to study organic matter transformations (Baldock and Preston, 1995; Leinweber and Schulten, 1999). By using solid state ^{13}C CPMAS NMR, the composition of insoluble organic matter could be analyzed directly from bulk material without pre-treatment or chemical extraction.

The foundation of these NMR techniques lies in the quantification of resonating proton nuclei in a magnetic field. With the help of this technique, the four sorts of C binding groups can be quantified (alkyl-C, O-alkyl-C, aromatic-C and carbonyl-C). Although, the quantification quality of these solid state NMR signals into concentrations of C groups was considered challenging until recently (Smernik and Oades, 2000), the introduction of variable contact time (VCT) experiments (Conte *et al.*, 1997) has highly improved NMR analysis quantitivity.

When the four C binding groups are sufficiently quantified in a sample, this attained quantitivity can be recalculated into absolute amounts of biopolymers in the analyzed samples. Hereby the distribution of C groups in the sample is coupled to the known (average) C group composition and chemical structure of the four groups of biopolymers. If the physical characteristics (total and volatile solids content) of the sample are also known, the absolute amount of biopolymers (in kg) can be quantified mathematically. Ultimately, the C_{org}/N_{org} ratio of the whole sample is then possible to define. Next to Veeken *et al.* (2001) in composting science, similar approaches have been used by Hedges *et al.* (2002) and Nelson and Baldock (2005) in soil science to determine the biochemical composition from organic samples.

In the following section, the methodology of both the biopolymer and the microbial yield model are given. To validate the hypothesis presented earlier, the results of two composting experiments were used. The experimental setup and data of these experiments is also presented in the following section.

5.2 Materials and methods

5.2.1 Experimental design and composition of the composting substrates

The samples used for the ^{13}C CPMAS NMR analyses were collected from an extensive and an intensive straw amended swine manure composting experiment. The extensive composting method (EC) simulated a passively aerated and periodically turned process using natural convection for its aeration as described in Szanto *et al.* (2007b) and Veeken *et al.* (2002a). The duration of the experiment was 4 months, where the compost substrate was mixed and turned manually once a month. The intensive composting experiment (IC) had a closed reactor design with forced aeration and the compost mass was manually turned once a week during the process of one month (Veeken *et al.*, 2001). The summarized results of the two experiments are included in Table 5.1.

Table 5.1 Composting matter composition of the EC (sample nr.=6) and IC experiments (sample nr.=2) (Data from Veeken *et al.*, 2001, Veeken *et al.*, 2002a and Szanto *et al.*, 2007b)

Parameter	**Unit**	**Extensive Composting**					**Intensive Composting**				
Sampling	[d]	0	30	63	91	118	0	7	14	21	28
Weight	[kg FW]	1080	810	570	465	445	42	25.6	21.45	19.44	17.96
TS	[g.kg FW^{-1}]	282	324	390	427	411	380	550	590	580	620
VS	[g.kg TS^{-1}]	725	641	542	521	499	810	790	770	750	720
C_{org}	[g.kg TS^{-1}]	314	283	299	247	228	355	359	360	322	343
N_{total}	[g.kg TS^{-1}]	35.2	29.8	27.1	24.1	23.9	38	33.6	31.1	32.7	34.2
NH_4^+	[g.kg TS^{-1}]	10	3.6	2.8	0.9	0.5	14.3	10.4	9.5	9.1	8.9
NO_3^-	[g.kg TS^{-1}]	0.03	0.05	0.12	0.30	0.80	0*	0	0	0	0
N_{org}	[g.kg TS^{-1}]	25.2	26.2	24.2	22.9	22.6	23.7	23.2	21.6	23.6	25.3
VFA	[g.kg TS^{-1}]	57	42	6	0.2	0.12	46.2	1.6	0.1	0	0
pH	[-]	8.4	8.7	8.6	8.5	8.3	7.4	8.6	8.4	8.8	8.5
C_{org}/N_{org}	[-]	12.5	10.8	12.3	10.8	10.1	15.0	15.5	16.7	13.6	13.6
NMR data#	[% of total signal]										
0-50 ppm range		15.5	21.4	20.6	22.4	22.1	27.2	21.7	15.2	15.4	14.7
50-110 ppm range		64.4	58.1	57.8	55.5	51.1	55.6	60.6	65.3	65.3	63.3
110-160 ppm range		11.4	11.5	12.7	12.8	15.5	9.2	10.4	12.2	13.0	13.6
160-220 ppm range		8.7	9.1	8.8	9.3	11.3	8	7.3	7.3	8.0	8.3

*Remarks: * where 0 is presented, the concentrations were beneath threshold level of detection; # Details of NMR data acquisition can be found in section 1.2.2; d: days; FW: fresh weight; TS: total solids; VS: volatile solids: N_{total}: total ($N_{Kjeldahl}+NO_2^-+NO_3^-$) nitrogen, where $N_{Kjeldahl}$ is based on Kjeldahl (1883); N_{org}: organic nitrogen ($N_{total}-(NH_3+NH_4^++NO_2^-+NO_3^-)$); C_{org}: organic carbon; VFA: volatile fatty acids.*

5.2.2 ^{13}C CPMAS NMR analysis

Samples for the NMR analyses were obtained by milling the air dried samples in a Retsch SM 2000 (Germany) cutting mill, and then crushing the dried material in a planet ball mill (Retsch, Germany) to particles smaller than 0.05 mm. The solid state ^{13}C CPMAS NMR spectra were obtained on a wide bore AMX 300 spectrometer (Bruker, Germany) operating at 75.47 MHz. The following parameters were used: spinning rate of 4.5 kHz; acquisition time of 0.033 s; 90° pulse length of 4 μs; contact time of 1.0 ms, recycle delay of 1 s, and line broadening of 50 Hz (Conte *et al.*, 1997). For each spectrum, 3600 cycles were accumulated. Variable contact time (VCT) experiments were performed for several compost samples to quantify the recorded NMR spectra. Back-extrapolation of VCT curves (consisting of 4-11 data points with cross-polarisation contact times ranging from 0.1 to 7 ms) to a contact time of 0 ms for the various chemical shift regions improved the quantification reliability of classical ^{13}C CPMAS NMR as explained by Lagen and Jager (2003). The regions applied for the determination of C functional group distribution differ slightly from that of Nelson and Baldock (2005). Here, the divisions are 0-50 ppm (alkyl C), 60-110 ppm (O-alkyl C), 110-160 ppm (aromatic C) and 160-220 ppm (carbonyl C) (see Tables 5.1 and 5.2).

5.2.3 Biopolymer model calculations

The biopolymer model makes use of the distribution of C groups in organic matter that were attained by the ^{13}C CPMAS NMR analysis of the compost samples. Mathematically, the four types of C groups that can be distinguished (alkyl, O-alkyl, aromatic and carbonyl) sufficiently allow the setting up of four equations to calculate the four biopolymer concentration variables from the relative peak areas of NMR measurements. The procedure to calculate the mass fraction of the biopolymers is comprehensively described by Veeken *et al.* (2001) and a similar method was used by Nelson and Baldock (2005).

Table 5.2 shows the spectral distribution of C groups in relation to the compositions of biopolymers. For the N content of protein 0.266 was applied as this value corresponds to bacterial and fungal composition (Cowie and Hedges, 1992).

Table 5.2 The biopolymer composition used for the combined biopolymer and microbial yield model

Biopolymer	**Relative composition**	**MW**	**C#**	**N/C**	**C fractions of biopolymers in %**			
		[g.mol^{-1}]	[C]	[-]	Alkyl	O-Alkyl	Aromatic	Carbonyl
Aliphatics	$CH_{2.06}O_{0.13}$	292	16	0	77.1	12.0	4.1	6.8
Protein	$CH_{1.83}O_{0.28}N_{0.46}$	137	5.4	0.266	46.9	16.7	9.4	27.0
Polysaccharides	CH_2O	162	6	0	1.4	97.6	1.0	0.0
Lignin	$CH_{1.48}O_{0.09}$	183	9.9	0	15.1	30.3	45.2	9.5

Remarks: MW: molecular weight; C#: number of C atoms; H: hydrogen; O: oxygen; N/C: reciprocal value to the C/N ratio (as only protein contains nitrogen)

5.2.4 The microbial yield model calculations

A fraction of the hydrolyzed free biopolymers will be emitted from the composting organic matter mainly in the form of NH_3, CO_2, and H_2O (Figure 5.1). The rest will be assimilated by microbial biomass for the building of microbial tissue. The difficulties of combining microbial growth with the biopolymer model have already been introduced in section 5.1.3. Figure 5.2 illustrates how the process of free biopolymer depletion and production occurs with the assistance of microbial biomass.

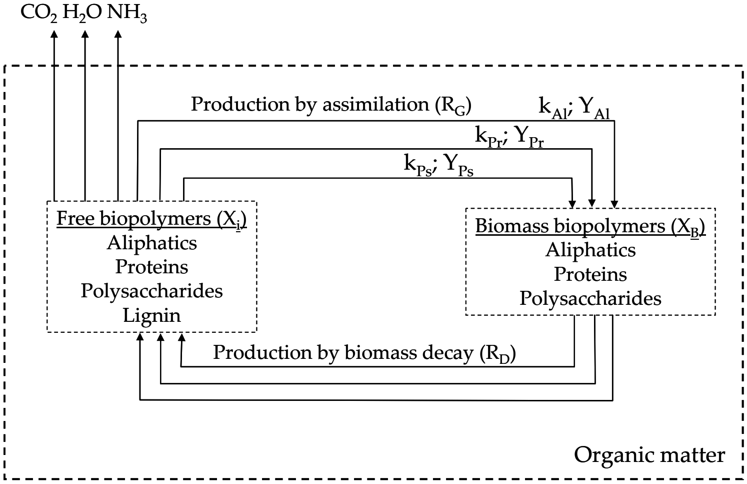

Figure 5.2 The combined biopolymer and microbial yield model scheme

Remarks: ---: boundary of the organic matter matrix; k: degradation constant [d^{-1}]; Ps: polysaccharides; Pr: proteins; Al: aliphatics; Y: biomass yield [$kg_{biomass}$ $kg_{biopolymer}^{-1}$]; R_G: microbial biomass production rate [$kg_{biomass}$ d^{-1}]; R_D: microbial decay rate [kg d^{-1}]; X_i: free biopolymer [kg]; X_B: biomass biopolymer [kg].

During the degradation of free biopolymers (X_i) an important feature is that the hydrolyzed matter is taken up according to the needs of microbial biomass. Therefore, the yield of the different microbial biopolymer groups will differ (Figure 5.2). The decay of microbial biomass produces free biopolymers at the microbial decay rate of R_D. As was explained, the degradation and production of free biopolymers by a continuous cycle of microbial assimilation and decay can not be measured accurately by analytical instruments. As free biopolymers do not differ formally from the microbial ones, analytically only an overall empirical degradation rate can be established.

Mathematically, the original ^{13}C CPMAS NMR signal can be used to model the proportion of free and microbial biopolymers for an intrinsic degradation rate:

$$C_i = X_i + \alpha_i \cdot X_B \qquad (i=1\ldots4) \qquad (5.1).$$

Here C is the empirical amount of biopolymer i as observed by ^{13}C CPMAS NMR (kg), X_i the amount of free biopolymer i (kg), α_i the mass fraction of biopolymer i in microbial biomass and X_B the total microbial biomass amount (kg). Subscript i denotes aliphatics, proteins, polysaccharides and lignin. The free biopolymers are degraded during composting and produced by the decay of microbial biomass. Theoretically, the intrinsic degradation rate of free biopolymers during composting could be described by:

$$\frac{dX_i}{dt} = -R_i + \alpha_i \cdot R_D \qquad (5.2).$$

Here next to the above explained parameters, t is time (d), R_i is the degradation rate of free biopolymer i as observed by ^{13}C NMR (kg d^{-1}). This R_i can also be understood as the rate of ammonification for nitrogenous compounds (see Figure 5.1). R_D the decay rate of microbial biomass (kg d^{-1}). Note that no decay rate, therefore no free biopolymer degradation is quantified in this chapter. The microbial biomass production rate (R_G) is defined as:

$$R_G = Y\sum_{j=1}^{4} R_j \qquad (j=1\ldots4;\ j\neq i) \qquad (5.3),$$

where R_G is the microbial biomass production rate (kg d^{-1}) and Y is the yield of microbial biomass on substrate. R_j is the degradation rate of the degraded free biopolymer j. The index j is used instead of i to mark difference between the total amount of free biopolymers present in the composting matter and the fraction of it that is degraded by microorganisms. The yield of microbial biomass is assumed constant. The change in intrinsic amount of biopolymer i degradation during composting is given by:

$$\frac{dC_i}{dt} = \frac{dX_i}{dt} + \alpha_i \cdot \frac{dX_B}{dt} \qquad (5.4).$$

Substitution of Equation 5.2 and 5.3 in Equation 5.4 results in:

$$\frac{dC_i}{dt} = -(1-\alpha_i \cdot Y)R_i + \alpha_i \cdot Y\sum_{j\neq i}^{4} R_j \qquad (5.5).$$

Equation 5.5 shows that the observed intrinsic degradation of biopolymer i (C_i) does not only depend on the degradation of the free biopolymer i (first term) but also on the incorporation of biopolymers in microbial biomass (second term). As the yield of microbial biomass (denoted by Y) can be assumed constant (Heijnen, 1999), the intrinsic degradation is also independent of the decay rate of microbial biomass (R_D) (Equation 5.5).

Hydrolysis (or ammonification for nitrogenous components) is generally the rate determining step in the degradation of solid substrates and can be described by first order kinetics (Vavilin *et al.*, 1996):

$$R_i = k \cdot C_i \qquad (5.6),$$

where k is the first order degradation rate (d^{-1}).

For the simultaneous quantification of the intrinsic turnover rates of the four biopolymers matrix calculations are required. Putting the available data into a matrix form gives:

$$\frac{dC}{dt} = Z \cdot R \tag{5.7}$$,

where C is the vector with elements C_i, R the vector with elements R_i and the Z vector contains the total amount of biopolymers (kg) measured in the composting mass defined as:

$$Z = \alpha_i \cdot Y - I_{i,j} \tag{5.8}$$,

where I is the identity matrix required to represent the identity function. When the yield on microbial biomass and the microbial biomass composition are known, the vector R can be solved according to:

$$R = Z^{-1} \cdot \frac{dC}{dt} \tag{5.9}$$.

The degradation rate of each biopolymer (R_i) as function of time can then be obtained, applying the central difference approximation to calculate the first derivative from the measured C_i:

$$\left(\frac{dC_i}{dt}\right)_{t=t+0.5dt} = \frac{C_{i,t+dt} - C_{i,t}}{dt} \tag{5.10}$$.

From the time series of R_i and the associated central averaged amounts of C_i, k can be found by linear regression using Equation 5.10.

5.3 Results and discussion

5.3.1 Composting processes

Details of the composting experiments can be found in Veeken *et al.* (2001), Veeken *et al.* (2002a and 2002b) and Szanto *et al.* (2007b). In this section, only the volatile solids changes are explained as they comprise C and N related degradation. Loss of water and concentration of total solids were calculated based on absolute amounts (kg) for the determination of absolute molecular distribution and C/N ratio as described in Veeken *et al.* (2001). Degradation of VS was calculated as listed in Veeken *et al.* (2002b) on the basis of total weight, mean TS and mean VS of the compost bed.

The absolute amount of a biopolymer in the course of composting is calculated as:

$$M_{biopolymer} = M \cdot TS \cdot VS \cdot F_{biopolymer} \tag{5.11}$$

where $M_{biopolymer}$ is the mass of a biopolymer (kg), M the total weight of the compost bed (kg), TS is the total solids content (g kg^{-1} FW), VS the volatile solids content (g kg^{-1} TS) and $F_{biopolymer}$ is the mass fraction of a biopolymer on VS basis.

Using total weight for the reporting of N emissions and retentions is not generally used in composting science (Figure 5.3). However, the content of N compounds on a

TS or VS basis does not provide useful information on the changes occurring in the composting bed. This is because the TS and VS fractions simultaneously change during composting processes (Veeken *et al.*, 2002a).

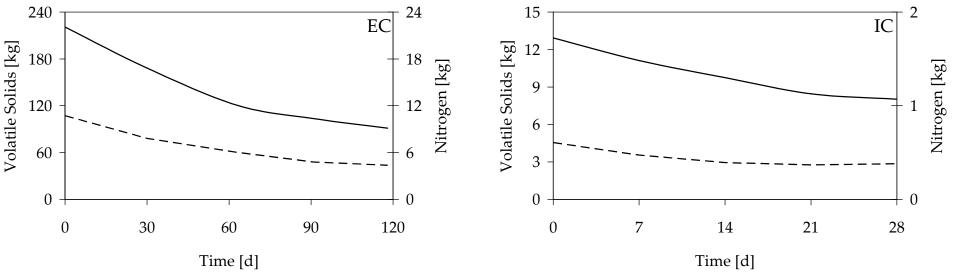

Figure 5.3 Losses of the VS (volatile solids) fraction and total amount of N (nitrogen) from the EC and IC experiments

Remarks: continuous line: amount of volatile solids in experiment [kg]; dashed line: amount of N_{total} *(total nitrogen (*$N_{Kjeldahl}+NO_2^-+NO_3^-$*, where* $N_{Kjeldahl}$ *is based on Kjeldahl (1883)) in experiment [kg].*

The EC experiment (Figure 5.3) shows that 55 % of the initially available organic matter was degraded within the first 3 months. About 59 % of the initially available N_{total} was lost from the compost bed. Veeken *et al.* (2002b) showed that only 3% was emitted as NH_3 and no NH_4 and NO_3 were accumulated in the compost bed. Therefore, it can be assumed that N was lost as N_2 or N_2O via nitrification-denitrification.

The IC experiment shows a 38 % degradation of organic matter in the 4-week composting period. Here, the pH of the compost beds initially increased, likely because of the degradation of available VFA. Later, this trend slowed due to NH_3 volatilization. Although the N losses amounted to only 37 % of the initially available N_{total}, the concentration remained fairly constant as a high amount of TS was lost with the degraded organic matter. Measurements from the off-gas and the condensate confirmed that practically all N loss occurred in the form of NH_3.

The C_{org}/N_{org} ratio has changed little in the EC experiment (Table 5.1). The initially low value of 12.5 has decreased to 10.1 after some fluctuations in the 4-month experiment. The IC experiment has shown a higher initial C_{org}/N_{org} ratio of 15. After an initial increase probably because of the volatilization of ammoniacal N, this has decreased to 13.6 after 4 weeks.

5.3.2 Validation of the biopolymer model

5.3.2.1 Validation of the biopolymer model with the correlation of C_{org}/N_{org} ratio's

C_{org} and N_{org} concentrations for the compost substrate are presented in Table 5.1. The C_{org}/N_{org} ratio was determined by chemical analyses as described by Veeken *et al.*, 2001 and Veeken *et al.*, 2002a. Using the attained NMR data and the biopolymer model, the four biopolymer concentrations and the resulting C_{org}/N_{org} parameters can be calculated. The data are listed in Table 5.3.

Table 5.3 Biopolymer compositions and C_{org}/N_{org} ratio data calculated from the extensive (EC) and intensive composting (IC) experiment results

Parameter	**Unit**	**EC**					**IC**				
Sampling	[d]	0	30	63	91	118	0	7	14	21	28
Aliphatics	[g.kg VS^{-1}]	0	60	57	69	27	151	98	23	11	0
Protein	[g.kg VS^{-1}]	260	262	243	260	335	213	189	193	220	229
Polysaccharides	[g.kg VS^{-1}]	602	539	534	506	433	532	583	622	595	588
Lignin	[g.kg VS^{-1}]	138	140	166	165	205	104	129	162	174	183
C_{org}/N_{org}	[-]	12.4	12.3	13.2	12.4	9.6	15.1	17.0	16.7	14.6	14.1

The concentrations of aliphatics show an increasing trend for the EC experiment followed by a sharp decrease in the last month of the process. The reducing pattern of aliphatics is monotonous for the IC experiment and ends with a concentration below threshold level. Protein concentrations exhibit similar degradation patterns during the two experiments. The concentrations based on VS content fluctuate in narrow ranges except for the final data of the EC experiment where a slight increase was recorded. Polysaccharides show the highest level of degradation in concentration, and the lignin content remains relatively stable with small fluctuations in both processes. Comparing the C_{org}/N_{org} ratio values from Table 5.1 and Table 5.3 allows the correlation of the analytical data with the biopolymer model results for the EC and IC experiments (Figure 5.4).

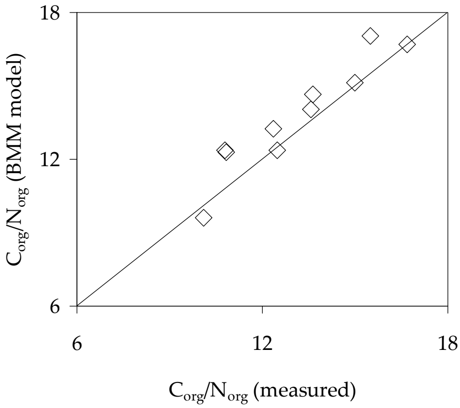

Figure 5.4 C_{org}/N_{org} ratio data (◇) correlation from the elemental analysis (Table 5.1) and the biopolymer model (Table 5.3)
Remarks: continuous line is a 1:1 correlation line.

Figure 5.4 demonstrates that a good correlation is achieved between the analytically measured C_{org}/N_{org} ratios and those calculated from the biopolymer model. The relatively small deviations from the 1:1 correlation line can be attributed to unavoidable inhomogeneity in the samples and uncertainty of the analyses applied. The good correlation indicates that the biopolymer model can adequately describe organic matter composition and changes in composting substrates.
However, these calculations can only offer an empirical degradation of the four biopolymers. Differentiating original organic matter degradation from microbial biomass is only possible if the composition and yield rate of microbial biomass is known.

5.3.2.2 Validation of the biopolymer model based on the microbial biomass composition

Microorganisms are also part of the composting organic matter. Therefore, their biopolymer composition should be applicable to validate the biopolymer model. Applying Equations 5.2 and 5.3, the biopolymer composition of biomass (α_i) was obtained from the ^{13}C CPMAS NMR spectra of fungal and bacterial biomass (Baldock *et al.* 1990; Golchin *et al.* 1996). The chemical shift contribution of the four regions does not differ significantly for bacterial and fungal biomass (Baldock *et al.*, 1990) and amounted to 25% for 0-50 ppm, 60% for 50-110 ppm, 3% for 110-160 ppm and 12% for 160-220 ppm from the NMR signal. The biopolymer composition of biomass based on these data could be determined for aliphatic compounds at $\alpha_{Al} = 0.06$, for protein at $\alpha_{Pr} = 0.45$, for polysaccharides at $\alpha_{Ps} = 0.52$ and for lignin at $\alpha_{Li} = -0.03$. The small negative value for the lignin fraction is due to the *a priori* definition of the four biopolymers (Table 5.2). This calculated composition is similar to the experimentally determined biomass composition of 50% proteins, 40% polysaccharides, 10% aliphatics and no lignin (Schlegel, 1993). Moreover, the calculated elemental composition on basis of the mass fraction and definition (Table 5.1) of $CH_{1.89}O_{0.59}N_{0.18}$ is close to the generally applied elemental composition of biomass of $CH_{1.8}O_{0.5}N_{0.2}$ (Heijnen, 1999). Both agreements confirm that the method to calculate the microbial biopolymer composition based on NMR data following Equations 5.2 and 5.3 is justified. Synthesizing above distributions, an adapted biopolymer composition of $\alpha_{Al} = 0.08$, $\alpha_{Pr} = 0.47$, $\alpha_{Ps} = 0.45$ and $\alpha_{Li} = 0.0$ is applied for biomass in the next section.

5.3.3 Incorporation of the microbial yield model in the biopolymer model

5.3.3.1 Empirical biopolymer degradation during manure composting

Section 1.3.2.1 showed that biopolymer concentrations fluctuate with sometimes significant increases during the composting processes (Table 5.3). As the simultaneous changes in TS and VS fractions during the process do not allow direct comparisons, the amounts of biopolymers in the composting matter are given here in absolute terms (i.e. in kg) instead of concentrations (see Figures 5.5 and 5.6). Using these values the empirical degradation rates can be determined directly.

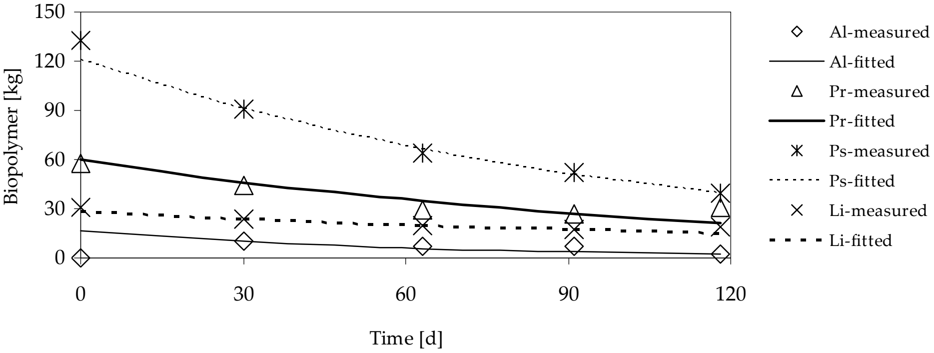

Figure 5.5 Biopolymer amounts measured during the EC process
Remarks: Al – aliphatics; Pr – proteins; Ps – polysaccharides; Li – lignin

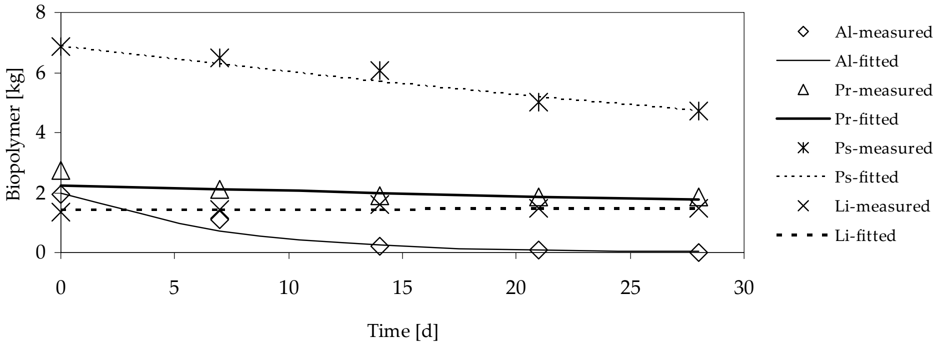

Figure 5.6 Biopolymer amounts measured during the IC process
Remarks: Al – aliphatics; Pr – proteins; Ps – polysaccharides; Li – lignin

The Figures 5.5 and 5.6 demonstrate the results of biopolymer calculations from the EC and IC experiments. The measured values refer to the calculated values based on the original analytical measurements. The fitted values are iterated from the measured values by applying Equation 5.11:

$$C_t = C_0 \cdot e^{-k.t} \qquad (5.11),$$

where C_t is the concentration of a biopolymer group in the substrate at a given time, C_0 is the original concentration of the biopolymer group at the start of the experiment, k stands for the degradation constant [d^{-1}] and t represents time in days.

The measured values of Figure 5.5 show an increasing amount of aliphatics that would indicate negative degradation values after the first month of composting. This is followed by a slight degradation at the second and third month and finally a drop towards the end of the 4-month process. Polysaccharides show rapid degradation leaving only 28 % of the initial amount after 4 months. Protein is slightly degraded in the first 3 months of the extensive process, then its amount increases again in the last month (Figure 5.5). Finally, 53 % of the originally present protein remains in the composted matter. Lignin groups exhibit a relatively constant degradation in the first 3 months and 60 % is retained after 4 months.

Measured values from the IC experiment show a continuous decrease of aliphatics (Figure 5.6) in the four weeks of composting time. Proteins decrease 66 % of the original amount in the process. The decrease is largest in the first period just as in case of the EC process. Polysaccharides show a decrease of 30 %. As lignin degradation does not occur at thermophilic conditions, its amount remains relatively constant throughout the intensive process.

If it is accepted that the cycle of microbial yield and decay are responsible for the observed fluctuation at the EC experiment, then the real degradation rates of free biopolymers have to be much higher than indicated by the conventional TS, VS and N concentration measurements. If the biopolymer composition of biomass is known, the intrinsic degradation rates of the four biopolymers are possible to calculate with the help of Equations 5.5 and 5.10.

5.3.3.2 Intrinsic biopolymer turnover during manure composting

Empirical turnover rates (in % degraded) could be calculated from the data determined in the previous section. Based on the microbial yield model and the microbial composition described previously, these data could be used to determine the intrinsic turnover rates containing microbial yield for both experiments. As the results show in Table 5.4, these values turned out to be higher than the original (empirical) degradation values for aliphatics, protein and polysaccharides (Table 5.4). As lignin is not built into microbial matter, its degradation values remain the same for both scenarios.

Table 5.4 Extent of turnover (%) and conversion rates (d^{-1}) of biopolymers at different microbial yield (Y) values from the EC and IC experiments

Biopolymers	**% turnover**		**Y=0**		**Y=0.5**	
	Empirical	Theoretical	k	RE	K	RE
EC						
Aliphatics	-*	-*	-0.002	0.362	0.005	0.044
Protein	47	155	0.017	0.121	0.021	0.114
Polysaccharides	70	113	0.011	0.090	0.015	0.004
Lignin	39	39	0.006	0.038	0.006	0.038
IC						
Aliphatics	100	113	0.069	0.062	0.075	0.136
Protein	33	115	0.018	0.405	0.075	0.009
Polysaccharides	32	65	0.014	1.000	0.029	0.273
Lignin	-9	-9	-0.004	7.947	-0.004	7.947

*Remarks: * not possible to determine as the initial amount of aliphatics was 0 kg in the compost bed; k: degradation rate constant [d^{-1}]; RE: relative sum of residual errors [%]; turnover represents the % of the initially available biopolymers degraded during the EC and IC experiments.*

For the turnover calculations, a typical microbial yield constant and a few assumptions had to be determined. It was assumed, that (i) the microbial yield (Y) is the same for the different biopolymer substrates, (ii) Y is constant for temperature and (iii) microbial biomass composition is constant. Two microbial yield scenarios were investigated thoroughly. The scenario where microbial yield equals zero (Y=0) corresponds to the original set of calculations where no microbial yield is taken into account. Y=0 is used instead of the original data to emphasize that the calculations were performed for the central averaged values. For the extent of microbial yield Y=0.5 was chosen as according to Heijnen (1999), it is a typical value for thermophilic aerobic conditions.

In Table 5.4, the empirical (Y=0) turnovers of aliphatic compounds show missing data for the EC and data of 100 % reduction for the IC experiment. The missing data is the result of the threshold amount of aliphatics at the start of the EC experiment. The intensive composting experiment has shown a rapid degradation of aliphatic compounds. However, the actual turnover value is likely to be smaller than 100 %. The microbial biomass present in the compost bed also had to contain 8 % aliphatics (see section 5.3.2.2). Lignin is only known to be degraded by fungi and actinomycetes that survive in temperature conditions below 50 °C (Tuomela *et al.*, 2000). As the IC experiment has shown thermophilic conditions, the negative degradation of lignin here is likely the result of sample inhomogeneity. This is confirmed by the 39 % degradation measured in the partly mesophilic EC process.

The correction for microbial biomass yield results in significantly higher degradation rates of aliphatics, proteins and polysaccharides. Logically the intrinsic turnover of lignin is not affected, as lignin is not part of microbial biomass. There are three negative degradation values (or rather production of the biopolymers) in Table 5.4: the lignin degradations and the degradation of aliphatics from the EC experiment. These values can be assumed zero and are likely to originate from sample inhomogeneity and analytical inaccuracy. The negligible changes in lignin values are also confirmed by the high relative RE values in Table 5.4. The aliphatics, protein and polysaccharides degradation constants are not only higher when the microbial yield (Y=0.5) is incorporated, also their residual errors are in most cases somewhat lower. The latter indicates that the description of degradation is better if the role of microbial yield is considered. Although not presented here, a scenario/sensitivity analysis with microbial yields of 0.4 and 0.6 (the ± 20 % scenarios of Y=0.5) has also confirmed the better fit with microbial degradation. These undisclosed calculations showed that a higher yield brings about higher theoretical degradation rates and also a higher incorporation of C and N in microbial biomass.

The model cannot yet calculate the amount of biopolymers incorporated in microbial biomass, as no reliable decay rate of microorganisms could be found in literature. If such data were available for the decay rate, the contribution of microbial biopolymers could also be quantified from the model. This way, we could differentiate between microbial production and free biopolymer degradation, thus giving a more realistic interpretation of decomposition dynamics as suggested by Horwath and Elliott (1996).

5.4 Conclusion

The investigated approach proved valid to calculate the composition of organic matter in terms of the four biopolymers. The data calculated from the ^{13}C CPMAS NMR data of the EC and IC composting experiments were confirmed by conventional analysis. In the first section of the chapter it was also suggested, that the intrinsic turnover rates of the biopolymers could only be assessed when microbial biomass yield was taken into account. The analysis of experimental data showed that the microbial yield model could indeed explain discrepancies in the empirical turnover of the biopolymers that otherwise could not be accounted for by first order degradation kinetics. Taking microbial biomass yield into account resulted in higher degradation rates for aliphatics, polysaccharides and proteins from free organic matter. The degradation rate of lignin was not affected, as lignin is not part of microbial biomass.

The comparing of C_{org}/N_{org} data from elemental analysis and the biopolymer model showed an excellent quality correlation. The validation by microbial biopolymer comparison was also successful. The biopolymer model proved a good estimation of the empirical degradation, but it could only give indications on immobilized N if the microbial yield model was added. While the concept of microbial yield role on the turnover characteristics of biopolymers has been clarified in the chapter, no complete calculation could be made here. Without a relevant decay rate for microbial biomass, it was not possible to quantify the fraction of microbial biopolymers from the amount of free biopolymers. This prevented the establishment of the amount of N susceptible to emissions. However, the role of microbial assimilation was presented and validated adequately.

Summarizing, it was shown that the biopolymer and microbial yield model combined with the application of ^{13}C CPMAS NMR techniques can provide a new approach for N loss estimation from manure composting. The quantification of the C_{org}/N_{org} ratio over time allows an improved insight in the NH_3 dynamics processes of manure composting. It is acknowledged that other composting parameters can contribute to the extent of N emitted from composting organic matter. Still, the quantification of microbial (immobilized) N and mineral (ammoniacal) N over time grants essential information on composting related N loss. This is expected to provide an enhanced basis to the estimation of N losses from manure composting without the application of time consuming experiments.

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6 SUMMARY AND GENERAL CONCLUSIONS

6.1 Introduction

NH_3 loss from solid manures poses a significant environmental problem. These manure related losses are the main source of anthropogenic NH_3 emissions in industrialized countries. The majority of the emissions occur after manure has been removed from the animal housing. Composting is offered here as a potential biological method to improve the manure management chains by stabilizing solid manures in an early phase. As the N retaining capacity of composting methods is debated, this feature has to be evaluated for its applicability as a treatment step. It is reasoned in this thesis that the assessment requires a chain approach. When a process is viewed as a part of a chain, the consequences are that (i) besides focusing on the process, also the end-product quality is assessed; (ii) a total material balance is required instead of a concentration-based balance. This means that absolute values of N compounds have to be calculated for the establishment of a proper process balance. As a result, the shifting of a nitrogenous emission to the latter stage of the chain (transport, storage and land application) or the swapping of one N emission to another can be better predicted and possibly reduced or prevented.

Chapter 1 describes the characteristics of manure management chains and the general features of manure composting. Here, a practice-oriented classification of composting methods is introduced. This classification is based on the comparison of a set of key parameters. These key parameters are identified as moisture content, structural parameters, C/N ratio and pH for the substrate; and O_2 level/aeration and temperature for the composting process. In addition, two more parameters are introduced for this classification: substrate optimization and process optimization. Both are understood as the possibility of parameter adjustment for the reduction of N loss and NH_3 emissions. This classification provides three distinct categories: (i) aerobic storage, (ii) extensive and (iii) intensive composting.

Finally, Chapter 1 focuses on the volatilization, nitrification-denitrification and assimilation processes of NH_3 in composting. Against this background, the following thesis objectives are formulated to improve scientific knowledge in:

- the relations among the key composting parameters on NH_3 dynamics processes,
- the level of achievable NH_3 control in extensive and intensive composting methods,
- the effect of NH_3 dynamics on N turnover and N content of product,
- the relevance of composting in (swine) manure management chains.

6.2 NH_3 dynamics differences in manure composting methods

Chapter 2 evaluates the feasibility of solid manure composting with the help of available scientific literature. It focuses on two parameters: the C/N ratio of the starting substrate and the aeration rate during the process. The previously introduced three methods i.e. aerobic storage, extensive and intensive composting are considered and compared.

The lack of data is the most striking feature of the accessed and evaluated literature. The information found indicates a serious lack of data to establish absolute (kg) N balances for many experiments. This is required as concentration values are not suitable to assess either the nutrient recycling or the environmental impact of composting processes. The reviewed information also indicates that amendments and bulking materials are not studied efficiently. Influence of amendments on the total solids content and C/N ratio is well documented, but assessment of the structural parameters is often neglected. The review also found insufficient information on the importance of alternative N conversion routes besides nitrification and denitrification. A deeper knowledge of this topic might show a clearer picture on how NH_3 dynamics influence subsequent N levels in the latter phases of the process.

Where useful data were found, the assessment shows that NH_3 and total N emissions vary widely for the storage and composting processes. This is likely to be the result of the high level of flexibility in the composting process. While processes can be defined well, the actual substrate and operating characteristics can result in big differences in N retaining efficiency of the three methods.

Literature shows that aerobic storage is often not more than in essence an anaerobic bed. The diffusion driven aeration does not allow for efficient stabilization of the organic matter and leads to relatively high NH_3 and greenhouse gas accumulation and emissions. In extensive composting, air is supplied to the compost bed through the natural convection principle. Literature shows that extensive methods offer a limited range of control tools, but they produce good quality composts in general. This method is expected to enable a significant fraction of NH_3 to be nitrified and denitrified, probably because of a relatively low aeration flux. Therefore, NH_3 is likely to be assimilated and nitrified instead of being emitted or accumulated. Intensive composting methods can offer the possibilities of high process and emission control. The process related N loss may not appear higher than with the extensive methods, but the emitted NH_3 can be trapped and treated. An important feature of intensive composting processes is the high amount of NH_3 emissions that is likely to be in relation with the high aeration rates. These aeration rates are suspected to prevent gaseous NH_3 to re-enter the N cycle in the composting matter.

One of the key findings of this assessment is that the indicatory value of the C/N ratio to estimate NH_3 losses depends on the aeration rate and the aeration mode. The higher the aeration rate, the less the initial C/N ratio can be used to estimate N loss from a composting process. In general, C/N ratio optimization in the starting material has more influence on the reduction of NH_3 losses from storage and extensive composting. Intensive composting studies indicate that the positive influence of optimized substrates or processes decrease with higher aeration rates.

In many of the reviewed literature, it is reported that the initially available TAN is the key reason behind the high N losses of composting processes. However, the evaluated experiments show comparable ultimate N_{total} losses at different initial TAN values. This implies that composting processes can only immobilize N on a larger scale if assimilation conditions are optimal. If that is true, the role of biodegradable, C-rich amendment is decisive to the process. Still, the aeration rate appears to be a key factor in composting NH_3 dynamics. The NH_3 flushing effect of a higher airflow can only be partially reduced by the optimization of the C/N ratio.

6.3 Nitrification-denitrification in extensive composting

An extensive composting experiment was carried out using straw amended swine manure from organic swine farming systems (Chapter 3). The manure-amendment mixture was composted in passively aerated reactors to estimate the effect of regular (monthly) turning on NH_3 dynamics, organic matter turnover and greenhouse gas emissions. The reactor design with a grid floor and isolating walls enabled a one dimensional natural convection flow in the contained compost bed. Two reactors were monthly turned and mixed, and two were left static (undisturbed) until the end of the four-month experiment. The 'turned' reactors showed high organic matter degradation (57±3 % of the initial organic matter) compared to only 40±5 % in the undisturbed piles. The turned reactors had low NH_3 and N_2O emissions, while the static ones gave insignificant NH_3 but very high N_2O emissions (9.9 ± 0.5% of the initial N). Prevalence of anaerobic regions in the static system resulted in high CH_4 emissions (12.6 ± 0.6% of the degraded organic matter [kg]).

The monthly turning of the compost bed appeared to have a major positive influence on the overall biodegradation of and water removal from the compost beds. It is likely to be the result of the reestablishment of a more porous bed structure by the turning and mixing activities. This agitation did not bring about higher natural convection velocities. It seems logical that the accelerated degradation leads to a decreased particle size and causing so a reduced permeability. In the turned reactors, turning and mixing ensured a homogeneous end-product. Here, the higher temperatures are expected to result in efficient pathogen and weed seed termination. The turned reactors functioned as extensive composting processes; the static reactors showed more signs of aerobic storage. These reactors were partly anaerobic and highly compacted especially in the lower regions of the beds.

The turning also appeared to lead to very different NH_3 dynamics and nitrogenous emissions compared with the static reactors. Both turned and static reactors had low NH_3 emissions, but no significant accumulation of NH_4^+ was observed in the final compost. It is proposed here that the unaccounted N is lost through the joint process of nitrification-denitrification, which is confirmed by presence of NO_2^- and NO_3^- in the compost samples. Neither of the compounds was accumulated in the reactors, possibly because the process conditions facilitate conversion to N_2O and N_2.

The static system showed high N_2O emissions. This is probably a result of the prevailing anaerobic regions in combination with the high NH_3 content and the absence of readily available C to allow microbial assimilation. In the turned system, CH_4 was present inside the compost bed, but only low amounts were emitted. This is likely to be the consequence of CH_4 oxidation in the anoxic top sections of the beds. The compacted static beds indicate occurrence of NH_3 oxidation in the thermophilic regions. This was probably done by CH_4 oxidizing bacteria that can also utilize NH_4^+, as nitrifying bacteria are not active at higher temperatures.

Compared to the uncontrolled emissions of untreated manures, extensive composting is proven here to be able to process animal manures with low C/N ratios without significant emissions of NH_3 and N_2O. If the structure is optimalized during the process, the process time is shortened and the environmental impact due to nitrogenous emissions is reduced. Loss of N during composting is inevitable but from an environmental point of view, inert N_2 emissions are favored to emissions of NH_3 or N_2O.

6.4 NH_3 volatilization in intensive composting

In Chapter 4, the NH_3 volatilization process is described, modeled and validated. The validation is carried out with help of experimental and literature data on forced aeration, swine manure composting processes. It was already suggested in Chapter 2 that the main parameters to influence NH_3 volatilization are pH, temperature and the aeration rate. The presented model describes the relationship of these parameters to NH_3 equilibriums and volatilization in the compost bed. There are two chemical equilibriums to consider: the balance of NH_3 and NH_4^+ in the liquid phase and the equilibrium between the liquid and the gas phase. In the model, it is shown that the first is an acid-base equilibrium, determined by the pH and the temperature. The second equilibrium is established by NH_3 partial pressures of the liquid and gas phase. This equilibrium is strongly influenced by the aeration rate that constantly reduces the partial pressure of NH_3 in the gas phase.

In the second half of Chapter 4, the model calculations are validated with the results of intensive composting experiments. The validation shows that the model can adequately describe NH_3 volatilization in a composting process. NH_3 emissions correlate well with the pH of the liquid phase. The aeration rate also exhibits a strong influence on NH_3 volatilization throughout the experiment. This latter phenomenon shows that (i) aeration rate and NH_3 volatilization have a direct link and (ii) that the airflow has a flushing effect that hinders assimilation and nitrification processes. The successful validation also underlines that pH, temperature and airflow are indeed the key parameters responsible for the extent of NH_3 emissions from manure composting processes. As these parameters are hard to alter, the recommendation is given to either increase microbial assimilation of NH_3-N through the reintroduction of NH_3 with air recirculation, or to entrap and concentrate the removed NH_3 for future use as liquid fertilizer.

6.5 NH_3-N assimilation in extensive and intensive composting

Chapter 2 has shown that C/N ratio is a key factor in the indication of N loss from a composting process. It also showed that the directness of this link between C/N ratio and N loss is subject to change with a differing aeration rate. Chapter 5 investigates whether an improved C/N alternative is available by means of a combined, two-step model. This model approaches N loss through organic matter turnover at the biopolymer level. Biopolymers as aliphatics, proteins, polysaccharides and lignins are the constituents of organic matter. Each of these four groups exhibit differing patterns in degradation and microbial assimilation of their C or N compounds. This combined model consists of two parts where the first part is a biopolymer degradation model. This first part can be used to quantify the degradation rate of the four biopolymers during manure composting. However, previous calculations of Veeken *et al*. (2001) with the model resulted in biopolymer turnover patterns deviating from the expected first order degradation kinetics. This paper argues that the cyclical growth and decay of microorganisms is the reason for such a deviation. Therefore, the second part of the combined model describes and quantifies the role of microbial growth in biopolymer degradation. It is expected that combining microbial growth with degradation of the free biopolymers can sufficiently describe the theoretical biopolymer degradation. Through this combined model, an organic C/N ratio parameter (C_{org}/N_{org}) can be quantified that has a more direct link with composting N loss. The analytical characterization is realized by a state-of-the-art 13-carbon cross polarization magic angle spinning nuclear magnetic resonance (^{13}C CPMAS NMR) method. The model is validated with the results of an extensive and an intensive swine manure-wheat straw composting experiment.

The biopolymer data calculated from the ^{13}C CPMAS NMR analysis were also confirmed by the results of a conventional composition analysis. The assessment of the experimental data shows that the microbial growth model can indeed explain discrepancies in the empirical turnover of the biopolymers that otherwise could not be accounted for. When microbial biomass yield is taken into account, the results give a higher theoretical degradation rate for aliphatics, polysaccharides and proteins. As lignin is not part of microbial biomass, the degradation rate of lignin is not affected. The calculated C_{org}/N_{org} data from elemental analysis and the same data from the biopolymer degradation model show an excellent correlation. The validation by comparing the different estimations on microbial organism biopolymer contents was also successful. The combined model therefore proves a good estimation of the empirical degradation. However, it can only give indications on the extent of immobilized N as a relevant decay rate is lacking in literature. With a decay rate for microbial biomass, it would be possible to quantify the fraction of microbial biopolymers from the amount of free biopolymers. This would allow the establishment of the amount of N susceptible to emissions.

Chapter 5 shows that once a reliable decay rate is found, the combined biopolymer degradation and microbial growth model can provide a new basis for N loss estimation for manure composting. The quantification of the C_{org}/N_{org} ratio over time allows an improved insight in the NH_3 dynamics processes of manure composting.

6.6 General conclusions

The new composting research approach using a chain approach and a novel, practice oriented classification method seems justified for the evaluation of composting methods and their NH_3 dynamics. It allows the identification of significant differences in the low-tech, extensive and the intensive, forced aeration composting designs. While intensive methods tend to have NH_3 volatilization as the main route in NH_3 dynamics, nitrification-denitrification is more relevant for extensive methods. This difference has consequences for the assimilation route and the quality and quantity of N lost from the processes.

Nitrification-denitrification appears to be the main NH_3 dynamics route in frequently turned extensive composting methods. Turning of the compost bed restores bed porosity and achieves homogenization of the compost bed. As a result, the co-existence of aerobic and anaerobic regions in the compost bed facilitates the simultaneous occurrence of nitrification and denitrification. Combined with the natural convection induced low aeration rate, the result is the complete conversion of NH_3 to the environmentally inert N_2. The improved bed structure also results in a largely aerobic degradation with little CH_4 and N_2O emissions compared to the conventional aerobic storage methods.

NH_3 volatilization cannot be prevented from intensive composting processes applying high rates of aeration. High rate NH_3 volatilization from intensive composting reduces the possibility of NH_3-N assimilation as latter is a much slower process. This thesis shows the mechanism of NH_3 volatilization during intensive composting processes and identifies the key factors influencing NH_3 emissions. The results prove that pH and temperature are the key factors in the liquid phase, while aeration rate is crucial in the gas phase. Although emitted NH_3 cannot be retained in the compost bed, the trapped NH_3 can be concentrated to form a rich liquid fertilizer free of pathogens. The relatively short process times often do not allow for truly ripe products in intensive composting processes, but they do provide an end-product that is suitable as soil conditioner. Unlike extensive methods with limited control, intensive composting installations are more applicable on central-scale operations. The dilemma of the process remains whether high aeration rates with a fast process or lower aeration rates with less nitrogenous emissions are required.

NH_3-N assimilation was researched from a new point of view in composting research. The validation of the combined model on biopolymer degradation and microbial yield shows good results. While the lack of a reliable decay rate did not allow the completion of the model, the validation does offer a good insight in the working of microbial growth and nutrient assimilation. Availability of a relevant decay rate will allow for the completing of the calculations and provide a good quality basis to assess N loss and NH_3 emissions from composting processes. The novel NMR method provides a clear picture on the composition of C binding groups leading to the quantification of the four biopolymers. The presented approach is a new development in composting science and it is expected to provide an improved basis to NH_3 dynamics in composting processes.

The practical use of the above findings includes the differentiated evaluation of extensive and intensive composting methods as potential options for manure management chains. The presented research shows that both composting methods can function better than storage as a manure treatment option. The land application of stored but untreated manures has adverse environmental effects in the form of NO_3^- leaching to the groundwater, acidification, and greenhouse emissions (N_2O, CH_4). By composting these manures, land emissions can often be reduced or completely prevented. The main advantage of composting methods appears to be their ability to offer control over the extent and form of the nitrogenous losses. When an assessment of composting integration considers all environmentally adverse emissions, composting is likely to become a more attractive option. Disadvantageous emissions can be reduced with the described extensive and intensive composting techniques, and they should more often replace aerobic storage in manure management chains in the future.

7 SAMENVATTING EN ALGEMENE CONCLUSIES

7.1 Inleiding

NH_3 verlies uit vaste mest is een belangrijk milieuprobleem. Deze verliezen vertegenwoordigen de grootste fractie van antropogene NH_3 emissies in industriële landen. De meerderheid van zulke emissies vindt plaats nadat de mest is verwijderd uit de stallen. Compostering is een biologische behandelingsmethode die hier uitkomst kan bieden. Het stabiliseert mest in de beginfase van de mestbeheer keten. Omdat de N-fixatie efficiëntie van compostering nog een onderwerp van discussie is, dient deze eigenschap geëvalueerd worden om de toepasbaarheid van compostering te bepalen. In dit proefschrift wordt beredeneerd dat dit niet via een proces, maar via een ketenbenadering moet gebeuren. Als een proces beschouwd wordt als deel van een keten, zijn de consequenties dat (i) naast het proces zelf, ook de eigenschappen van de eindproducten bekeken moeten worden en (ii) een totale massabalans moet en wordt gemaakt in plaats van een concentratiebalans. Dit betekent dat de absolute waardes van de N-emissies moeten worden berekend om een juiste procesbalans te kunnen maken. Hiermee kan de verschuiving van N-emissies naar een latere stap in de mestketen (opslag, transport en applicatie) of een verandering van het type N emissie beter worden voorspeld en mogelijk worden voorkomen of verminderd.

Hoofdstuk 1 beschrijft de kenmerken van vaste mestketens en de algemene kenmerken van mestcompostering. Ook een praktische classificatie van composteringsmethoden wordt hier weergegeven. Deze classificatie is gebaseerd op de vergelijking van de belangrijkste composteringsparameters. Deze sleutelparameters zijn geïdentificeerd als substraatparameters (vochtgehalte, fysieke structuur, C/N gehalte en pH) en procesparameters (O_2 gehalte/beluchting en temperatuur). Ook twee nieuwe parameters zijn toegevoegd: optimalisatie van het substraat en optimalisatie van het proces. Deze geven aan of er binnen een methode een mogelijkheid bestaat om het substraat of het proces aan te passen voor minder N verlies of NH_3 uitstoot. Hieruit kunnen drie composteringsmethoden worden gedefinieerd als (i) aerobe opslag, (ii) extensieve and (iii) intensive compostering.

Ten slotte wordt in Hoofdstuk 1 vervluchtiging, nitrificatie-denitrificatie en assimilatie verloop (microbiële inbouw) van NH_3 in composteringsprocessen nader bekeken. Op basis hiervan worden de volgende thesis objectieven bepaald:

- de relaties tussen de sleutelparameters en het effect op de NH_3 dynamiek,
- het behaalbare niveau van controle over de NH_3 dynamiek in compostering,
- de invloed van de NH_3 dynamiek op N omzetting en eindproductkwaliteit en
- de relevantie van compostering voor (varkens)mestketens.

7.2 Verschillen in NH_3 dynamiek bij mest composteringsmethoden

Hoofdstuk 2 evalueert de haalbaarheid van mestcompostering met hulp van wetenschappelijke literatuur. De focus is gericht op twee parameters (i) het C/N gehalte van de mest bij de opstart en (ii) het beluchtingsdebiet gedurende het proces. De eerder genoemde drie methoden als aerobe opslag, extensieve en intensive compostering worden hier bediscussieerd en vergeleken.

Een gebrek aan bruikbare data is het meest opvallende uit het gemaakte literatuuroverzicht. Het blijkt dat in literatuur vaak onvoldoende data worden geleverd om een absolute (kg) N balans van een composteringsproces te maken. Dit is noodzakelijk omdat concentraties niet geschikt zijn om de nutriëntenbalans en de milieu-impact van een proces vast te stellen. De onderzochte informatie geeft ook aan dat de effecten van supplementaire materialen (stro, houtchips) op de NH_3 dynamiek onvoldoende zijn onderzocht. Invloed van een supplement op droge stof en C/N gehalte zijn weliswaar voldoende beschreven, maar onderzoek naar de fysieke structuur ontbreekt vaak. Dit literatuuroverzicht toont ook aan dat er weinig informatie bekend is over de alternatieve N omzettingen naast het proces van nitrificatie-denitrificatie. Een diepere kennis over deze onderwerpen is noodzakelijk om een duidelijker beeld te krijgen over hoe de NH_3 dynamiek de daaropvolgende N processen beïnvloedt tijdens compostering.

Daar waar bruikbare data zijn gevonden, laat de evaluatie zien dat NH_3 en N_{total} emissies op grote schaal variëren bij de aerobe opslag en extensieve composteringsprocessen. Dit wordt waarschijnlijk veroorzaakt door de grote mate van flexibiliteit van de composteringsprocessen. De composteringsmethode mag dan wel goed definieerbaar zijn, het substraat en de proceskarakteristieken kunnen in zeer uiteenlopende waardes van N-fixatie efficiëntie resulteren bij de drie verschillende composteringsmethoden. Uit de bestudeerde literatuur blijkt dat aerobe opslag in wezen vaak een anaeroob proces is. De door diffusie gedreven beluchting is niet voldoende efficiënt voor de stabilisatie van organische stof en leidt tot relatief hoge NH_3 en broeikasgas uitstoot. Bij extensieve compostering wordt de luchtstroom in het compostbed aangevoerd door natuurlijke convectie. Uit de literatuur blijkt dat extensieve methoden een beperkt assortiment aan controle opties bieden. Die zijn echter meestal voldoende om een goede kwaliteit compost te produceren. Bij deze methode kan een significante fractie van de NH_3 genitrificeerd en genitrificeerd worden, waarschijnlijk door de lage beluchtingsnelheid. Hierdoor is het te verwachten dat NH_3 geassimileerd en genitrificeerd wordt in plaats van geëmitteerd of geaccumuleerd.

Intensieve composteringsmethodes bieden meer mogelijkheden voor proces- en emissiecontrole. Het proces gerelateerde N verlies is vaak niet lager dan bij extensieve methoden, maar geëmitteerde N componenten kunnen bij deze methode opgevangen en behandeld worden. Een belangrijke eigenschap van intensieve compostering is de hoge NH_3 emissie. Dit is waarschijnlijk te wijten aan het hoge beluchtingsdebiet die gasvormig NH_3 belet weer aan de N cyclus van het composteringsmateriaal deel te nemen.

De literatuurevaluatie toont aan dat het mogelijkheid om NH_3 emissies in te schatten aan de hand van het C/N verhouding, vermindert met een toenemend beluchtingsdebiet en het is afhankelijk van de beluchtingsmode. Hoe hoger de beluchtingsnelheid, des te minder kan de C/N verhouding gebruikt worden om de NH_3 emissie te schatten. Optimalisatie van de C/N verhouding in het initiële substraat heeft meer invloed op de vermindering van NH_3 emissies bij mestopslag en extensieve compostering. Bij intensive composteringsmethoden neemt de positieve invloed van geoptimaliseerde substraten of processen op NH_3 emissies af met een toenemend beluchtingsdebiet.

In de literatuur wordt veelal vermeld dat de initieel beschikbare TAN de primaire oorzaak is van het hoge N verlies uit composteringsprocessen. Echter, de geëvalueerde experimenten laten zien dat de uiteindelijke N verliezen vergelijkbaar zijn bij zeer uiteenlopende initiële TAN waardes. Dit impliceert dat composteringsprocessen N immobiliseren wanneer de assimilatie voorwaarden optimaal zijn. Indien hiervan kan worden uitgegaan, is de rol van biologisch afbreekbare C-rijke supplementen beslissend voor het proces. Het beluchtingsproces blijft ook een sleutelrol spelen in de NH_3 dynamiek bij composteringsprocessen. Het NH_3 stripeffect bij een hoog beluchtingsdebiet kan alleen gedeeltelijk gecorrigeerd worden door optimalisatie van het C/N verhouding.

7.3 Nitrificatie-denitrificatie in extensieve compostering

Een experiment met extensieve compostering is uitgevoerd op een mengsel van varkensmest en tarwestro, beide afkomstig van een biologische boerderij (Hoofdstuk 3). Dit mengsel is in passief beluchte composthopen behandeld om de invloed van maandelijkse omkeren en mengen (omzetten) van de composthoop op de NH_3 dynamiek, de organische stof omzetting en de broeikasgasemissies (in het bijzonder CH_4 en N_2O) te bepalen. Het reactor design, met een roostervloer en geïsoleerde muren, liet een eendimensionale convectie luchtstroom door het compostbed toe. Twee reactoren werden maandelijks omgezet, de andere twee niet (stationair).

De gemengde reactoren vertoonden een hoge organisch stof afbraak (57±3 % van de initieel beschikbare organische stof) in vergelijking met de stationaire reactoren (40±5 %). De gemengde reactoren vertoonden lage NH_3 en N_2O emissies, terwijl de stationaire reactoren weinig significante hoeveelheden NH_3, maar heel hoge N_2O emissies produceerden ($9.9 \pm 0.5\%$ van $N_{initial}$). De aanwezigheid van anaerobe regio's in de stationaire systemen resulteerde ook in hoge CH_4 emissies (12.6 ± 0.6% van de afgebroken organische stof).

Het maandelijks omzetten van het compostbed heeft een positieve invloed op de totale biologische afbraak en de waterverdamping uit de reactoren. Dit is waarschijnlijk het resultaat van het herstellen van structuur in het compostbed door de mengactiviteit. Deze menging resulteerde niet in hogere natuurlijke convectiesnelheden aangezien een versnelde biologische afbraak resulteert in verkleinde deeltjesgrootte en daarmee de doorlatendheid (permeabiliteit) verlaagt. De mengactiviteit zorgde ook voor een homogeen eindproduct. Tevens kan worden verwacht dat de hogere temperaturen resulteren in een efficiënte afdoding van pathogenen en onkruidzaden. Terwijl gemengde reactoren functioneerden als extensieve composteringsprocessen, leken de stationaire reactoren meer op aerobe opslag. De stationaire reactoren waren deels anaeroob en zeer compact, vooral in de lagere zones van het bed.

Het mengen bleek ook tot een heel verschillende NH_3 dynamiek en N-emissiepatronen te leiden. De gemengde en stationaire reactoren gaven lage NH_3 emissies. Er werd geen significante accumulatie van NH_4^+ waargenomen in het compost product. Aangenomen wordt dat een deel van de N-fractie uit het compostbed is verdwenen door nitrificatie en denitrificatie. Dit wordt ondersteund door de aanwezigheid van NO_2^- en NO_3^- in het compost. Geen van deze componenten accumuleerde in de reactoren, waarschijnlijk omdat de procesomstandigheden de omzetting naar N_2O en N_2 vergemakkelijkten.

Het stationaire systeem liet hoge N_2O emissies zien. Dit is het gevolg van persistente anaerobe regio's in combinatie met een hoge NH_3 inhoud en de afwezigheid van beschikbare C, om microbiële assimilatie toe te laten. Hoewel CH_4 aanwezig was in het compost bed werd hiervan slechts een lage emissie gemeten. Dit is waarschijnlijk een gevolg van CH_4 oxidatie in de anoxische top zone van de bedden. De compacte, stationaire bedden gaven oxidatie van NH_3 in de thermofiele zones. Dit is mogelijk bewerkstelligd door CH_4 oxiderende bacteriën die NH_4^+ kunnen benutten, aangezien nitrificerende bacteriën inactief zijn bij hogere temperaturen.

Uit dit onderzoek blijkt, dat vergeleken met de ongecontroleerde emissies van onbehandelde mest, extensieve compostering een geschikte methode is om mest met een laag C/N gehalte zonder significante NH_3 en N_2O emissies te kunnen stabiliseren. Indien de structuur voldoende geoptimaliseerd is gedurende het proces, is een kortere procestijd en een lagere milieu-impact het gevolg. N verlies tijdens het composteringsproces is onvermijdelijk. Echter, vanuit milieuoogpunt is emissie van inert N_2 gunstiger dan van NH_3 of N_2O.

7.4 NH_3 emissie tijdens intensieve compostering

In Hoofdstuk 4 wordt het NH_3 vervluchtigingproces beschreven, gemodelleerd en gevalideerd. De validatie is uitgevoerd met hulp van experimenteel en literatuur data van geforceerd beluchte compostering van een mengsel van varkensmest en tarwestro. In hoofdstuk 2 werd gesteld dat de sleutelparameters om NH_3-vervluchtiging te beïnvloeden de pH, de temperatuur en het beluchtingsdebiet zijn. Het gepresenteerde model beschrijft de relatie van deze parameters met NH_3 evenwichten en vervluchtiging in het compost bed. Er zijn twee chemische evenwichten: het evenwicht van NH_3 en NH_4^+ in de vloeistoffase en het evenwicht tussen de vloeistof- en het gasfase. In het model is het eerste evenwicht een zuur-base equilibrium dat wordt bepaald door de pH en de temperatuur. Het tweede evenwicht wordt bepaald door de NH_3 partiële druk in de gasfase. Dit evenwicht wordt sterk beïnvloed door het beluchtingsdebiet dat continu de NH_3 concentratie vermindert in de gasfase.

In de tweede helft van Hoofdstuk 4 worden de modelberekeningen gevalideerd met de resultaten van intensieve composteringsexperimenten. De validatie toont aan dat het model geschikt is om NH_3 vervluchtiging in een composteringsproces te beschrijven. De NH_3 emissies correleren goed met de pH van de vloeistof. Het beluchtingsdebiet vertoont een sterke invloed op NH_3 vervluchtiging gedurende het experiment. Dit toont aan dat (i) beluchtingsdebiet en NH_3 vervluchtiging een directe correlatie vertonen en (ii) de beluchting een strippend effect heeft, wat microbiële assimilatie en nitrificatie processen verhindert. De succesvolle validatie onderstreept dat pH, temperatuur en beluchting inderdaad de sleutelparameters zijn die bepalend zijn voor de mate van NH_3 emissies uit composteringsprocessen. Omdat deze parameters moeilijk aangepast kunnen worden, resteren er twee opties. De eerste optie is het recirculeren van NH_3 emissie in het compostbed om microbiële assimilatie te stimuleren. De tweede optie is het vangen en concentreren van NH_3 van de uitgaande gasstroom om als vloeibare meststof te dienen.

7.5 NH_3-N assimilatie in extensieve en intensieve compostering

In Hoofdstuk 2 werd aangetoond dat de C/N verhouding een sleutelfactor is voor de indicatie van N-verlies uit een composteringsproces. Tevens werd gesteld dat de verbinding tussen C/N verhouding en N verlies verandert met de snelheid van beluchting. Hoofdstuk 5 onderzoekt of het maken van een alternatief C/N verhouding parameter op basis van een model mogelijk is om NH_3 verlies in te schatten. Dit model benadert het N verlies op biopolymeer niveau.

Biopolymeren, zoals aliphaten, proteïnen, polysacchariden en lignines, zijn de vier bestanddelen van organische stoffen. Elke groep vertoont verschillende afbraak- en microbiële assimilatiepatronen met betrekking tot C en N. Het gecombineerde model is opgebouwd uit twee delen waarvan het eerste deel een biopolymeer afbraak model is. Dit deel kan gebruikt worden om de afbraaksnelheid van de vier biopolymeren te kwantificeren tijdens de mestcompostering. Eerdere berekeningen van Veeken *et al.* (2001) met het model resulteerden in biopolymeer omzettingspatronen die afweken van de verwachtte eerste orde afbraakkinetiek. In dit hoofdstuk wordt er vanuit gegaan dat groei en afsterving van micro-organismen de oorzaak zijn van de gevonden afwijking. Daarom wordt in het tweede gedeelte van het model de rol van microbiële groei in biopolymeer afbraak beschreven en gekwantificeerd. De verwachting is dat het combineren van de microbiële groei met de afbraak van vrije (niet micro-organisme gerelateerde) biopolymeren de theoretische biopolymeeromzetting wel adequaat kan beschrijven. Met dit gecombineerde model kan een organische C/N verhoudingsparameter (C_{org}/N_{org}) gekwantificeerd worden die een meer directe link heeft met N verlies uit compostering. De analytische bepaling van de organische stof samenstelling is uitgevoerd met de '13-carbon cross polarization magic angle spinning nuclear magnetic resonance' (^{13}C CPMAS NMR) methode. Het model is gevalideerd met resultaten van een extensieve en een intensieve compostering van een varkensmest en tarwestro mengsel.

De met ^{13}C CPMAS NMR analysetechniek verklaarde biopolymeer gehaltes werden bevestigd door de resultaten verkregen uit de conventionele analyses. De evaluatie van de experimentele data toont aan dat het meerekenen van de microbiële groei inderdaad de afwijkingen in het empirische omzettingspatroon kan verklaren. Wanneer de microbiële groei wordt verdisconteerd, resulteert dit in een hogere theoretische afbraaksnelheid voor aliphaten, polysacchariden and proteïnen. Omdat lignine geen bestanddeel is van micro-organismen wordt deze afbraaksnelheid niet beïnvloed door de berekeningen.

De uit biopolymeer groepen uitgerekende C_{org}/N_{org} data van de elementaire analyse en de zelfde data van het biopolymeer afbraak, vertonen een excellente correlatie. De validatie op basis van het vergelijken van verschillende schattingen van (biopolymeer)inhoud van micro-organismen was ook succesvol. Dit bevestigt dat het gecombineerde model een goede schatting kan geven van empirische afbraak. Echter, het kan alleen een indicatie geven voor de hoeveelheid geïmmobiliseerde N, omdat een relevante informatie over afstervingssnelheid ontbreekt in literatuur. Met een betrouwbare afstervingssnelheid is het mogelijk om de fractie van de microbiële biopolymeren van de vrije biopolymeren te kwantificeren. Hiermee zou het mogelijk zijn om de hoeveelheid N die kan vervluchtigen vast te stellen.

Hoofdstuk 5 toont aan dat als de afstervingssnelheid bekend is, het gecombineerde biopolymeermodel een nieuwe basis kan geven voor schattingen van N verlies bij (mest)compostering. De kwantificering van het C_{org}/N_{org} gehalte gedurende het composteringsproces geeft een verbeterd inzicht in de NH_3 dynamiek.

7.6 ALGEMENE conclusies

De nieuwe aanpak van composteringsonderzoek met een ketenbenadering en een nieuwe op de praktijk geënte classificatiemethode, blijkt een goed basis om de relatie tussen composteringsprocessen en NH_3 dynamiek te evalueren. Dit maakt de identificatie van belangrijke verschillen mogelijk tussen de low-tech, extensieve en de geforceerd beluchte, intensieve ontwerpen van composteringsprocessen. De intensieve composteringsmethoden hebben NH_3 vervluchtiging als de hoofdroute in de NH_3 dynamiek; de route van nitrificatie-denitrificatie is relevanter bij extensieve methoden. Dit verschil heeft gevolgen voor de hoeveelheid van microbiële assimilatie en de mate en wijze van N verliezen uit de processen.

Nitrificatie-denitrificatie blijkt de NH_3 dynamiek hoofdroute te zijn in regelmatig omgezette extensieve composteringsprocessen. Mengen van het compostbed zorgt voor herstel van bedporositeit en maakt het compostbed homogener. De co-existentie van aerobe en anaerobe zones in het compostbed maken het simultaan optreden van nitrificatie en denitrificatie mogelijk. Gecombineerd met het lage beluchtingsdebiet van het natuurlijke convectieproces, is het resultaat een complete omzetting van NH_3 naar N_2. De verbeterde structuur van het bed resulteert ook in meer aerobe afbraak van C en N met weinig CH_4 en N_2O emissies in vergelijking met de conventionele aerobe opslagtechnieken.

NH_3 vervluchtiging kan niet worden voorkomen in intensive composteringsprocessen met hoge beluchtingsnelheden. De hoge mate van NH_3 vervluchtiging uit intensive compostering verkleint de kans op NH_3-N assimilatie omdat dat laatste een veel langzaamere proces is. Dit proefschrift beschrijft het mechanisme van NH_3-vervluchtiging en identificeert de sleutelparameters die emissies van NH_3 beïnvloeden. De resultaten bewijzen dat naast TAN, de pH en de temperatuur de sleutelparameters zijn in de vloeistoffase, terwijl het beluchtingsdebiet cruciaal is in de gasfase. Hoewel de geëmitteerde NH_3 niet in het compostbed kan worden gefixeerd, kan de NH_3 in het uitgaande gas worden opgevangen en in een geconcentreerde vorm worden gebruikt als vloeibare mest. De relatief korte procesduur maakt een voldoende rijp compostproduct vaak onmogelijk, maar het eindproduct kan wel gebruikt worden als bodemverbeteraar. In tegenstelling tot extensieve methoden met beperkte controle, zijn intensieve composteringsinstallaties toepasbaar op grote schaal. Het dilemma van het proces is de keuze tussen een hoog beluchtingsdebiet met snelle afbraak en veel NH_3-emissies, of lagere beluchting met een trager proces maar met minder N verlies.

NH_3-N assimilatie is vanuit een nieuwe invalshoek benaderd in composteringsonderzoek. De validatie van het gecombineerde model voor biopolymeer afbraak en microbiële groei geeft goede resultaten. Het gebrek aan een betrouwbare afstervingsnelheid verhindert de afronding van het model, maar de validatie geeft goed inzicht in de werking van microbiële assimilatie en nutriënten inbouw. Beschikbaarheid van een afstervingsnelheid zal het afronden van het model mogelijk maken. De nieuwe NMR methode verschaft een duidelijke analytische basis wat de kwantificatie van de vier biopolymeren mogelijk maakt. De gepresenteerde benadering is een nieuwe ontwikkeling en naar verwachting kan het zorgen voor een verbeterde kennisbasis van NH_3 dynamiek in compostering.

Het praktische nut van bovenstaande bevindingen ligt in de gedifferentieerde evaluatie van extensieve en intensieve composteringsmethoden als potentiële opties voor mestbeheer ketens. Het gepresenteerde onderzoek toont aan dat beide composteringsmethoden beter kunnen functioneren dan de conventionele, aerobe opslag. Het toedienen van opgeslagen maar niet behandelde mest op land heeft nadelige milieueffecten zoals het indringen van NO_3^- in het grondwater, verzuring van NH_3 en broeikasgas emissies (N_2O, CH_4). Mestcompostering kan deze problemen verkleinen of voorkomen. Het belangrijkste voordeel van deze methoden is de beschikbaarheid van controle mechanismes over de mate en vorm van N verliezen.

In conventionele evaluaties lijkt de optie compostering vaak nadelig in vergelijking met opslag van mest. Echter, als alle ongunstige milieu emissies worden beschouwd, kan compostering een gunstigere keuze zijn. De hier beschreven extensieve en intensieve methoden geven de mogelijkheid om nadelige emissies te verminderen. Compostering van mest zou aerobe opslag vaker moeten vervangen in ketens van mestbeheer.

ABOUT THE AUTHOR

Gábor Szántó was born in Veszprém (Hungary) in 1975. He completed a water management secondary school in 1994 (Barcs, Hungary) and attained a BSc in water management-environmental studies at the Eötvös József College in 1997 (Baja, Hungary). He visited Wageningen University (then Wageningen Agricultural University) initially as a Tempus fellow in 1996 and 1997. In 1998, he was offered a Matra fellowship to follow MSc studies in Environmental Sciences. Specializing in biological treatments of organic wastes, he completed his MSc in 2000. In the years to follow, composting remained his main research area. From 2001, he continued his work as a PhD fellow at the sub-department of Environmental Technology (WUR). From 2007 until today, he is the program coordinator of PROVIDE, a scientific project on East African sanitation and waste management, at the Environmental Policy Group of Wageningen University.

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