Short term carbon and nitrogen transformations following pig and cattle slurry incorporation in soils

Transformations azotées et carbonées à court terme consécutivement à l'incorporation de lisier bovin et porcin au sol.

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Abstract.

Carbon mineralization and nitrogen biotransformations were studied in a laboratory experiment, for 24 days, at 16°C. Thirteen pig slurries and five cattle slurries were labelled with $(^{15}NH_4)_2SO_4$ *and added to a loamy soil (*S_1*, pH 5.4 organic matter 2%) and to two loamy sand soils (*S_2 *et* S_3*, pH 6.7 and 5.5, organic matter 3.9%).*

The rates of organic carbon mineralization of the slurries were high, and significantly higher in S_1*, compared to* S_2 *and* S_3 *soils. Carbon mineralization was well described by a two-compartment model, the first compartment being the soluble fraction of organic matter determined by Van Soest's method, and the second corresponding to the non-soluble fraction. The high level of carbon decomposition strongly stimulated the immobilization of ammonium. Gross mineralization also varied greatly with soils and slurries. Net mineralization was observed for all treatments, on* S_1*, whereas net immobilization was observed in 28 % of cases, and concerned mainly treatments on* S_3*. Nitrification of the ammonium in slurries was complete on day 24 on* S_2 *and* S_3*, but not on* S_1 *soils ; rates of nitrification varied greatly between soils, during the active phase of nitrification following the latent period.*

A simple model describing nitrogen and carbon fluxes was constructed from the relationships between the chemical and biochemical composition of the slurries, carbon and nitrogen mineralization and nitrogen immobilization.

Key words : slurry, ^{15}N, nitrogen biotransformations, carbon mineralization

Résumé

La minéralisation apparente du carbone et les biotransformations des formes azotées du lisier ont été étudiées en laboratoire, sur une durée de 24 jours, à la température de 16°C. Treize lisiers de porc et cinq lisiers de bovin enrichis en azote 15 par addition de $(^{15}NH_4)_2SO_4$ ont été apportés sur un sol limoneux (S_1, de pH 5,4 et de taux de matière organique 2%) et deux sols limono-sableux (S_2 et S_3, ayant respectivement un pH de 6,7 et 5,5 et de taux de matière organique égaux 3,9%).

Le taux de minéralisation du carbone organique des lisiers est significativement supérieur sur S_1, comparativement à S_2 et S_3. La minéralisation du carbone en fin d'expérience est bien décrite par un modèle comprenant deux compartiments correspondant à : i) la fraction soluble déterminée par la méthode Van Soest, et ii) la fraction insoluble. L'importante activité de décomposition du carbone organique stimule fortement l'immobilisation de l'azote ammoniacal, qui représente 20 à 70% de l'azote ammoniacal apporté, le jour 24.

La minéralisation brute du système sol-lisier varie fortement selon les sols et les lisiers. On mesure un flux de minéralisation nette pour tous les traitements, sur S_1 ; on observe par contre une organisation nette de l'azote dans 30% des cas, sur les sols 2 et 3.

La nitrification de l'ammonium des lisiers est achevée le jour 24, sur S_2 et S_3, mais pas sur S_1 ; les vitesses de nitrification varient considérablement selon les sols, au cours de la phase active succédant à la phase de latence.

Les relations établies entre la composition chimique et biochimique des lisiers, la minéralisation du carbone et de l'azote et l'immobilisation de l'azote permettent de proposer une modélisation simple des flux d'azote et de carbone, à la fin de la nitrification de l'ammonium du lisier.

Mots-clés : lisier, ^{15}N, biotransformations de l'azote, minéralisation du carbone.

1. Introduction

Nitrate availability after slurry landspreading is determined by : i) the amounts of ammonia and organic nitrogen supplied, and ii) the rates of gaseous losses, rates of nitrification/immobilization of ammonia, and mineralization of the slurry organic nitrogen. Morvan et al (1996, 1997) showed in field experiments that gross immobilization / mineralization processes were high and mainly occurred during the first few days following the slurry spreading and that nitrification also occurred rapidly, but after a lag period.

Nitrogen transformations after addition of crop residues to soils have been investigated in many studies. Immobilization and mineralization appear to be linked to carbon decomposition, and mainly depend on : i) chemical and biochemical composition of the fresh organic matter (Azam et al, 1985, Mary et al, 1996), ii) the availability of inorganic nitrogen during C decomposition (Recous et al, 1995), iii) the accessibility of organic matter to the microbial biomass (Darwis,1993, Angers et al 1997), and iv) soil characteristics (Nicolardot et al, 1986, Sparling et al, 1996).

The composition of slurries differ markedly from those of crop residues ; it can be presumed that the rates of C and N transformations may differ significantly from those observed with crop residues. Kirchmann and Lundvall (1993), for example, observed a different pattern of inorganic nitrogen evolution after addition of slurries to a soil than that usually measured after crop residues incorporation (Mary et al, 1996).

Pig and cattle slurry composition is characterized by great variability, due to : i) animal species, age and feed supply, and ii) aerobic or anaerobic transformations of the organic matter during storage (Van Faassen and Van Dijk, 1987). In fact, Kirchmann and Lunvall (1993) showed that the rates of nitrogen transformations differed significantly both between pig and cattle slurries, and between fresh or digested pig slurries.

Since there is little published information about the effect of slurry composition upon carbon and nitrogen transformations after the addition of slurry to soils, the purpose of our experiment was to study this effect, on a time scale corresponding to the duration of nitrification of the ammonia fraction of the slurry.

It is also becoming increasingly necessary to design and validate simple operational dynamic models, for prediction of the amount and rates of « production » of the nitrate available after slurry spreading. Such simple models could be useful for « tactical » decision support systems, and enable the decision makers to optimize the agronomic utilization of slurries, to calculate the risk of pollution. We propose therefore a simple model describing short term C and N biotransformations.

2. Material and methods

2.1. Slurry composition and soil characteristics

Thirteen pig and five cattle slurries were sampled in farms around Rennes, in Brittany. pH, dry matter content, ammonia ($N\text{-}NH_4^+$) and total nitrogen (N_{tot}), total inorganic (TIC) and organic (TOC) carbon contents were determined. These parameters were characterized by a considerable variability (table 1), in agreement with the results of Sommer and Husted (1995). The C:N ratios of the organic fraction were rather low, and ranged from 8.2 to 27 ; the neutral detergent soluble fraction, obtained by Van Soest's method (Linères and Djakovitch, 1993), trended to be higher than the soluble fraction of crop residues.

	minimum	maximum	median	mean
pH	6.8	8.8	7.6	7.6
dry matter (%)	1.9	19.2	1.4	1.8
$N\text{-}NH_4$ ($g\ l^{-1}$)	0.26	5.34	3.1	3.2
N_{tot} ($g\ l^{-1}$)	0.87	9.60	6.1	5.7
TIC ($g\ l^{-1}$)	0.02	2.27	0.91	0.85
TOC ($g\ l^{-1}$)	13.30	81.30	34.5	38.5
$TOC{:}N_{tot}$	3.7	17.2	8.0	7.9
TOC : Norg	8.2	27.2	16.2	16.2
SOL (% TOC)	38	85	50.3	52.0

Table 1.
Statistical parameters calculated from chemical and biochemical analyses of the eighteen slurries

The characteristics of the three soils are given in table 2.

	Soil 1	Soil 2	Soil 3
Clay	14.3	19.3	18.5
Silt	72.7	48.8	44.6
Sand	13.0	31.9	36.9
pH (water)	5.4	6.7	5.5
N org (%)	0.120	0.200	0.210
C org	1.14	2.29	2.27
OM (%)	2.0	3.94	3.90

Table 2.
Selected physico-chemical characteristics of the three soils

2.2. Incubation procedure

The experiment was conducted at an average temperature of 16°C for 24 days. Soil samples of 500 g dry weight basis were placed in 2000 ml wide-mouth glass jars. The ammonium fractions of the slurries were enriched with ^{15}N, using a solution of $((^{15}NH_4)_2SO_4)$ 10% atom excess, which was thoroughly mixed with the slurry. The amount of slurry added to the soils were calculated to ensure rates of nitrogen supply in the soil, comparable with those usually measured in the field, after slurry spreading. The amounts of ammonia nitrogen added varied from 85 to 95 ppm for the pig slurries, and from 43 to 63 ppm for the cattle slurries. The soil water content was adjusted to 199 mg g^{-1} soil, and remained constant until the end of the experiment. Each treatment was replicated twice.

CO_2 evolved was captured in traps containing 15 ml 1M NaOH. The sampling times were 1,3,8, 14 et 24 days for CO_2. The sampling dates were 3, 8 and 24 days for the inorganic N analysis and were 8 and 24 days for the ^{15}N analysis.

2.3. Analytical procedures

The carbonates trapped in the NaOH were precipitated with excess $BaCl_2$; the remaining NaOH was assayed by 0.1 N HCl titration using phenolphtalein as indicator.

The same analytical procedures were used for ^{14}N and ^{15}N analysis as in Morvan et al (1997).

Flux calculations

Gross N rates were calculated using the FLUAZ model described in detail by Mary et al (1998). FLUAZ combines a numerical model for solving the balance mass equations and a non linear fitting program for optimizing the N rate parameters. A single labelled treatment (NH_4^+ labelled in our case) was used to calculate the rates of ammonium and nitrate immobilization (i_a and i_n respectively), mineralization (m), nitrification (n) and volatilization (v). FLUAZ use was limited to treatments that presented a consistent ^{15}N balance on days 8 and 24 ; gross nitrogen rates were calculated for 14, 8 and 11 treatments, on soils 1, 2 and 3 respectively.

The apparent C mineralization rate of the slurry was calculated assuming that the priming effect was negligible, and that the TIC supplied by the slurries was volatilized and trapped during the first day.

3. Results and discussion

3.1. Carbon mineralization of the organic fractions of the slurries

Carbon mineralization rates were high during the first five days after the start of the experiment, and remained significant until day 24 (fig 1). The cumulative amounts of C mineralized varied widely between the slurries, ranging from 17 to 43 % of the added C. Carbon mineralization rates measured in soils 2 and 3 were very similar, and significantly lower than the C-CO_2 evolved on soil 1.

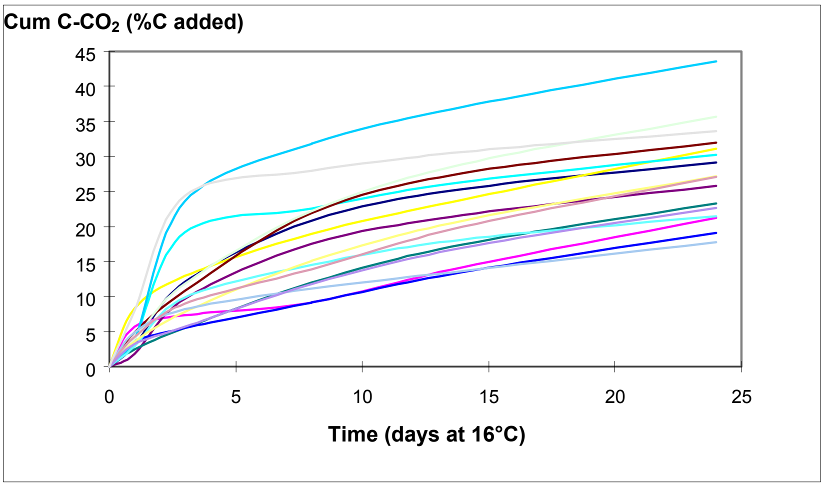

Figure 1
Mineralization kinetics observed on soil 1 for the 18 slurries
(similar patterns were observed for soils 2 and 3).

The cattle slurries were characterized by a lower rate of mineralization, in agreement with the results of Kirchmann and Lundvall (1993). The kinetics also differed considerably between slurries, the relative differences being higher during the first few days, compared to those on day 24.

Kirchman and Lundvall (1993) obtained similar kinetics and rates of C-CO_2 evolution, after the addition of fresh and digested slurries to a soil. These authors found that carbon mineralization rates ranged from 20 to 43 %, at 25 °C, twelve days after slurry incorporation (comparable with our results, on day 24, if a Q_{10} of 2 for carbon transformations is considered for the 15-25 °C temperature range). The rate of evolution of C-CO_2 was also similar to the rates of C mineralization of plant residues, such as wheat straw (Mary et al, 1996) or maize roots (Azam et al, 1985), when decomposition was not limited by the soil inorganic N content (Recous et al, 1995).

The initial high rates of C mineralization have been attributed to the rapid decomposition of the easily decomposable components of applied organic matter of low molecular weight ; Reinertsen et al (1984) postulated that fresh organic matter decomposition in the early stages was largely dependent on the sizes of the water soluble C pool, and of an intermediately available C pool. Our results are in good agreement with this hypothsesis : we found that carbon mineralization rates were closely correlated to the neutral detergent soluble fraction, over the first few days (similar correlation coefficients for all three soils, and equal to 0.95, 0.94 and 0.91 on days 3, 8 and 14 respectively).

3.2. Gross and net fluxes of nitrogen immobilization and mineralization

The gross mineralization (m) and immobilization (i) fluxes varied widely between slurries (fig 2) and were mainly apparent during the first eight days, the 0-8 days mineralization accounting on average for 78 % of the total nitrogen mineralization.

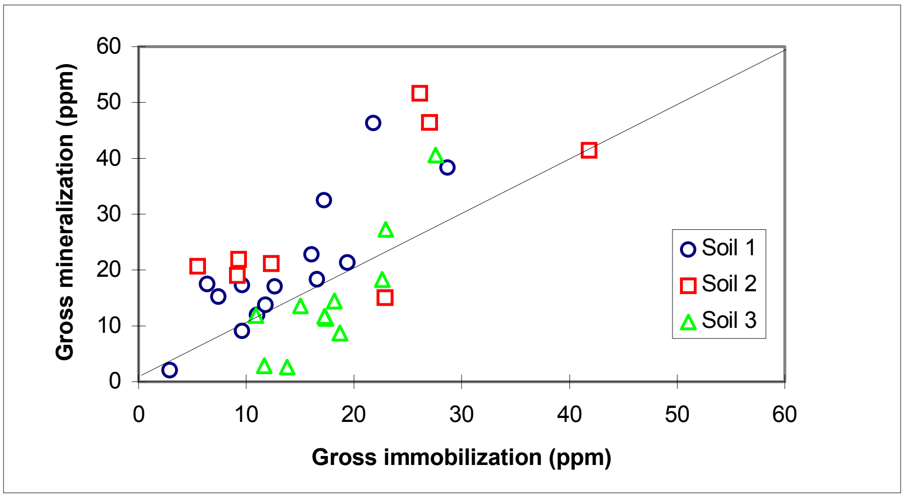

Figure 2
Comparison of gross nitrogen immobilization and mineralization (ppm)
of slurries, calculated on day 24.

The gross processes depended on soil type, gross immobilization being lower on soil 1, than on soils 2 and 3, whereas nitrogen mineralization on soil 1 tended to be intermediate between the higher fluxes measured on soil 2 and the lower ones measured on soil 3.

Net fluxes were obtained from the difference (m-i), and varied from -11 to +29 ppm on day 24 ; net mineralization was dominant, and observed for all treatments, on soil 1. Despite the low C:N ratios of the organic fractions of the slurries, net immobilization was observed in 29 % of the cases, and mainly on soil 3. These contrasting results are consistent with those of Kirchmann and Lundvall (1993) , who did not find any net mineralization after the incubation of cattle and anaerobic pig slurry, in contrast to that of fresh and anaerobically digested pig slurry. These authors also pointed out that the net immobilization occurring during the early stages was significantly correlated to the concentrations of fatty acids, which could represent 10 to 30 % of the total C, and act as very rapidly decomposable C sources.

3.3. C-N relationships

- Gross immobilization (i) has been related to carbon mineralization in the following expression (Recous et al, 1995) :

$$i = \frac{Y}{r_{bio}.(1-Y)}.C_{\min} = R.C_{\min}$$

where r_{bio} is the C:N ratio of the newly-formed microbial biomass, Y the C assimilation yield, and C_{min} the amounts of C mineralized. The 'R' ratio values were calculated for each soil (table 3), assuming that these remained constant over the short duration of the experiment.

	R	Interval confidence 95% level	R²
Soil 1	0.076	0.070 - 0.082	0.78
Soil 2	0.089	0.080 - 0.098	0.85
Soil 3	0.107	0.101 - 0.114	0.88

Table 3.
Values of R, given by the relationship : i = R.Cmin, confidence interval at the 95% level, and value of the determination coefficient.

The results are consistent with the values calculated by Aita (1996) and Darwis (1993), during wheat straw decomposition, which ranged from 0.080 to 0.125. The significantly different values of R indicate variable values of r_{bio} or Y, or both parameters, between the soils. Assuming that the r_{bio} value was the same for each soil, and supposed equal to a usual value of 10, the R values could be used to calculate Y values of 0.44, 0.47 and 0.52 on soils 1,2 and 3 respectively.

3.4. Nitrification

The few sampling dates didn't permit a fine description of the typical pattern of nitrification kinetics, usually Follow Mickaelis Menten kinetics (Le Pham et al, 1984). We did however observe that the lag period was nearly three days on soils 1 and 3, but shorter on soil 2. This was followed by an active nitrification phase (fig 3). Ammonium depletion was complete by day 24 on soils 2 and 3, whereas significant amounts of N-NH_4 (2-32 ppm) still remained on soil 1. Apparent rates of nitrification over the 3-8 days period varied greatly between soils, ranging from 6.0 to 9.1 mg N kg^{-1} soil on soil 2, and from 2.4 to 3.3, and from 3.2 to 4.2 mg N kg^{-1} soil on soils 1 and 3.

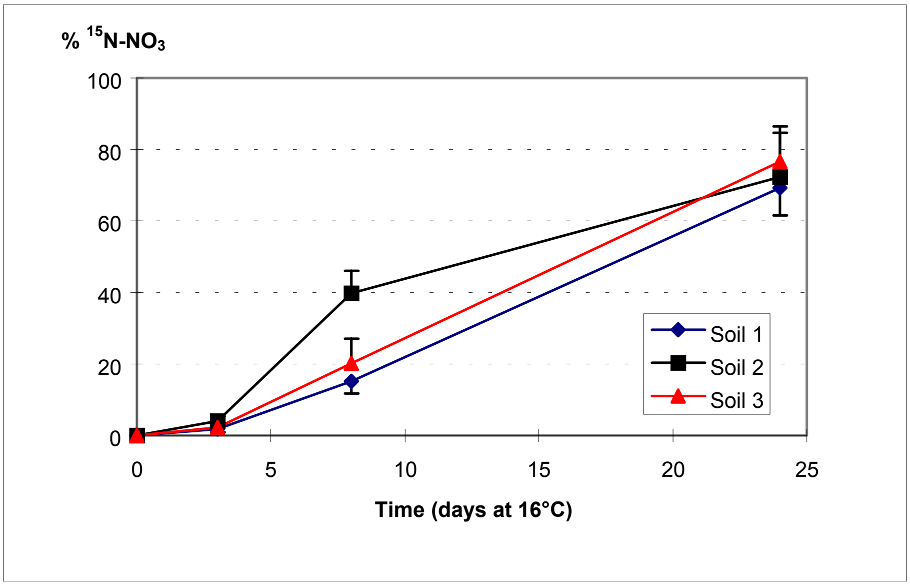

Figure 3.
Plot of the mean percentage of ^{15}N-NO$_3$, for each soil (vertical bars indicate the standard deviation calculated after pooling the treatments, for each soil)

3.5. A simple model of slurry C and N transformations

Previous results were used to make certain assumptions and calibrate a simple dynamic model describing C and N transformations following slurry addition to soils during the period of slurry ammonium nitrification (fig 4). Microbial growth, maintenance and death was not considered in this simplified approach, implying that remineralization and recycling were neglected. Direct assimilation of organic nitrogen compounds by the microbial biomass was also neglected. Given these limitations, the gross immobilization and mineralization could be linked to carbon mineralization by means of simple stoechiometric relationships (table 4).

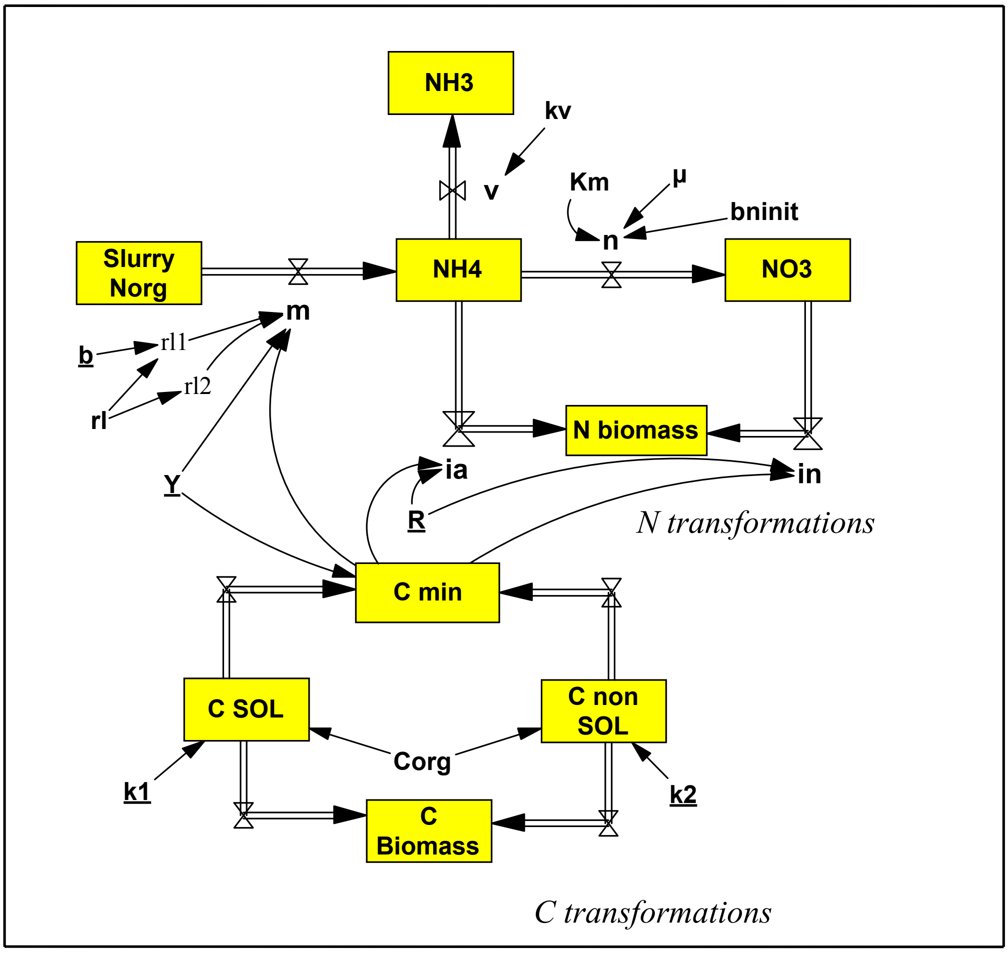

Figure 4.
Flow chart of C and N slurry transformations after addition of slurry to soils (input parameters obtained by numerical fitting are underlined)

Total organic C supplied	C_{org}	µg g^{-1} soil	input
C soluble fraction	SOL	dimensionless	input
Slurry organic N applied	N_{org}	µg g^{-1} soil	input
Ammonia supplied	NH_4	µg g^{-1} soil	input
C_{org}:N_{org} ratio	rl	dimensionless	input
C:N ratio of the soluble fraction	rl_1	dimensionless	rl_1 = b. rl
C:N ratio of the non soluble fraction	rl_2	dimensionless	rl_2 = f(Corg, SOL, rl, rl_1)
C assimilation yield	Y	dimensionless	constant / soil
i : Cmin ratio	R	µg N µg^{-1} C	constant / soil
decay constant rate for volatilization	k_v	day^{-1}	input
decay constant rate for SOL C pool	k_1	day^{-1}	constant / soil and slurry type
decay constant rate for non SOL C pool	k_2	day^{-1}	constant / soil and slurry type
specific growth rate of nitrifiers	µ	day^{-1}	constant / soil
rl_1:rl ratio	b	dimensionless	constant
Initial nitrifying biomass	bn_{init}	cells µg^{-1} soil	constant / soil
Mickaelis constant	K_m	µg g^{-1} soil	constant

Table 4.
Input parameters and relationships used in the model

Relationships

$$C_{\min} = (1-Y).[SOL.C_{org.}(1-e^{-k1.t}) + (1-SOL).Corg.(1-e^{-k2.t})]$$

$$i = i_a + i_n = R.C_{\min}$$

$$m = \frac{1}{rl_1}.SOL.C_{org}.(1-e^{-k1.t}) + \frac{1}{rl_2}.(1-SOL).C_{org}.(1-e^{-k2.t})$$

$$n = \int_0^t \mu.bn.\frac{[NH_4]}{K_m+[NH_4]}$$

$$v = \int_0^t kv.[NH_4]$$

The following assumptions were made :

- the rate of decomposition of the slurry carbon could be described by a two-compartment model, as suggested by the great variability of carbon mineralization kinetics and rates. The easily decomposable compartment was assumed to be the neutral detergent soluble fraction (SOL), the second pool consisting of the non-soluble fraction,
- the C:N ratio of the SOL fraction (r_{l1}) was assumed to be linked to the global C:N ratio of the total organic fraction of the slurry (rl_1 = b.rl)
- the C:N microbial ratio (r_{bio}) and the assimilation yield of the microbial biomass (Y) were presumed to remain constant throughout the experiment.

Nitrification rate was modeled by Mickaelis Menten kinetics ; the effect of pH on the rate of nitrification was not considered.

The model requires few parameters : i) the amounts of soluble and total organic carbon supplied by the slurry, ii) the amounts of ammonia and organic nitrogen, and iii) the rate of volatilization. The other input parameters are constants, such as the b parameter, or depend only on soil type (Y, R, µ, bn_{init}), or on the soil and slurry type (pig or cattle slurry) (k_1, k_2). Such parameters were obtained by numerical optimization procedures carried out on the data used for the FLUAZ calculations. The required input parameters are given in table 4.

The main results were that :

- the great variability in the kinetics and final rates of C mineralization observed between slurries could be well described by a two-compartment model (R^2 = 0.97 between predicted and measured values). Accurate prediction of C mineralization was obtained by using the **same k_1 and k_2** decay constants values for all pig slurries, and the **same k_1 and k_2** values which differed from those of the pig slurries, for cattle slurries. This is of great interest for the purpose of an operational model,
- the C-N relationships provided reasonable predicted values for i and m, on days 8 and 24, if the the ratio rl_1:rl was equal to 1.23,
- the adjusted values of apparent assimilation yield ranged from 0.52 to 0.61 for the different soils ; they were in good agreement with the values given by many authors, and explained the differences due to the soil, for i and m,
- this simple model was able to provide an accurate prediction of the amounts of nitrate available during nitrification of the ammonia of the slurry, and reasonable prediction at the end of nitrification (fig 5).

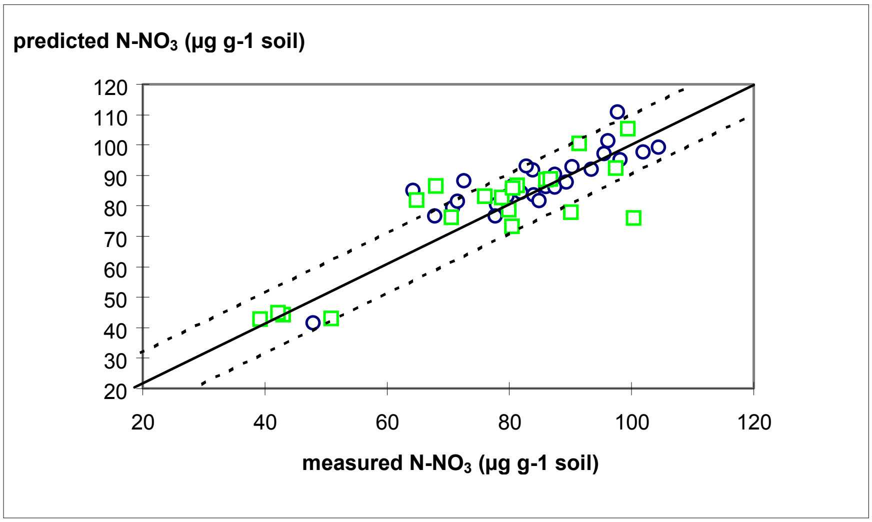

Figure 5.
Comparison of measured and predicted amounts of nitrate (µg g^{-1} soil),
on day 24. (blue rounded points were obtained with treatments used to fit the model parameters; green squared points were obtained with independent datas)

4. Conclusion

We have shown that the great variability observed between the carbon and nitrogen biiotransformations of different slurries can be related to the chemical and biochemical composition of these latter.

A simple dynamic model, requiring few parameters, was calibrated on three soils and gave an accurate description of the short term nitrogen transformations. The discrepancies between measured and predicted gross N fluxes might be explained by the fact that remineralization was not taken into account. Further investigations will need to be made : i) to quantify the turnover and recycling of the microbial biomass, and ii) to model the effects of the soil characteristics.

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