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COMPARISON OF FIVE ORGANIC WASTES REGARDING THEIR BEHAVIOUR DURING COMPOSTING: PART 2, NITROGEN DYNAMIC

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Abstract

This paper aimed to compare household waste, separated pig solids, food waste, pig slaughterhouse sludge and green algae regarding processes ruling nitrogen dynamic during composting. For each waste, three composting simulations were performed in parallel in three similar reactors (300L), each one under a constant aeration rate. The aeration flows applied were comprised between 100 and 1100 L/h. The initial waste and the compost were characterized through the measurements of their contents in dry matter, total carbon, Kjeldahl and total ammoniacal nitrogen, nitrite and nitrate. Kjeldahl and total ammoniacal nitrogen and nitrite and nitrate were measured in leachates and in condensates too. Ammonia and nitrous oxide emissions were monitored in continue. The cumulated emissions in ammonia and in nitrous oxide were given for each waste and at each aeration rate. The paper focused on process of ammonification and on transformations and transfer of total ammoniacal nitrogen. The parameters of nitrous oxide emissions were not investigated. The removal rate of total Kjeldahl nitrogen was shown being closely tied to the ammonification rate. Ammonification was modelled thanks to the calculation of the ratio of biodegradable carbon to organic nitrogen content of the biodegradable fraction. The wastes were shown to differ significantly regarding their ammonification ability. Nitrogen balances were calculated by subtracting nitrogen losses from nitrogen removed from material. Defaults in nitrogen balances were assumed to correspond to conversion of nitrate even nitrite into molecular nitrogen and then to the previous conversion by nitrification of total ammoniacal nitrogen. The pool of total ammoniacal nitrogen, i.e. total ammoniacal nitrogen initially contained in waste plus total ammoniacal nitrogen released by ammonification, was calculated for each experiment. Then, this pool was used as the referring amount in the calculation of the rates of accumulation, stripping and nitrification of total ammoniacal nitrogen. Separated pig solids were characterised by a high ability to accumulate total ammoniacal nitrogen. Whatever the waste, the striping rate depended mostly on the aeration rate and on the pool concentration in biofilm. The nitrification rate was observed as all the higher as the concentration in total ammoniacal nitrogen in the initial waste was low. Thus, household waste and green algae exhibited the highest nitrification rates. This result could mean that in case of low concentrations in total ammoniacal nitrogen, a nitrifying biomass was already developed and that this biomass consumed it. In contrast, in case of high concentrations, this could traduce some difficulties for nitrifying microorganisms to develop.

Keywords: Organic waste, composting, nitrogen dynamic, ammonification, nitrification, ammonia emissions, nitrous oxide emissions.

1. Introduction

Concern with nitrogen dynamic in composting aims to identify the ways allowing to reduce ammonia and nitrous oxide emissions either by keeping nitrogen in compost or through its conversion into molecular nitrogen. Indeed, nitrous oxide is a powerful greenhouse gas and ammonia emissions contribute to bad odours around composting plants and take part to the eutrophication of ecosystems and to acid rains. More, losses in nitrogen reduce the fertilizer value of the compost.

In their review on environmental impacts of biological treatments of organic waste, Mallard et al. (2006) estimated ammonia emissions during composting around 0.2 kg N-NH_3/Mg DM for green waste and around 4.5 for wastewater sludge, between 0.6 and 1.2 for household waste, between 1.4 and 9.4 for pig and cattle manure and between 4 and 6 for biowaste. Komilis and Ham (2006) found that these emissions were 2, 4.4 and 34 kg N-NH_3/Mg DM for respectively paper, green waste and food waste whereas Pagans et al. (2006) found that these emissions were 0.47, 0.17 and 7.67 kg N-NH_3/Mg OM for respectively organic fraction of municipal solid waste, raw sludge and animal by-products. Emissions of nitrous oxide, expressed as equivalent CO_2 regarding green house effect, range between 2 and 50 kg CO_2/Mg DM for biowaste, between 5 and 125 for household waste, between 10 and 1700 for pig and cattle manure and around 340 for wastewater sludge (Mallard et al., 2006).

These results indicated that there is a wide variation of ammonia and nitrous oxide emission resulting from different waste nature and composting conditions.

Assuming microorganisms use 15-30 parts of carbon for each part of nitrogen, low C/N ratios were often considered being responsible for higher emissions of ammonia (Okereke and Meints, 1985, Pagans et al., 2006, Tiquia and Tam, 2000, Zhu, 2007), whereas high C/N ratios would allow to immobilize and even fix nitrogen (Liang et al., 2006). However, as reported by Kirchmann and Witter (1989), many authors did not observe any reduction of ammonia emissions as C/N was increased. Then, some claimed for the account of the biodegradabilities of carbon and nitrogen instead of its chemical concentrations (Liang et al., 2006; Paillat et al., 2005; Paré et al., 1998). Indeed, Liang et al. (2006) observed that the addition of sucrose reduced nitrogen losses during composting of manure with straw whereas the addition of paper had low influence on ammonia volatilization. Liang et al. (2006) also reported that Subair (1995) and Witter (1986) found that low amounts of glucose were effective in reducing emissions of NH_3 when composting liquid hog manure and sewage sludge with straw.

Many papers also dealt with the influence of the aeration rate, the temperature and the pH on the emissions of ammonia. Thus ammonia emissions were found all the higher as the aeration rates (de Guardia et al., 2008; Körner and Stegmann, 2003; Liang et al., 2004), the temperatures (Pagans et al., 2006; Witter and Lopez-Real, 1987) and the pH (Beck-Friis et al., 2001; Cronje et al., 2002; Ekinci et al., 2000; Pagans et al., 2006) were high.

Waste nature and composting conditions were investigated in order to account for nitrification and denitrification too. The concentrations of nitrite and nitrate measured in composting materials were usually low (Lemus and Lau, 2002), which could result whether to low nitrification rates or most probably to denitrification following nitrification. In addition, since molecular nitrogen produced through denitrification is low compared to N_2 concentration in air, denitrification can not be easily quantified by measurement of N_2 in exhaust gazes. Then, nitrification and denitrification were usually considered on basis of a qualitative approach when the nitrogen balance was not coherent. The oxygen concentration, the concentration in NH_4^+/NH_3 and the temperature in composting material were invoked to account for nitrification and denitrification rates (Bishop and Godfrey, 1983; Eiland et al., 2001; Körner et al., 1999; Körner and Stegmann, 2003; Tiquia and Tam, 2000; Wong et al., 2001). The increase of nitrate, when most of the biodegradable matter was biodegraded and when the concentration in total ammoniacal nitrogen and the temperature decreased, was interpreted as being due to both the availability of oxygen and the achievement of optimal temperatures for nitrification. In contrast, others considered denitrification occurred even when oxygen concentration was higher than 15% and they attributed the increase of nitrate to a slow-down of denitrification resulting from a diminishing of biodegradable organic matter (Lemus and Lau, 2002; Liang et al., 2006).

In agreement with theory, ammonification leads to the release of total ammoniacal nitrogen, which then adds to total ammoniacal nitrogen initially present in the waste. Then, this pool of total ammoniacal nitrogen is either immobilized as organic nitrogen, accumulates in compost, is emitted as ammonia or is converted into nitrate then molecular nitrogen through nitrification and denitrification. Thus, the removal of nitrogen from material results mostly from the transformations and the transfer of total ammoniacal nitrogen. However, few papers (de Guardia et al., 2008) took into account the amount of organic nitrogen ammonified in the calculation of the rates of accumulation, stripping and nitrification.

More, although Martins and Dewes (1992) underlined the influence of ammonification on ammonia emissions and although the peak of ammonia emissions occurred when biological activity was maximum (Körner et al., 1997), i.e. at the peak of material temperature (Bhoyar et al., 1979), the correlation between ammonification and organic matter biodegradation was poor studied. However, in agreement with the

assumption that ammonification was closely tied to carbon biodegradation and to organic nitrogen content of the biodegradable fraction, de Guardia et al. (2008) and Liang et al. (2006) assumed a correlation between organic nitrogen ammonified, ΔNorg, and organic carbon removed, ΔCorg:

$$\Delta Norg \approx \Delta Corg \times \left[1/\left(TC / Norg\right)\right]$$

with TC/Norg, the ratio of carbon to organic nitrogen of either the biodegraded fraction (Liang et al., 2006) or of the initial substrates (de Guardia et al., 2008).

This state of the art showed that there was still a need for a better understanding of processes ruling nitrogen dynamic during composting. This study aimed to compare five organic waste, i.e. household waste, separated pig solids, food waste, pig slaughterhouse sludge and green algae, regarding their behaviour towards organic nitrogen mineralization, ammonia striping, NH_4^+/NH_3 accumulation in compost, nitrification and denitrification. Composting conditions like aeration and temperature were also investigated as potential parameters of ammonification, accumulation, striping and nitrification. Composting experiments were performed in lab-pilots under forced aeration.

Nomenclature

C_{bio}	biodegradable carbon	N-nit	nitrogen nitrified
Cbio/Nbio	C/N ratio of the biodegradable fraction	NK	Kjedahl nitrogen
COD	chemical oxygen demand	Norg	organic nitrogen
CV	coefficient of variation	NO_2^-	nitrite
C/N	carbon to nitrogen ratio	NO_3^-	nitrate
DM	dry matter	OM	organic matter content
FW	food waste	OM_0	initial content in organic matter
GA	green algae	P	pool of NH_4^+/NH_3 contained in initial waste and released by ammonification
HW	household waste	PSS	pig slaughterhouse sludge
NH_4^+/NH_3	total ammoniacal nitrogen	SPS	separated pig solids
NH_3	ammonia	TC	total carbon
N_2O	nitrous oxide	WC	wood chips

2. Methods

2.1. Materials used and performance of experiment

The waste were collected on site less than 24h before each composting simulation. The household waste (HW) was collected at a composting plant (Launay-Lantic, Brittany, France). After three days in a rotating drum, the household waste were submitted to mechanical sorting to extract impurities. Finally, they were mixed

with yard waste to achieve their composting. Here, HW was sampled after mechanical sorting and before composting. The food waste (FW) was collected at a cafeteria. The separated pig solids (SPS) were sampled at a pig livestock. They corresponded to the solid fraction obtained following centrifugation of pig slurry. The pig slaughterhouse sludge (PSS) was collected at the wastewater treatment plant of a slaughterhouse. The green algae (GA) were collected on the beach of St Michel en Grèves in Brittany. They were rinsed then, drained for 24h before the composting experiments. The household waste, the food waste, the pig slaughterhouse sludge and the green algae were mixed with calibrated wood chips (WC), which dimensions ranged between 12.5 and 30 mm. Moisture content of the mixtures was comprised between 56 and 70%. In the case of PSS, the sludge was sampled between January and October of the same year. Except for PSS, the same waste was loaded in three similar reactors. These consisted in insulated cylindrical chambers (300L) in which air was blown at the bottom then crossed the material. A constant aeration rate was applied on each reactor meaning the behaviour of each waste was studied as it was submitted to three different aeration rates. The aeration rates were comprised between 100 and 1100 L/h. The value of the highest aeration flow was chosen on basis of airflows applied at real scale. The medium and the lowest ones were selected in order to, whether limit biodegradation thanks to oxygen supply (PSS at 105 L/h), or achieve complete stabilisation i.e. avoid limitation by drying too fast the material. The in-coming airflow, the material temperature and its total mass were measured in continue thanks to respectively a volumetric gas meter, three Pt100 probes and weigh sensors. The exhaust gases were collected at the top of the reactors and the condensates formed were trapped in bottle condensers. The condensates and the leachates were weighed every day then, analysed. Concentrations of oxygen, carbon dioxide, methane, ammonia and nitrous oxide were measured in both the in-coming and out-going airflows. The emissions of ammonia were measured for each waste and at each aeration rate whereas nitrous oxide emissions were measured for only household waste, food waste and green algae. The material was turned once, twice or three times during composting. The composting was stopped when the oxygen consumption rate seemed constant and around zero. The experiments lasted from 27 to 50 days. The details relating to initial and final characteristics of the mixtures and to experimental conditions were given in Table 1 in Part 1 of this pair of articles.

2.2. Pre-treatments and chemical characterization of the waste and of the mixtures

As much as possible, in order to reduce losses through drying, the chemical characterization was applied on moistened waste i.e. without any drying. Thus, taking into account its low particle dimensions, separated pig solids and composted ones were characterized without any drying neither grinding. The characterization of the composted mixtures containing wood chips made other risks i.e. under or over-estimate one of its components.

Thus, for mixtures of green algae with wood chips, the strategy consisted to separate the composted waste from the wood chips by mechanical sieving and even manual separation. For mixtures of household waste with wood chips and pig slaughterhouse sludge with wood chips, mechanical screening was coupled with aqueous extractions. For food waste, the initial waste and the mixture obtained after composting were dried then ground before characterization. Taking into account wood chips pieces dimensions and that they biodegraded slower than studied waste, the method assumed that the wood chips were inert meaning wood chips obtained after composting were not characterized. Whatever the pre-treatment, the same was applied on initial and composted waste.

Thus, as mentioned earlier, separated pig solids and composted ones were characterized without any drying neither grinding. Fresh and composted green algae were cut in a food grinder without any drying, and then, they were characterized. Taking into account that the composted household waste and composted pig slaughterhouse sludge remained adsorbed on the wood chips, the separation was achieved thanks to mechanical sieving coupled with aqueous extractions. Such extraction also reduced losses through drying since volatile compounds adsorbed on solids, i.e. composted waste or wood chips, were trapped in the aqueous extracts. Then, the aqueous extract was characterized with the standard methods used for liquids. The solids were dried then analysed. The global composition was obtained by adding each phase contribution. Taking into account sanitary risks, i.e. pathogens and odours, initial food waste and composted mixtures, i.e. food waste plus wood chips, were not submitted to aqueous extractions. The high dimensions of food waste particles led to dry then grind initial waste and composted mixtures before their chemical characterization. In this case, the wood chips were assumed inert regarding the duration of the experiments and their contribution was subtracted from the characterization applied on the final global mixture i.e. composted food waste plus wood chips

The initial and composted wastes were characterized for their content in dry matter (DM), organic matter (OM), total carbon (TC), chemical oxygen demand (COD), Kjeldahl nitrogen (NK), total ammoniacal nitrogen (NH_4^+/NH_3), nitrite (NO_2^-) and nitrate (NO_3^-). Whatever the waste, the compost or the composted mixture, three samples at the minimum were pre-treated then analysed. If the coefficient of variation (CV) was inferior to 5%, then the analysis was registered. If not, some additional samples were submitted to pre-treatment and analysis. In the case of analysis practised on moistened material, the heterogeneity was higher than for dried and ground materials, which led to characterize 5 to 15 samples to get CV inferior to 5%.

The contents in TC, COD, NK, NH_4^+/NH_3, NO_2^- and NO_3^-, of the condensates and of the leachates, were measured too. Each sample collected was analyzed three times leading to CV inferior to 5%.

Details relating to the pre-treatments and standard methods applied for chemical characterization were given in Part 1.

2.3. Methods for calculation of the rates of ammonification, accumulation, stripping and nitrification

Organic nitrogen content was obtained by subtracting total ammoniacal nitrogen from Kjeldahl nitrogen. Then, thanks to the knowledge of the mass of waste loaded in the reactor and of the mass of the composted waste and thanks to characterizations applied on initial and composted waste, it was possible to calculate the mass of organic nitrogen in the initial waste and in the composted one. The rate of ammonification was obtained by dividing the mass of organic nitrogen removed during composting by the mass of organic nitrogen contained in initial waste.

Ammonification leading to the release of total ammoniacal nitrogen and the removal of nitrogen from material being due at first to the transformations and to the transfer of total ammoniacal nitrogen (Figure 1), both were considered in the calculation of the rates of accumulation, striping and nitrification of total ammoniacal nitrogen. Then, the pool P was defined as the addition of the mass of total ammoniacal nitrogen contained in initial waste plus the mass of total ammoniacal nitrogen released by ammonification:

$$P = N_NH_4^+ / NH_{3\,0} + \Delta Norg \; .$$

The mass of total ammoniacal nitrogen released following ammonification, ΔNorg, corresponded to the mass of organic nitrogen removed during composting and mentioned above.

Thus, the accumulation rate was the ratio of the mass of total ammoniacal nitrogen contained in composted waste to the mass of pool P i.e. the mass of total ammoniacal nitrogen contained in initial waste plus the mass of total ammoniacal nitrogen released by ammonification, both potentially participating to accumulation.

The striping rate was the ratio of the mass of nitrogen emitted as ammonia to the mass of total ammoniacal nitrogen, which could potentially be emitted i.e. the mass of the pool P. Considering that nitrogen in condensates was mostly as NH_4^+/NH_3 and that it came from condensation of the out-going gas, it was added to nitrogen emitted as ammonia.

In agreement with Figure 1, total ammoniacal nitrogen transformed by nitrification can be calculated by subtracting from the pool P the masses of total ammoniacal nitrogen accumulated plus the mass of total ammoniacal nitrogen striped as ammonia plus total ammoniacal nitrogen collected in condensates and in leachates. Then, as for the calculation of the rates of accumulation and striping, the rate of nitrification was

calculated by dividing the mass of total ammoniacal nitrogen nitrified by the mass of P i.e. the mass of total ammoniacal nitrogen which could be potentially transformed by nitrification.

Figure 1 here

3. Results and discussion

3.1. Chemical characteristics of the initial and composted waste

The chemical characteristics of household waste, separated pig solids, food waste, pig slaughterhouse sludge, green algae and wood chips were given in Table 2 in Part 1. Considering all the studied waste, the mean value of TC was 572.1 g/kg OM with a coefficient of variation (CV) equal to 9% and the mean of COD concentrations was 1570 g O_2/kg OM with a CV equal to 18.0%. In contrast, the waste differed significantly to each other regards to their contents in organic matter and in Kjeldahl and total ammoniacal nitrogen. Thus, OM content was the lowest for green algae, 53.3% DM, and the highest for food waste, 91.4% DM. The N-NK concentrations ranged between 17 and 60 g N-NK/kg DM corresponding respectively to household waste and pig slaughterhouse sludge. The highest concentrations in N-NH_4^+/NH_3 were observed for separated pig solids and pig slaughterhouse sludge whereas NH_4^+/NH_3 was under detection level (0.01 g/kg DM) in household waste. Since drying was responsible for high losses in total ammoniacal nitrogen, and taking into account that not any aqueous extraction was practiced for food waste, N-NH_4^+/NH_3 was not measured within. The chemical characterization showed that the wood chips differed from the waste mainly regards to their contents in nitrogen, which were inferior to 1.0 g N-NK/kg DM and under detection level for NH_4^+/NH_3. No nitrate neither nitrite were detected in the initial substrates.

The chemical characteristics of composted waste were given in Table 3 in Part 1. During composting, the concentrations in N-NK and N-NH_4^+/NH_3 increased or decreased depending on the waste and on the aeration rate. No nitrate neither nitrite were detected in the composted waste.

3.2. Ammonia and nitrous oxide emissions

The cumulated emissions of ammonia and nitrous oxide measured on green algae were given Figures 2a and 2b as an illustration of NH_3 and N_2O emission profiles. As it was often mentioned in literature, the peaks of NH_3 and N_2O occurred either at the peaks of oxygen consumption rate or after material turning.

The highest levels of ammonia emissions were observed for pig slaughterhouse sludge, between 4.8 and 36.1 g N-NH_3/kg OM_0 (Table 1). They ranged between 2.9 and 10.8 g N-NH_3/kg OM_0 for the food waste and the

green algae (Table 1). The ammonia emissions were the lowest for the separated pig solids and the household waste i.e. inferior to 1.7 g N-NH_3/kg OM_0 for SPS and to 0.1 for HW (Table 1). These data agree with ranges reported by Mallard et al. (2006). For a given waste, except for pig slaughterhouse sludge, the losses of nitrogen as ammonia emissions were all the higher as the aeration rate applied was high, which was in agreement with literature (de Guardia et al., 2008; Körner and Stegmann, 2003; Liang et al., 2004). However, this increase with aeration rate depended on the waste too. Indeed, this increase was significant for food waste, pig slaughterhouse sludge and green algae and almost negligible for household waste (Table 1). More, for pig slaughterhouse sludge, although nitrogen emitted as ammonia, i.e. in gas plus condensates, accounted for more than 80% of nitrogen removed from material at the two highest aeration rates, there was a decrease of ammonia emissions from 36.1 to 26.4 g N-NH_3/kg OM_0 while the aeration rate was increased from 486 to 1066 L/h (Table 1). This decrease could be due to a lower ammonification rate at 1066 L/h than at 486 L/h (Table 2), which may result from limitation of biodegradation because of a higher kinetic of drying at 1066 L/h.

Concerning nitrous oxide emissions, these were negligible during composting of household waste and food waste. They ranged between 2.2 and 4.5 g N-N_2O/kg OM_0 for the green algae i.e. in the same range as ammonia emissions (Table 1).

Figure 2 here

Table 1 here

3.3. Nitrogen balance

Taking into account neither nitrite nor nitrate were found in initial waste and in composts, total nitrogen in initial waste and composts corresponded to Kjeldahl nitrogen. Initial contents in Kjeldahl nitrogen and its removal rates were given in Table 1 for each waste. Separated pig solids were characterized by low removal rates of initial content in nitrogen, between 5.8 and 8.3%, whereas these were comprised between 36.7 and 43.1%, 43.3 and 57.0%, 48.4 and 66.2% and 39.6 and 56.3% for respectively household waste, food waste, pig slaughterhouse sludge and green algae (Table 1). During composting, nitrogen was either kept, either exported from material in leachates or emitted as ammonia, nitrous oxide and molecular nitrogen in exhaust gases. Losses of nitrogen as percent nitrogen removed from material were also given in Table 1. The nitrogen losses in leachates depended mostly on the amount of leachates i.e. on one hand on the substrates, their moisture content and their water holding capacity, and on the other, on aeration flow. However, the nitrogen losses in leachates also depend on nitrogen dynamic in the composting material i.e. on transformations and transfer of nitrogen. Table 1 shows that, in this study, these losses were all the higher as the aeration rate was low. Thus, these losses

represented until 50% of nitrogen removed from pig slaughterhouse sludge at 105L/h. Losses as ammonia represented from 0 to 83% of nitrogen removed. The cumulated losses of nitrogen i.e. in the leachates, in the condensates, as ammonia and as nitrous oxide, accounted for 1 to 91% of nitrogen removed from the material. Except for pig slaughterhouse sludge, more than 45% of nitrogen removed was always lacking in nitrogen balance (Table 1). For the household waste, this default was even superior to 97% (Table 1). N lacking in nitrogen balance was considered as molecular nitrogen emitted following nitrification and denitrification as usually assumed in literature. Figure 3 gives an illustration of the concentrations in N-NK in initial waste and of nitrogen kept in material, lost in leachates and emitted as NH_3, N_2O and N_2 in each experiment performed. In case of separated pig solids and pig slaughterhouse sludge, nitrous oxide was not measured and it was accounted as N_2 emissions. Thus, nitrogen removed from material was emitted mainly as N_2 for household waste and green algae whereas it was emitted mainly as NH_3 for pig slaughterhouse sludge (Figure 3).

Figure 3 here

3.4. Influence of ammonification on nitrogen removal and on ammonia emissions

Taking into account that the total ammoniacal nitrogen was not quantified in the food waste and composted ones, food waste was excluded from part of the following discussion.

The ammonification rates were given in Table 2. As mentioned earlier, the removal of nitrogen from material results at first from the transformations and the transfer of total ammoniacal nitrogen (Figure 1). More, ammonification leads to the release of total ammoniacal nitrogen. Then, ammonification has a potential influence on removal rates of nitrogen from material. Figure 4 confirmed this influence. Indeed, the removal rate of Kjeldahl nitrogen was shown closely correlated to the removal rate of organic nitrogen through ammonification. Thus, the removal rates of Kjeldahl nitrogen and the ammonification rates were around 40% for household waste and between 50 and 70% for pig slaughterhouse sludge and green algae. Separated pig solids exhibited some negative ammonification rates. Thus, in the case of separated pig solids, the immobilization of total ammoniacal nitrogen as organic nitrogen in biomass and humic substances was superior to its release by ammonification. In contrast, for household waste, pig slaughterhouse sludge and green algae, immobilization was lower than ammonification. It was not possible to identify any direct influence of the aeration rate on the removal rate of Kjeldahl nitrogen (Table 1) neither on the ammonification rate (Table 2).

Table 2 here

Figure 4 here

In literature, many authors suggested that ammonification was linked to the biodegradation of the organic matter. Liang et al. (2004) proposed a linear relationship between both as:

$$\Delta Norg \approx \Delta TC \times \left[1/\left(C_{bio} / N_{bio}\right)\right]$$

with ΔNorg, the amount of organic nitrogen ammonified during composting, ΔTC, the amount of carbon removed during composting, and C_{bio}/N_{bio}, the ratio of carbon to nitrogen concentrations of the biodegraded fraction. ΔTC was previously calculated in Part 1. Both ΔNorg and ΔTC are given in Table 2. Figure 5 gives an illustration of ΔNorg as function of ΔTC. Although the regression coefficients of the linear correlations are low for pig slaughterhouse sludge and separated pig solids, C_{bio}/N_{bio} ratios were calculated for each waste thanks to the measurement of the slopes corresponding to $[1/(C_{bio}/N_{bio})]$ (Table 2). Figure 5 illustrates well that the ammonification ability differs significantly from one waste to another. Thus, the green algae were the waste which biodegradation was responsible for the highest removal in organic nitrogen, i.e. the highest release in total ammoniacal nitrogen, per unit mass of carbon removed. However, although C_{bio}/N_{bio} was lower for green algae than for pig slaughterhouse sludge, 5 against 10, since biodegradability of pig slaughterhouse sludge is much higher than the one of green algae, the composting of pig slaughterhouse sludge until stabilisation will release more total ammoniacal nitrogen than green algae. In contrast, taking into account that C_{bio}/N_{bio} ratio was superior for household waste than for green algae, 45 against 5, and that the biodegradability of household waste was superior to the one of green algae, composting of household waste was responsible for a lower release of total ammoniacal nitrogen than green algae. The negative value of C_{bio}/N_{bio} obtained for separated pig solids illustrated that for separated pig solids, immobilization of total ammoniacal nitrogen as organic nitrogen was higher than ammonification.

Figure 5 here

For a given waste, the proposed relationship shows that the total ammoniacal nitrogen released by ammonification is all the higher as C_{bio}/N_{bio} is low and as biodegradation rate is high, leading potentially to higher emissions of ammonia. Figure 6a confirmed that the ammonia emissions were all the lower as the ratio C_{bio}/N_{bio} was high. However, it was not possible to observe any reduction of ammonia emissions when the content in biodegradable carbon increased (Figure 6b). In contrast, the ammonia emissions were all the higher as N_{bio} contained in initial material was high (Figure 6c). Then, here, the decrease of ammonia emissions when C_{bio}/N_{bio} increased was due to the decrease of N_{bio} rather than to the increase of C_{bio}.

Figure 6 here

3.5. Accumulation versus striping or nitrification of NH_4^+/NH_3

The rates of accumulation, striping and nitrification were calculated for each experiment in order to identify the parameters ruling the transformations of the pool P defined as total ammoniacal nitrogen initially contained in waste plus total ammoniacal nitrogen released by ammonification. The accumulation rate, the striping rate and the nitrification rate were represented on Figure 7 as function of the aeration rate, the concentration of the pool P in the biofilm, the mean temperature of the material during composting and its content in biodegradable carbon. The concentration of P in the biofilm was estimated by dividing the amount of P by the mean amount of water in the material during composting:

$$mH_2O_{mean} \approx \left[mH_2O_0 + mH_2O_{end}\right]/2 .$$

The mean temperature, the maximum temperature and the mean content in water in the material during composting are given in Table 3.

At first, it can be noted that separated pig solids is characterised by a high ability to retain NH_4^+/NH_3 (Figure 7a), pig slaughterhouse by a high sensitivity to striping (Figure 7b) and household waste and green algae by a high ability to nitrification (Figure 7c).

Considering processes, it seemed that the accumulation rate decreased slightly when the aeration rate increased (Figure 7a). Except for household wastes, which were characterized by a high ability to nitrify, the accumulation rate decreased strongly when the pool concentration increased (Figure 7d). These results confirm the influence of ammonification rate on ammonia emissions and are in agreement with the basic knowledge on mass transfer between liquid and gaseous phases. It was not possible to find any evident influence of the mean temperature (Figure 7g) and of the initial content in biodegradable carbon (Figure 7j) on the accumulation rate.

As result of the decrease of accumulation when the aeration rate and the pool concentration increased, Figures 7b and 7e confirmed the increase of the striping rate when the aeration rate and the pool concentration increased. In opposition to assumptions of the literature, the mean and the maximum temperatures (Table 3, Figure 7h) were not evident parameters of ammonia emissions. Thus, the striping rate of separated pig solids was inferior to 10% whereas its mean temperature during composting was around 50°C. It was not found any correlation between the striping rate and the initial content in biodegradable carbon (figure 7k).

The nitrification rate seemed poorly influenced by the aeration rate (Figure 7c). It should be mentioned that, except for pig slaughterhouse sludge at 105 L/h, the oxygen supply was never limiting (Part 1) , meaning that such limitation could not be invoked to explain the discards regards to nitrification rates. The low decrease of the nitrification rate of pig slaughterhouse sludge when the aeration rate was increased was a result of its low

ability to retain total ammoniacal nitrogen and its high sensitivity to striping. Although it is not so evident, it seemed that the rate of nitrification decreased when the pool concentration increased (Figure 7f), and that nitrification was maximum when temperature was around 35°C and decreased with lower or higher temperatures (Figure 7i). This result agreed with literature in which high concentrations in total ammoniacal nitrogen and high temperatures were assumed to slow down and even inhibit nitrification (Bishop and Godfrey, 1983; Eiland et al., 2001; Körner et al., 1999; Körner and Stegmann, 2003; Tiquia and Tam, 2000; Wong et al., 2001). The content in biodegradable carbon (Figure 7l) was not found influent of nitrification process, neither the pH of the initial wastes, ranging between 6.6 and 8.7.

Back considering specific behaviour of each waste, the separated pig solids were characterised by a high ability to retain NH_4^+/NH_3 (Figure 7a), which was supported by a medium concentration of NH_4^+/NH_3 in the biofilm (Figure 7d). Comparing to other wastes studied, separated pig solids were constituted of finer solid particles. Thus, assuming a high specific surface, this last may also explain this high retention capacity. As result of its high accumulation capacity, the striping rate of separated pig solids was low and poorly sensitive to the aeration rate (Figure 7b). Other parameters like pH and conductivity should be investigated in order to explain its behaviour and especially its low nitrification ability.

The pig slaughterhouse sludge were characterized by their rather high ability to striping (Figure 7b), which can be explained by their higher concentrations in NH_4^+/NH_3 in comparison with the other waste (Figure 7e). These higher concentrations explained its low accumulation ability too (Figure 7d). At 105 L/h, the pH of pig slaughterhouse sludge ranged between 8.4 and 8.7. Although the pH at 105 L/h was higher than at 486 and 1066 L/h, ammonia striping was lower. The increase of the striping rate with the aeration rate was interpreted as being responsible for the simultaneous decrease of its accumulation (Figure 7a) and nitrifying (Figure 7c) abilities. However, the nitrifying ability of pig slaughterhouse sludge reached 25% at the lowest aeration rate (105 L/h) which could mean that pig slaughterhouse sludge was able to nitrify provided the residence time of NH_4^+/NH_3 was sufficient. In other words, in the case of pig slaughterhouse sludge, the nitrification kinetic seemed lower than the striping one leading to low nitrification rates. However, further specific experiments are needed for explaining this behaviour regarding nitrification.

The household wastes were characterized by their high ability to nitrification (Figure 7c) which reduced their accumulation and striping abilities around zero. All the total ammoniacal nitrogen released by ammonification was nitrified. The higher ability to nitrification of household waste coincided with an initial concentration in NH_4^+/NH_3 around zero (Table 1 in Part 1) which could mean that nitrification was already in progress in initial

substrates and that a nitrifying biomass was already present within. The household waste are characterised by a high content in paper i.e. cellulose, which could favour the development of nitrifying microorganisms too.

Finally, the green algae were characterized by their rather high ability to nitrification (Figure 7c). This could be partly explained by the fact that these algae develop in seawaters with high concentrations in phosphorus and nitrogen. As for household waste, this ability coincided with low concentrations in NH_4^+/NH_3 in initial materials (Table 1 in Part 1). Although the striping rates of green algae were rather low, their increase with the aeration rate was also favoured by the rather high concentrations in NH_4^+/NH_3 in the biofilm (Figure 7e).

Figure 7 here

Taking into account the previous observations, the nitrification rate was represented as function of the initial concentration in total ammoniacal nitrogen in the waste. Figure 8 let think that the concentration in NH_4^+/NH_3 in the initial waste was an indicator of the nitrification ability of the waste. Indeed, the higher was this concentration in the waste, the lower was the waste ability to nitrification. Thus, the low concentrations in NH_4^+/NH_3 in initial materials could mean that nitrifying microorganisms are already present within and that nitrification is already in progress. Moreover, high concentrations of NH_4^+/NH_3 could mean that nitrifying microorganisms develop very slowly as demonstrated by Blouin et al. (1990). These results also suggest that nitrification ability is an intrinsic property of the waste and then that process conditions have a low influence on this ability. However, further experiments should be performed in order to characterise the nitrifying biomass in the waste. These should be completed by a chemical and biochemical characterisation in order to identify if pH, conductivity or some biochemical fractions influenced the development of the nitrifying microorganisms.

Figure 8 here

4. Conclusion

Household waste, separated pig solids, food waste, pig slaughterhouse sludge and green algae were compared regarding processes ruling nitrogen dynamic in composting. The removal rate of total nitrogen was demonstrated being closely correlated to the ammonification rate. The ratio of biodegradable carbon to ammonifiable organic nitrogen, C_{bio}/N_{bio}, was calculated for each waste. The green algae were responsible for the highest release of total ammoniacal nitrogen per unit mass carbon biodegraded whereas household waste led to the lowest one. In contrast, the biodegradation of separated pig solids led to the immobilization of NH_4^+/NH_3. The waste content in ammonifiable organic nitrogen, N_{bio}, and the aeration rate applied were found the most predominant parameters of ammonia emissions. Nitrogen balances showed that losses in leachates and as ammonia and nitrous oxide accounted for 1 to 91% of nitrogen removed from material. Except for pig

slaughterhouse sludge, the gap between nitrogen removed from material and losses in leachates and as ammonia and nitrous oxide exceeded 45% meaning a large part of nitrogen removed was nitrified, then, transferred to atmosphere as molecular nitrogen. Neither aeration rate nor biodegradable carbon content were found influent of nitrification rate. In contrast, the high nitrification rates of household waste and of green algae coincided with the lowest concentration in total ammoniacal nitrogen in initial waste. Then, nitrification rate was found closely correlated to this concentration. This could mean that, in case of low concentration in total ammoniacal nitrogen in initial waste, nitrification was already in progress and that in case of high concentrations, nitrifying microorganisms develop slowly. Further experiments have to be performed in order to quantify nitrifying microorganisms and to investigate if their development was correlated with chemical or biochemical characteristics of the wastes.

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Table 1:

Ammonia and nitrous oxide emissions and nitrogen balance

	Aeration rate	N_2O and NH_3 emissions		Initial content in N-NK	Removal rate of N-NK	Losses in nitrogen as percent total nitrogen removed from material (%)				Closure in nitrogen[4]
	L/h	g N-NH_3/kg OM_0 [1]	g N-N_2O/kg OM_0	g N/kg OM_0	%	Leach.[2]	Cond.[3]	N_2O	NH_3	%
HW	117	0.0	0.0	22.4	36.7	2.3	0.0	0.1	0.0	-97.6
	394	0.1	0.0	22.4	43.1	0.2	1.3	0.0	0.0	-98.5
	746	0.1	0.0	22.4	41.3	0.2	0.8	0.0	0.0	-99.0
SPS	166	1.1	nm[5]	43.1	5.8	0.0	35.2	nm	10.9	-53.9
	226	1.0	nm	43.1	5.9	0.0	27.0	nm	13.0	-60.1
	443	1.7	nm	43.1	8.3	0.0	25.0	nm	23.4	-51.6
FW	138	5.5	0.1	43.4	57.0	13.1	12.9	0.5	9.4	-64.1
	372	8.1	0.0	43.4	43.3	11.6	12.5	0.0	30.4	-45.4
	773	10.8	0.0	43.4	50.9	4.4	9.6	0.0	39.2	-46.8
PSS	105	4.8	nm	61.1	48.4	48.4	0.0	nm	16.2	-35.4
	486	36.1	nm	73.8	66.2	10.5	17.6	nm	56.3	-15.7
	1066	26.5	nm	55.0	57.5	7.1	0.5	nm	83.3	-9.2
GA	156	2.9	2.2	65.9	42.6	0.0	0.0	8.0	10.5	-81.5
	391	6.6	4.5	65.9	39.6	0.0	0.0	17.3	25.3	-57.5
	721	9.3	3.6	65.9	56.3	0.0	0.0	9.6	25.0	-65.4
	Mean					6.5	9.5	3.9	22.8	-58.8
	Max.	36.1	4.5			48.4	35.2	17.3	83.3	-9.2
	Min.	0	0.0			0.0	0.0	0.0	0.0	-99.0

[1] NH_3 in gases plus condensates

[2] Leachates

[3] Condensates

[4] Closure in nitrogen: [(Losses in nitrogen in leachates + condensates and as N_2O and NH_3) – (Nitrogen removed from material)]*100/(Nitrogen removed from material)

[5] nm: not measured

Table 2
Ammonification rate and Cbio/Nbio ratio of the biodegradable fraction

	Aeration rate	Ammonification rate	ΔTC	ΔNorg.	Cbio/Nbio
	L/h	**%**	**g C/kg OM_0**	**g N/kg OM_0**	
HW	117	36.7	415.4	8.2	
	394	43.1	427.4	9.7	
	746	41.3	380.6	9.3	**45**
Mean			**407.8**	**9.1**	
CV (%)			6.0	8.3	
SPS	166	-4.8	196.2	-1.4	
	226	-7.5	210.6	-2.1	
	443	-0.6	*208.7*	*-0.2*	**-166**
Mean			**205.2**	**-1.7**	
CV (%)			3.8	-31.2	
PSS	105	63.5	330.3	33.5	
	486	71.4	287.7	44.8	
	1066	52.0	328.3	21.0	**10**
Mean			**315.4**	**33.1**	
CV (%)			7.6	36.0	
GA	156	55.9	208.2	35.9	
	391	50.2	197	32.2	
	721	62.1	178.2	39.9	**5**
Mean			**194.5**	**36.0**	
CV (%)			7.8	10.7	

Table 3
Mean temperature, maximum temperature and mean content in water in material during composting

	Aeration rate	T mean	T max	Mean content in water
	L/h	°C	°C	kg H_2O/m^3 reactor
HW	117	38.5	55.2	198.5
	394	34.8	57.2	186.7
	746	34.4	57.1	169.8
SPS	166	51.5	66.5	275.0
	226	47.6	65.5	285.0
	443	47.1	64.2	279.8
FW	138	35.4	48.3	124.3
	372	32.6	47.3	118.8
	773	32.3	48.0	117.8
PSS	105	45.6	53.4	367.6
	486	45.9	68.4	354.3
	1066	43.4	66.7	317.7
GA	156	29.8	53.5	106.5
	391	27.8	40.7	105.0
	721	24.5	34.5	90.2

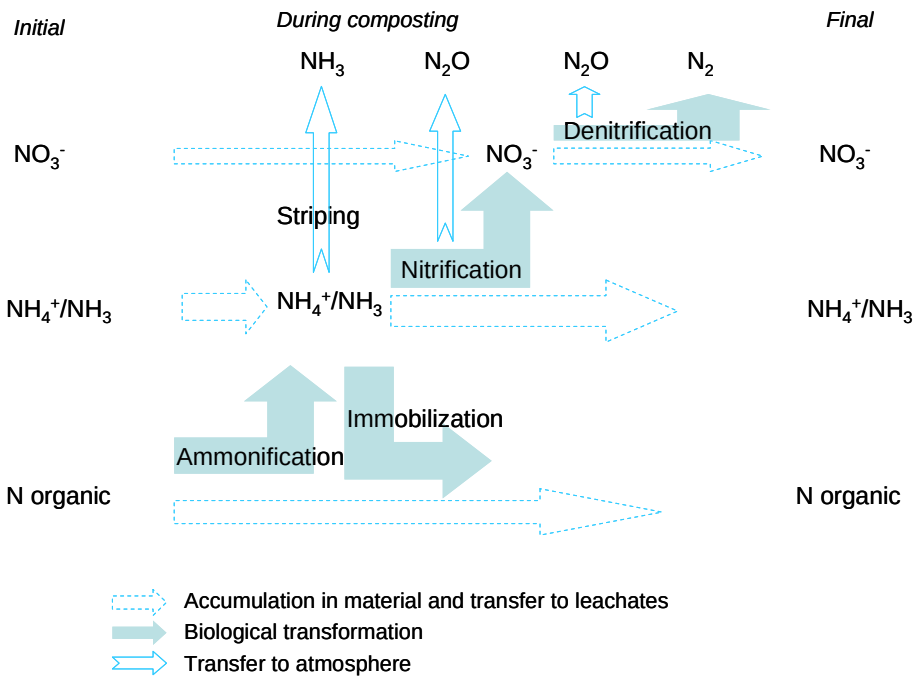

Figure 1: Nitrogen transformations and transfers during composting.

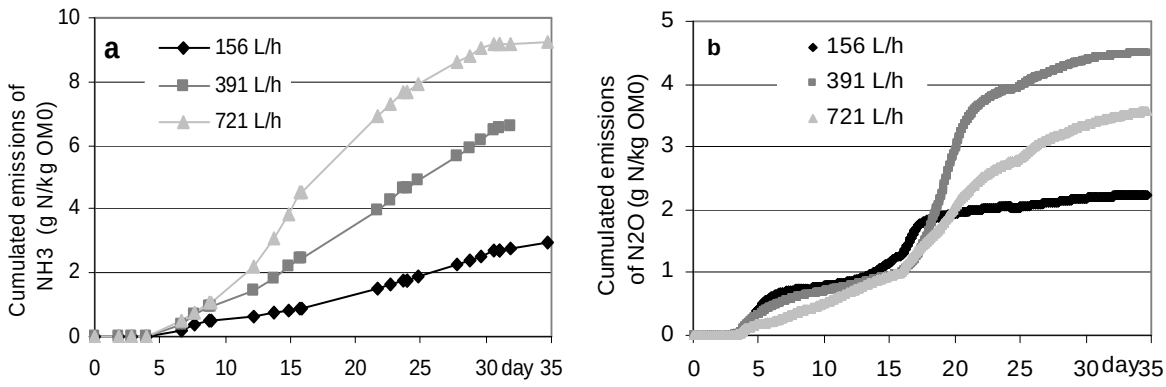

Figure 2: Cumulated emissions of ammonia and nitrous oxide during composting of green algae.

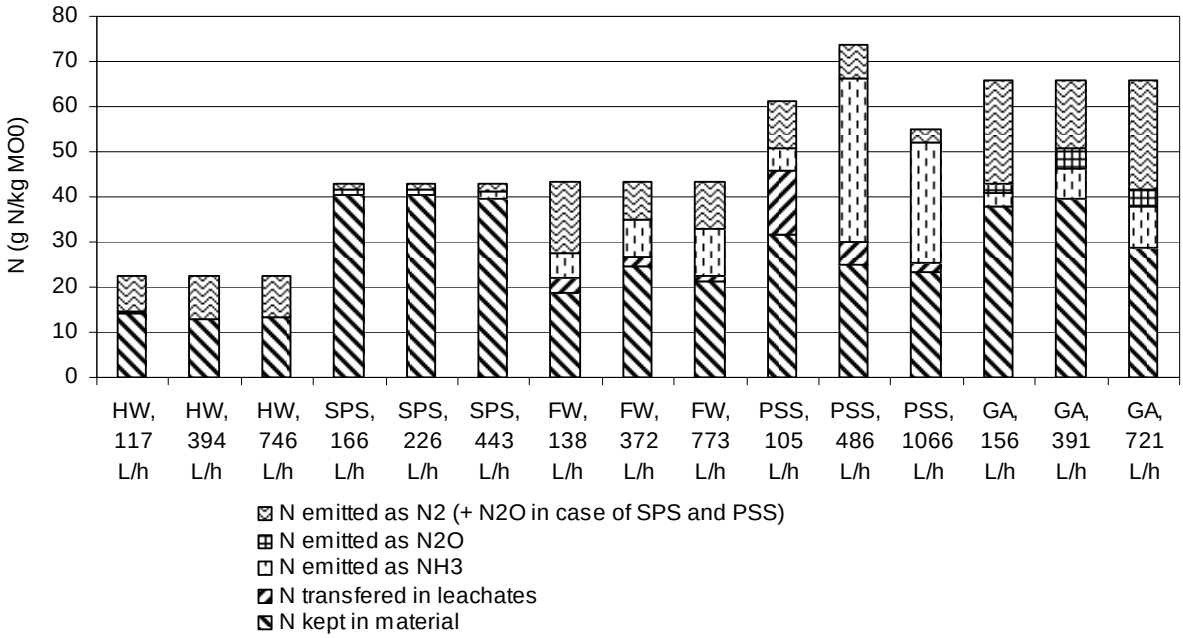

Figure 3: Accumulation and transfers of nitrogen as function of the aeration rate.

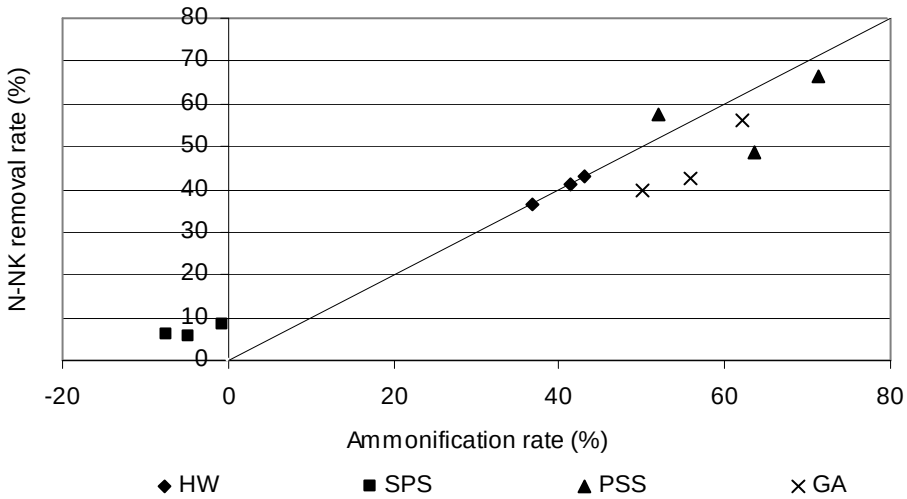

Figure 4: N-NK removal rate as function of ammonification rate.

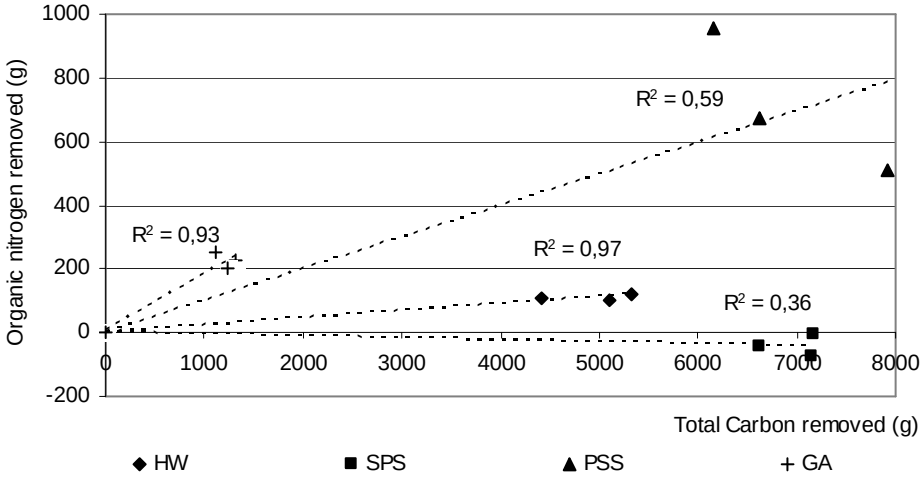

Figure 5: Organic nitrogen removal as function of carbon removal.

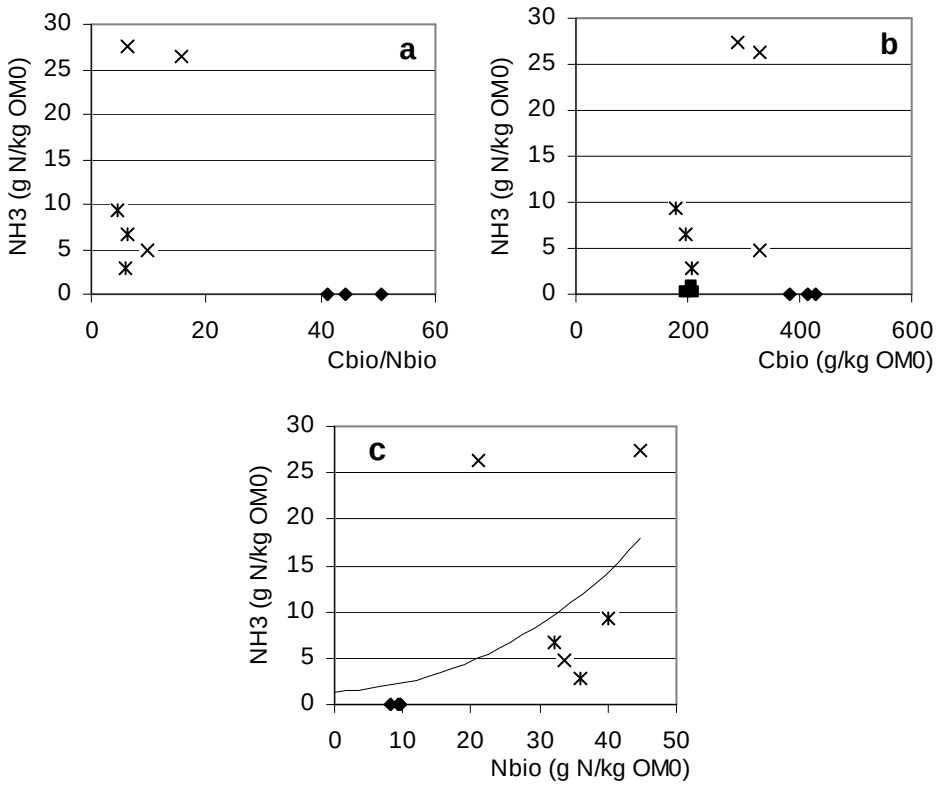

Figure 6: Influence of the contents in biodegradable carbon (C_{bio}), ammonifiable nitrogen (N_{bio}) and ratio C_{bio}/N_{bio} on ammonia emissions.

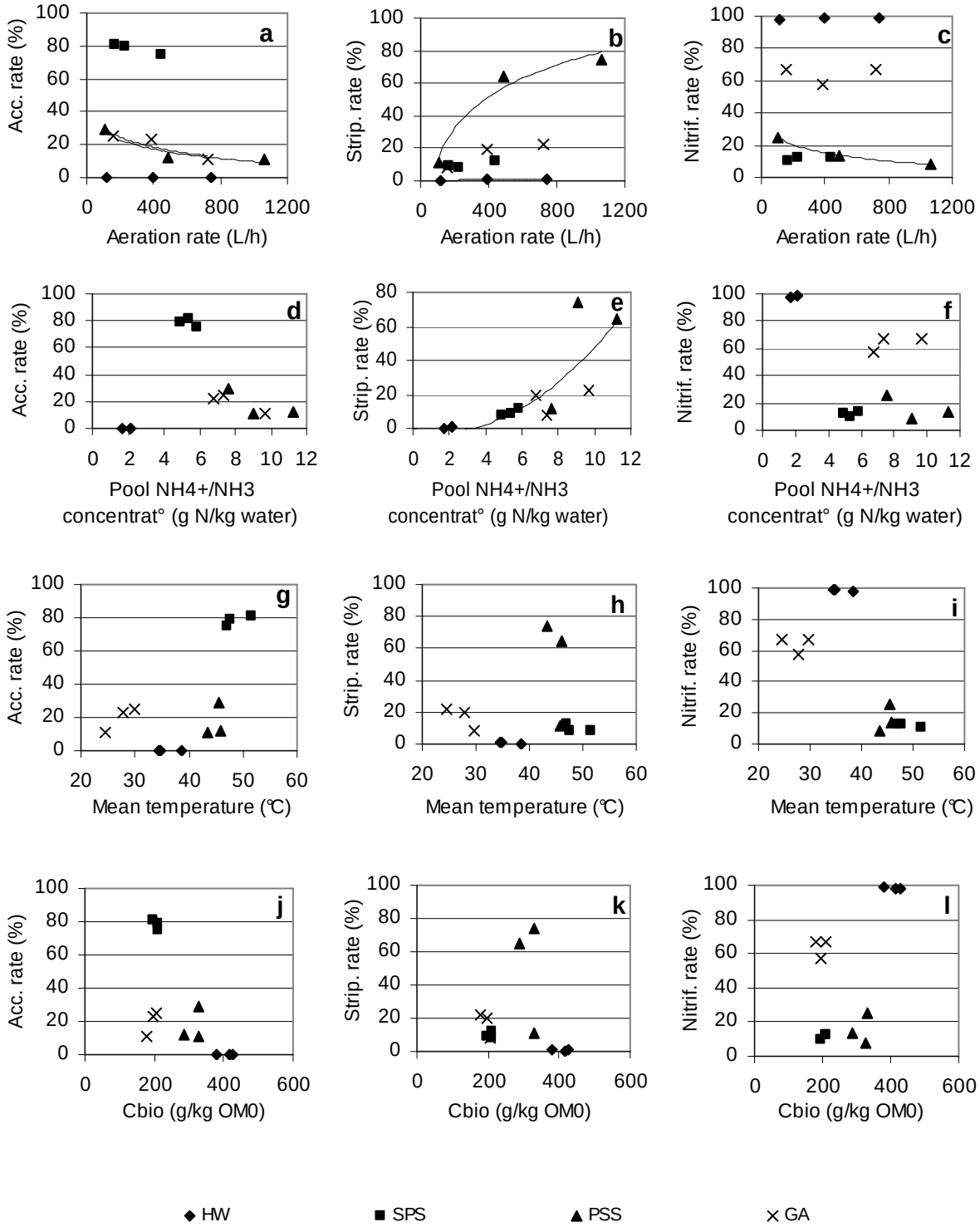

Figure 7: Accumulation. striping and nitrification rates as function of aeration rate. NH_4^+/NH_3 concentration. mean temperature and biodegradable carbon content.

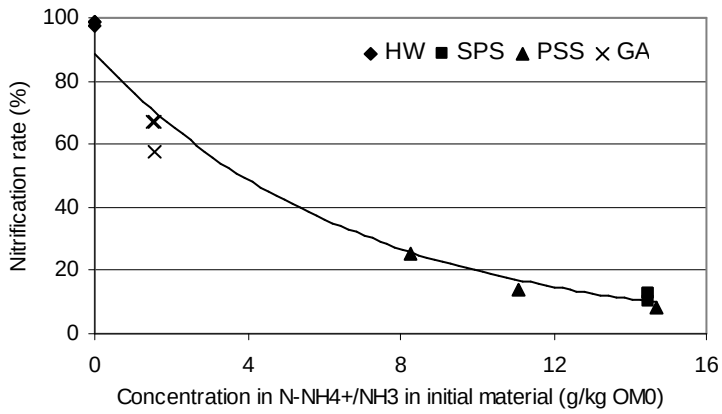

Figure 8: Nitrification rate as function of the concentration in NH_4^+/NH_3 in the initial waste