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Kinetics of C and N mineralization, N immobilization and N volatilization of organic inputs in soil

M. Pansu[a,*], L. Thuriès[b]

[a]IRD (ORSTOM), BP 64501, 34394 Montpellier Cedex 5, France
[b]Phalippou-Frayssinet S.A., Organic Fertilizers, 81240 Rouairoux, France

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Abstract

C and N mineralization data for 17 different added organic materials (AOM) in a sandy soil were collected from an incubation experiment conducted under controlled laboratory conditions. The AOM originated from plants, animal wastes, manures, composts, and organic fertilizers. The C-to-$N_{\rm AOM}$ ratios ($\eta_{\rm AOM}$) ranged from 1.1 to 27.1. Sequential fibre analyses gave C-to-N ratios of soluble ($\eta_{\rm Sol}$), holocellulosic ($\eta_{\rm Hol}$) and ligneous compounds ($\eta_{\rm Lig}$) ranging from 1.1 to 57.2, 0.8 to 65.2, and 3.5 to 25.3, respectively. Very different patterns of net AOM-N mineralization were observed: (i) immobilization for four plant AOM; (ii) moderate mineralization (4–15% AOM-N) for composts; (iii) marked mineralization (11–27% AOM-N) for 1 animal AOM, 1 manure and 2 organic fertilizers; and (iv) high rates of transformations with possible gaseous losses for some N-rich AOM.

The Transformation of Added Organics (TAO) model proposed here, described AOM-C mineralization (28 °C, 75% WHC) from three labile (L′), resistant (R) and stable (S) compartments with the sole parameters $P'_{\rm L}$ and $P_{\rm S}$ = fractions of very labile and stable compounds of AOM, respectively. Dividing the C-compartments by their C-to-N estimates supplied the remaining $N_{\rm AOM}$ fraction (RAONF). A $P_{\rm im}$ parameter split the TAO nitrogen fraction (TAONF = added N-RAONF) into two compartments, immobilized (imN) and inorganic (inorgN) N. A $P_{\rm im} > 0$ value meant that all the TAONF plus a fraction ($P_{\rm im} - 1$) of native soil inorganic N was immobilized. Additional N mineralization was predicted when necessary from imN by first order kinetics (constant $k_{\rm remin}$). The TAO version with two parameters $P_{\rm im}$ and $k_{\rm remin}$ allowed us to predict very different patterns of N mineralization and N immobilization. In a few cases, a further first order kinetic law (constant $k_{\rm v}$) was added to predict N volatilization from inorgN. Two hypotheses were tested: (i) $\eta_{\rm L'}$, $\eta_{\rm R}$, $\eta_{\rm S}$ (C-to-N of L′, R and S) = $\eta_{\rm Sol}$, $\eta_{\rm Hol}$, $\eta_{\rm Lig}$, respectively, (ii) $\eta_{\rm L'} = \eta_{\rm R} = \eta_{\rm S} = \eta_{\rm AOM}$. The first hypothesis was validated by these data, and the second was a good approximation of the former one. In all the cases, predictions were in good agreement with measured values.

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1. Introduction

Despite a large collection of experimental data, the fate of nitrogen (N) of organic inputs in soils remains difficult to interpret. Inorganic N can be produced by mineralization or immobilized by microbial biomass; it can be assimilated by plants, partially fixed within clays, leached in water or volatilized as NH_3, N_2O, NO_x or N_2. Tracer experiments illustrate the complexity of the fluxes (Mary et al., 1998), with a high turnover of ammonium (NH_4^+) largely re-immobilized by microbial biomass (Yevdokimov and Blagodatsky, 1993), and partly nitrified according to a growth law (Pansu et al., 1998a).

In most soil organic matter (SOM) models, N kinetics are derived from those of carbon (C). The initial input material is generally defined by two (Molina et al., 1983; Van Veen et al., 1984; Parton et al., 1987; Bradbury et al., 1993; Pansu et al., 1998b) or three (Verberne et al., 1990; Hansen et al., 1991) compartments. Some mineralization data have been used directly with SOM models (Hadas and Portnoy, 1994; Jans-Hammermeister and McGill, 1997; Trinsoutrot et al., 2000a) or have been adjusted to different specific models. In simplified systems with artificial extraction of inorganic N, a one-compartment model has been proposed by Stanford and Smith (1972). Other functions have been then tested: linear (Addiscott, 1983), parabolic (Broadbent, 1986),

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* Corresponding author. Tel.: +33-4674-16100; fax: +33-4674-16294.
E-mail address: pansu@mpl.ird.fr (M. Pansu).

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exponential plus constant (Bernal et al., 1998), or double exponential (Deans et al., 1986; Matus and Rodriguez, 1994). In other studies, double exponential expressions failed to estimate organic N pools (Dendooven et al., 1997) or were used for C- but not for N-pools (Bloemhof and Berendse, 1995; Trinsoutrot et al., 2000b).

Another option is to propose mechanistic models in order to follow specifically the decomposition of added organic matter (AOM) to the SOM part. The model of Bosatta and Ågren (1985) defined a quality theory applied to AOM constituents as a continuum. In the model of Henriksen and Breland (1999a), AOM was split into three biochemical compartments, and then assimilated into five soil compartments. Nicolardot et al. (2001) proposed one AOM compartment assimilated into three soil compartments. From a comparative statistical study on C mineralization, Thuriès et al. (2001) proposed splitting AOM into three compartments with only two descriptive parameters. In this paper, we aimed to extend this AOM-C to an AOM-N model in order to predict the C- and N-transformations of AOM.

Although pioneer studies on inorganic-N evolution from incubation experiments took into account a large diversity of AOM (Rubins and Bear, 1942), most of these can be classified in two large groups corresponding to homogeneous materials: (i) plant residues (Nordmeyer and Richter, 1985; Janzen and Kucey, 1988; Jensen, 1994; Bloemhof and Berendse, 1995; Quemada and Cabrera, 1995; Kaboneka et al., 1997; Dendooven et al., 1997; Mueller et al., 1998; Trenbath and Diggle, 1998; Henriksen and Breland 1999a,b; Trinsoutrot et al., 2000a,b; Nicolardot et al., 2001), and (ii) animal manures or composts (Leclerc, 1990; Thiénot, 1991; Hébert et al., 1991; Hadas and Portnoy, 1994; Mahimairaja et al., 1995; Jedidi et al., 1995; Sørensen and Jensen, 1995; Hadas and Portnoy, 1997; Bernal et al., 1998; Paré et al., 1998). Our objective was to model AOM-C and -N transformations of a large collection of AOM from plant, animal manure or compost origins.

2. Materials and methods

2.1. Added organic materials (AOM)

Different kinds of AOM from agri-food industry wastes and industrial-processed fertilizers (organic amendments and fertilizers) were tested (Table 1). The materials originated from (a) plant residues: wet and dry grape berry pellicle cakes (Wgrap, Dgrap), coffee cake (Coffk), cocoa cake (Kokoa), olive pulp (Olivp), (b) animal wastes: hydrolysed feather meal (Featm), native fine feather (Nfeat), guano (Guano), (c) animal manures from sheep (Shepm), and chickens (Chicm), and (d) industrial organic fertilizers: composted amendments (Compo series), and combined fertilizers (Gnofer, Comfer). A full description of these organic materials and their biochemical characterization by the Van Soest et al. (1991) method were given in Thuriès et al. (2001, 2002). The data used in this paper (Table 1) were: η_{AOM}, η_{Sol}, η_{Hol}, η_{Lig} = C-to-N ratios of AOM, soluble, holocellulosic (= hemicellulosic + cellulosic), and ligneous AOM fractions, respectively.

2.2. Incubation experiment

The incubation test using a sandy soil (top 0–20 cm layer; sand = 69.3%, clay = 11.5%, $pH_{(H2O)}$ 6.6, CEC = 5.5 cmol c^+ kg^{-1}, total C = 4.98 g kg^{-1}, total N = 0.59 g kg^{-1}) was previously described by Thuriès et al. (2001). 125 to 500 mg AOM in 50 g air-dried soil (AOM-C ranged from 8 to 102% of initial soil C, AOM-N from 26 to 93% of initial soil N) were incubated at 28 °C and 75% WHC. CO_2–C titrimetric measurements were made on 17 sampling occasions during six months. Organic C and total N in soil, AOM and soil + AOM mixtures were determined by dry combustion on a Fisons Instruments elemental analyser (Fisons, Crawley, UK).

Inorganic-N measurements were made at days 0, 1, 2, 5, 10, 21, 41, 90, 182 (when soil + AOM or control soil samples were removed from the incubation) according to the reference method NF–ISO 14256 (2000): (i) extraction by a KCl 1 mol l^{-1} solution, (ii) filtration through a 0.2-μm membrane and storage of filtrates at −20 °C, and (iii) determination of nitrate + nitrite and ammonium by spectrophotometric methods. In this paper, we considered total inorganic N (= ammonium + nitrate + nitrite). An aliquot of each soil + AOM sample was air dried and analysed for total N content in order to be able to estimate possible gaseous losses of N.

2.3. Data calculation and control

The inorganic N due to AOM at sampling occasion i can be written:

$$\mathrm{inorgN}_i = \frac{1}{n}\sum_{\alpha=1}^{n}(\mathrm{inorgN}^s_{i\alpha} - \overline{\mathrm{inorgN}^c_i}) \qquad (1)$$

where $\mathrm{inorgN}^s_{i\alpha}$ and $\overline{\mathrm{inorgN}^c_i}$ are inorganic N at sampling occasion i and replication α for sample (soil + AOM) and mean value of soil control, respectively; n = three replicates. Net N mineralization gives a mN_i positive value, whereas N immobilization gives a negative one. All units (Remaining Added Organic C Fraction RAOCF in Eq. (3), $\mathrm{inorgN}^s_{i\alpha}$, $\overline{\mathrm{inorgN}^c_i}$, inorgN_i and total-N) were expressed as a fraction of C input (Mary et al., 1996; Whitmore and Handayanto, 1997; Henriksen and Breland, 1999b; Trinsoutrot et al., 2000b), in order to facilitate the interpretation of N fluxes from AOM by using C-to-N ratios.

For p sampling occasions with n replicates, the pooled variance of inorgN_i was:

$$s^2_{\mathrm{inorgN}} = \frac{1}{np-p}\sum_{i=1}^{p}\sum_{\alpha=1}^{n}(\mathrm{inorgN}_{i\alpha} - \mathrm{inorgN}_i)^2 \qquad (2)$$

Table 1

AOM-C application rates in the incubation experiment, TAO-C parameter values (Thuriès et al., 2001), measured C-to-N data for AOM (η_{AOM}), soluble (η_{Sol}), holocellulosic (η_{Hol}), ligneous (η_{Lig}) AOM fractions, and parameters obtained for TAO-N with Eqs. (4) and (10) hypotheses

AOM origin	AOM	g kg^{-1} soil added C	TAO-C parameters Eq. (3)		C-to-N data				TAO-N parameters with C-to-N L′, R′, S Eqs. (4)–(6)			TAO-N parameters with C-to-N AOM Eqs. (5), (6) and (10)			F test	
			P'_{L}	P_{S}	η_{AOM}	η_{Sol}	η_{Hol}	η_{Lig}	P_{im}	k_{remin}	k_v	P_{im}	k_{remin}	k_v	Eq. (11)	Eq. (11a)
Plant	Coffk	4.999	0.055	0.394	27.13	57.21	39.35	18.00	1.170	0.00099	0	1.109	0.00064	0	1.001 NS	
	Wgrap	4.667	0.070	0.624	19.64	23.92	21.56	18.46	1.156	0.00209	0	1.136	0.00181	0	1.000 NS	
	Dgrap	4.605	0.058	0.670	21.99	23.29	39.43	18.56	1.713	0.00522	0	1.514	0.00410	0		1.299 NS
	Olivp	4.426	0.048	0.531	23.78	19.97	65.22	16.00	1.814	0.00419	0	1.505	0.00337	0		1.087 NS
	Kokoa	4.072	0.278	0.482	9.62	9.14	9.53	9.97	0.981	0.00246	0.00896	0.979	0.00257	0.00890		1.001 NS
Manure	Shepm	3.230	0.064	0.422	16.99	8.43	14.87	25.27	0.900	0	0	0.871	0	0	1.010 NS	
	Chicm	3.360	0.309	0.304	6.20	2.40	31.59	14.96	0.820	0.00163	0.0120	0.572	0.00404	0.0184		1.054 NS
Animal wastes	Nfeat	1.205	0.068	0.697	3.74	3.07	5.08	3.50	0.835	0.04850	0	0.487	0.00982	0		4.310 *
	Featm	1.064	0.450	0.089	3.10	2.38	4.13	4.17	0.703	0.00466	0.00694	0.611	0.00117	0.00316		1.016 NS
	Guano	0.392	0.637	0.130	1.12	1.10	0.80	6.60	0.497	0.0413	0.05270	0.484	0.04040	0.04840		1.001 NS
Fertilizer	Gnofer	0.617	0.394	0.108	2.87	1.96	3.94	5.08	0.665	0	0	0.601	0	0		1.345 NS
	Comfer	1.735	0.261	0.613	9.87	5.45	8.78	15.66	0.772	0.00208	0	0.601	0.00475	0		1.295 NS
Compost	Compo a	2.709	0.117	0.634	12.40	5.19	13.18	16.17	0.889	0.00054	0	0.787	0.00045	0		1.005 NS
	Compo b	3.434	0.097	0.680	14.74	8.00	21.60	14.98	1.084	0.00151	0	1.116	0.00202	0		1.029 NS
	Compo e	2.505	0.034	0.869	10.66	5.45	15.18	10.70	0.532	0	0	0.448	0	0		1.027 NS
	Compo +	3.035	0.079	0.750	13.12	8.64	57.89	11.70	1.145	0.00231	0	1.168	0.00246	0	1.005 NS	
	Compo p	2.816	0.032	0.776	14.16	1.40	30.63	18.70	0.760	0.00075	0	0.208	0	0		1.124 NS

Coffk, coffee cake; Wgrap, wet grape berry pellicle cake; Dgrap, dry grape berry pellicle cake; Olivp, olive pulp; Kokoa, cocoa cake; Shepm, sheep manure; Chicm, chicken manure; Nfeat, native fine feather; Featm, feather meal; Guano, bird guano; Gnofer, guano-based industrial fertilizer; Comfer, compost-based industrial fertilizer; Compo, industrial composted amendments.

with the corresponding confidence interval: $\mathrm{inorgN}_i \pm t_{0.975}^{np-p} s_{\mathrm{inorgN}}$.

2.4. Mathematical model

In order to predict C mineralization, Thuriès et al. (2001) selected two models amongst the seven tested: a parallel first order two-compartment model with three parameters (*m*4), and a parallel first order three-compartment model with four parameters (*m*5). Additionally, a simplification of *m*5 was proposed: the kinetic constants of very labile (k'_{mL}) and resistant (k'_{mR}) compartments could be considered as being independent of the AOM origin. Under the controlled conditions of the incubation (28 °C, 75% WHC), the following mean values were retained: $k'_{\mathrm{mL}} = 0.4 \pm 0.15\ \mathrm{d}^{-1}$ (half life $T_{1/2} = 1.7$ d), $k'_{\mathrm{mR}} = 0.012 \pm 0.003\ \mathrm{d}^{-1}$ ($T_{1/2} = 58$ d). Thus the proposed model *m*6 needed two parameters only: the fraction P'L of very labile compounds, and the fraction P_{S} of very stable ones (with a mineralization constant fixed to 0 for this six-month experiment). The fraction of intermediary resistant compounds was $P_{\mathrm{R}} = 1 - P'_{\mathrm{L}} - P_{\mathrm{S}}$, and RAOCF (remaining $\mathrm{C_{AOM}}$ plus AOM-C transformed into microbial biomass and humus) at a given time t from input time t_0 (d) can be written:

$$\mathrm{RAOCF} = P'_{\mathrm{L}}\,\mathrm{e}^{-0.4(t-t_0)} + (1 - P'_{\mathrm{L}} - P_{\mathrm{S}})\mathrm{e}^{-0.012(t-t_0)} + P_{\mathrm{S}} \tag{3}$$

Among the 17 AOMs tested in the experiment, Eq. (3) with P'_{L} and P_{S} values from Table 1, allowed us to predict RAOCF with determination coefficients of $r^2 > 99.5$ for seven series, $99 < r^2 < 99.5$ for five series, $98 < r^2 < 99$ for two series, and $93 < r^2 < 98$ for the three animal AOMs, i.e. Guano, Featm and Nfeat (best predicted with *m*4).

Let η_{L}, η_{R}, η_{S} be the C-to-N ratios of very labile, resistant and stable AOM-compartments, respectively; the remaining added organic N fraction (RAONF) can be expressed as:

$$\mathrm{RAONF} = \frac{P'_{\mathrm{L}}}{\eta_{\mathrm{L}}}\mathrm{e}^{-0.4(t-t_0)} + \frac{1 - P'_{\mathrm{L}} - P_{\mathrm{S}}}{\eta_{\mathrm{R}}}\mathrm{e}^{-0.012(t-t_0)} + \frac{P_{\mathrm{S}}}{\eta_{\mathrm{S}}} \tag{4}$$

The transformed (mineralized or immobilized) added organic N fraction (TAONF) can then be expressed from the total C (= 1 in this data, all values of C and N expressed as a fraction of initial C content) and C-to-N ratio of AOM (η_{AOM}) by:

$$\mathrm{TAONF} = \frac{1}{\eta_{\mathrm{AOM}}} - \mathrm{RAONF} \tag{5}$$

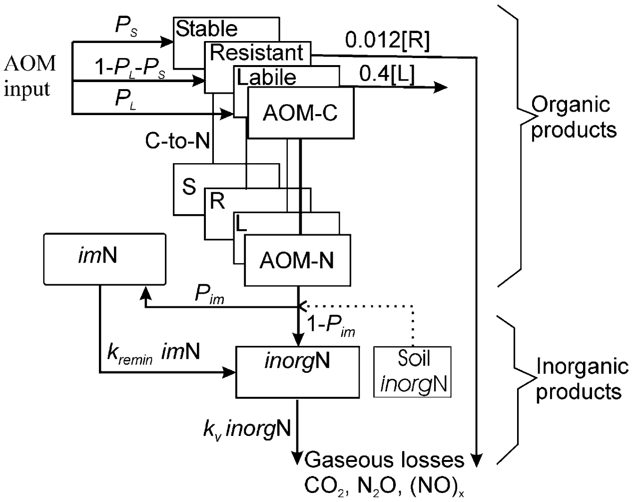

Fig. 1. The model TAO (Transformation of Added Organics, *Transformation des Apports Organiques*) for C mineralization, N mineralization, N immobilization and N volatilization of Added Organic Matters (AOM) in soil: inorgN, inorganic N from AOM; imN, immobilized N from AOM (and Soil-Inorg N if $P_{\mathrm{im}} > 1$).

In the proposed TAO model (Fig. 1), the fraction P_{im} splits the TAONF into 2 compartments: immobilized N ($\mathrm{imN} = P_{\mathrm{im}}$ TAONF) and mineralized N ($\mathrm{inorgN} = (1 - P_{\mathrm{im}})$ TAONF). Additionally, imN could be re-mineralized (decomposition of microbial cells) and inorgN could be partly volatilized according to first order kinetics, the complete equations become:

$$\mathrm{inorgN} = (1 - P_{\mathrm{im}})\mathrm{TAONF} + \int_{t_0}^{t} \mathrm{imN}\,k_{\mathrm{remin}}\,\mathrm{d}t - \int_{t_0}^{t} \mathrm{inorgN}\,k_v\,\mathrm{d}t \tag{6}$$

$$\mathrm{imN} = P_{\mathrm{im}}\,\mathrm{TAONF} - \int_{t_0}^{t} \mathrm{imN}\,k_{\mathrm{remin}}\,\mathrm{d}t \quad \text{for } t > t_0 \tag{6a}$$

otherwise $\mathrm{inorgN} = \text{initial } \mathrm{inorgN_{AOM}}$ and $\mathrm{imN} = 0$ for $t = t_0$

When $k_{\mathrm{remin}} = k_v = 0$, the system is entirely governed by the fraction P_{im}, and the two fractions P'_{L} and P_{S} from C mineralization curves. The curves TAONF, imN and inorgN are thus parallel. If the inorgN slope becomes greater than the TAONF slope, then k_{remin} must be greater than 0. If the inorgN slope becomes lower than the TAONF one, then N losses occur and k_v becomes greater than zero. A system where P_{im}, k_{remin} and k_v have simultaneously positive values is in active transformation with a phase of gaseous N losses from inorgN and maintenance of inorgN level from imN and organic $\mathrm{N_{AOM}}$. By these transfer processes, losses of inorgN give losses of total N from AOM. Conversely, a system where $P_{\mathrm{im}} = k_{\mathrm{remin}} = k_v = 0$ is a system where only N mineralization occurs from initial AOM without any N immobilization or N volatilization. In a system where $P_{\mathrm{im}} = 1$, the AOM organic N is entirely re-organized into SOM which mineralizes according to the k_{remin} value. In a system where $P_{\mathrm{im}} > 1$, N immobilization is greater than TAONF; this system immobilizes all TAONF plus a part ($P_{\mathrm{im}} - 1$) of the inorganic N from soil origin (expressed in the AOM-N unit).

Sensitivity analysis showed a linear response of predicted inorgN to change of parameters P_{im}, k_{remin} or k_v (data not shown). The P_{im} parameter had the greatest influence on inorgN, especially when P_{im} was used alone ($k_{\mathrm{remin}} = k_v = 0$). For example, in the Shepm prediction with P_{im} alone ($P_{\mathrm{im}} = 0.87$, Table 1), a random normal distribution of P_{im} with a relative standard deviation of 1% gave a random normal distribution of inorgN at 210 d with 10% RSD. A less accurate simulation could be performed with a positive value for the three parameters ($P_{\mathrm{im}} = 0.81$, $k_{\mathrm{remin}} = 0.0021$, $k_v = 0.016$), but the model predictions were more stable: a 1% RSD for P_{im} gave 5% and $< 1\%$ RSD for inorgN predictions at 90 and 210 d, respectively. The fluctuations of inorgN predictions to P_{im} changes were the greatest for the maximum or minimum values of inorgN curves. The predictions were less sensitive to k_{remin} or k_v fluctuations, with the greatest changes at the end of the incubation.

2.5. Model calculations

The P'_{L} and P_{S} parameters (Eqs. (3) and (4); Table 1) were given by Thuriès et al. (2001). As a first step, we calculated RAONF Eq. (4) with $\eta_{\mathrm{L}'}$, η_{R}, η_{S} assimilated to C-to-N data η_{Sol}, η_{Hol}, and η_{Lig}, respectively. These data must be checked (and if necessary η_{Hol} recalculated) according to the balance Eq. (7):

$$\frac{1}{\eta_{\mathrm{AOM}}} = \frac{P'_{\mathrm{L}}}{\eta'_{\mathrm{L}}} + \frac{P_{\mathrm{R}}}{\eta_{\mathrm{R}}} + \frac{P_{\mathrm{S}}}{\eta_{\mathrm{S}}} \tag{7}$$

TAONF was then calculated according to Eq. (5). The prediction of inorgN required the optimization of P_{im} only and, if necessary, k_{remin} and/or k_v (Eq. (6)). It was performed by Powell's method with the minimized criterion:

$$\mathrm{RSS} = \sum_j (y_j - \hat{y}_j)^2 \tag{8}$$

where y_j and $\hat{y}_j$ were data measurement and prediction of inorgN, respectively, at sampling occasion j. The alternative consisted of considering total N data with the minimized criterion:

$$\mathrm{RSSt} = \sum_{k=1}^{2} p_k^2 \sum_j (y_{kj} - \hat{y}_{kj})^2 \tag{9}$$

where k identified the data series (inorgN or total added N) associated with a weight coefficient p_k. The two possibilities were tested, and the first (Eq. (8)) then retained (similar accuracy; inorgN measurements more repeatable than total N ones). Although total added N data were not taken into account in the calculations, the predictions obtained were in accordance with these data. Hence, total added N data was used to validate the TAO approach.

In a second step, RAONF was calculated without the use of η_{L}, η_{R}, η_{S} determinations, C-to-N ratios of compartments L, R, S being equal to η_{AOM}. Eq. (4) became:

$$\mathrm{RAONF} = \frac{1}{\eta_{\mathrm{AOM}}}\left(P'_L\,\mathrm{e}^{-0.4(t-t_0)} + (1 - P'_{\mathrm{L}} - P_{\mathrm{S}})\mathrm{e}^{-0.012(t-t_0)} + P_{\mathrm{S}}\right) \tag{10}$$

with the other calculations remaining unchanged. Comparisons of the two methods were made by the test:

$$F = \frac{\mathrm{RSS}_4}{\mathrm{RSS}_{10}} \quad \text{if } \mathrm{RSS}_4 > \mathrm{RSS}_{10} \tag{11}$$

$$\text{else } F = \frac{\mathrm{RSS}_{10}}{\mathrm{RSS}_4} \quad \text{if } \mathrm{RSS}_{10} > \mathrm{RSS}_4, \tag{11a}$$

RSS_4 and RSS_{10} being RSS (Eq. (8)) with first (Eq. 4) and second (Eq. (10)) calculations, respectively.

3. Results

3.1. Classification of inputs according to inorganic-N production

Fig. 2 presents N-rich AOM incubation data showing net positive mineralization flux and positive rates of mineralization (slope). After six months of incubation, net mineralized N represented about 27% of total AOM-N for the two organic fertilizers Gnofer (C-to-N = 2.9) and Comfer (C-to-N = 9.9), 22% for Nfeat (animal waste, C-to-N = 3.7), and 11% for Shepm (manure = plant + animal origin, C-to-N = 17). The mineralized N decreased whereas C-to-N ratios increased, but there was no significant relationship. In contrast with the results of Thiénot (1991) and Corbeels et al. (1999), Shepm did not show a net N immobilization. The fraction of mineralized N was almost the same for the two organic fertilizers, and was higher than that for Nfeat and Shepm. The expected difference between the two fertilizers was shown. The guano-based fertilizer (Gnofer) mineralized 26% of its N during the first month of incubation, this level remaining stable during the following five months. The compost-based fertilizer (Comfer) mineralized about 10% of its N contact during the first week, the mineralization increasing afterwards linearly with the incubation time.

Fig. 3 shows the inorganic N immobilization by N-poor plant debris which has often been observed (Quemada and Cabrera, 1995; Trenbath and Diggle, 1998; Mueller et al., 1998; Henriksen and Breland, 1999b; Trinsoutrot et al., 2000b). From this incubation data at 180 d, the C-to-N threshold for mineralization/immobilization (Whitmore and Handayanto, 1997) was found to be ca. 19. All the AOM in Fig. 3, with C-to-N ranging from 19.6 (Wgrap) to 27.1 (Coffk), induced a marked N immobilization. The particular behaviour of Kokoa (Fig. 5), an AOM of plant origin, could be partly explained by its low C-to-N value (Table 1). Negative values of inorgN were observed during

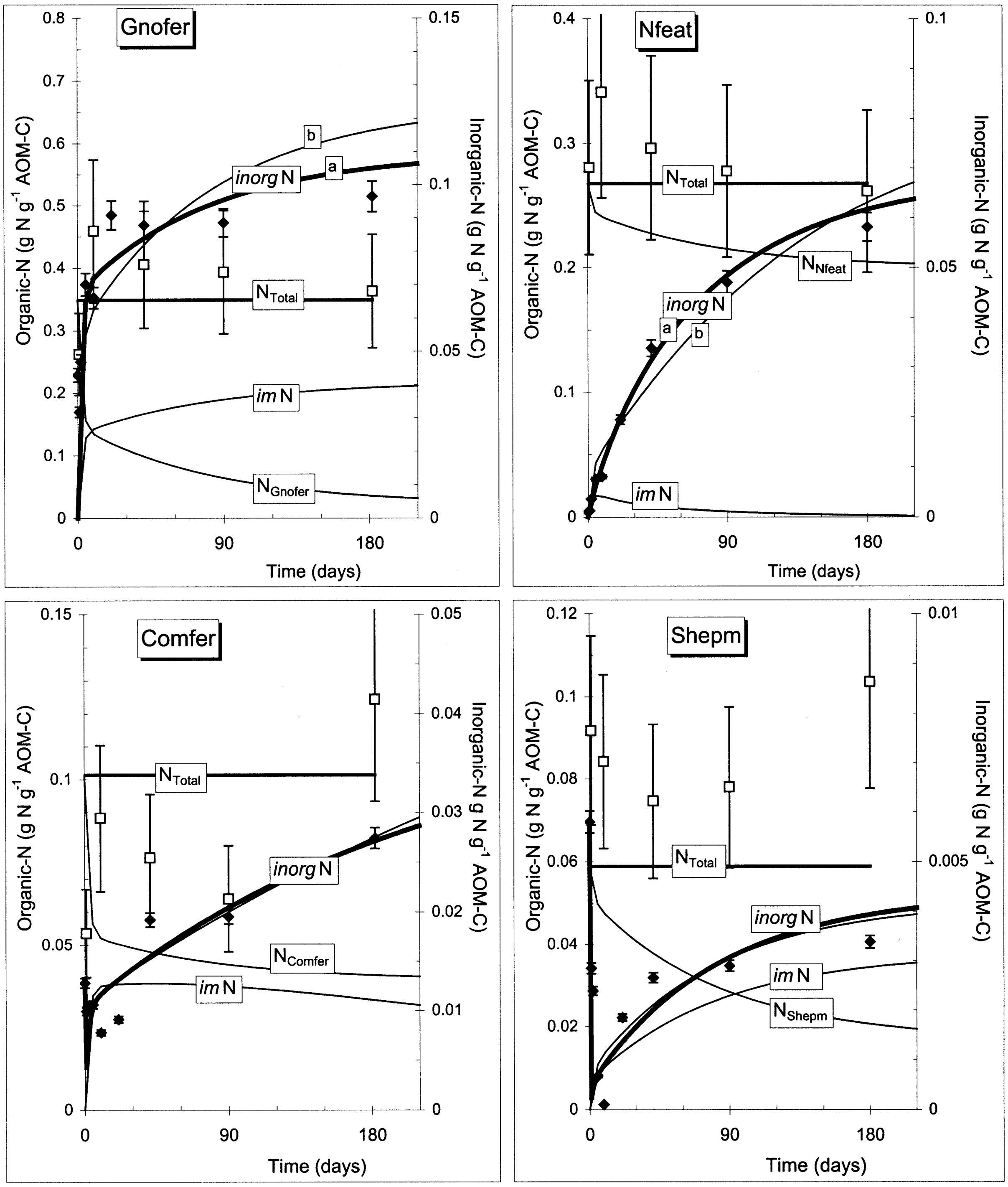

Fig. 2. Mineralization and immobilization of N from guano-based fertilizer (Gnofer), native fine feather (Nfeat), compost-based fertilizer (Comfer), sheep manure (Shepm). Points = experimental data with 95% confidence intervals (◆, inorgN from AOM; □, total N from AOM) continuous lines = TAO predictions of inorgN (bold lines: a, prediction with C-to-N of fractions; b, predictions with C-to-N_{AOM}), remaining N_{AOM} and immobilized N (thin lines).

6 months for Olivp and Coffk, 4 months for Wgrap and 5 months for Dgrap, respectively. All the inorganic N (from soil + AOM, Tot.inorg.N in Fig. 3) was immobilized within 3 months for Olivp and Coffk, and 1.5 months for Wgrap and Dgrap. In comparison, immobilization for the olive pulp studied by Thomson and Nogales (1999) lasted 3 months.

At 180 d, mineralized-N from composts (Fig. 4) represented 9% of total AOM-N for Compo a (mixture at composting time ct = 0), 4% for Compo b (ct = 41 d), 7% for Compo e (ct = 305 d), and 15% for Compo p (ct = 185 d). Immobilization of N is known to depend on the degree of composting (Bernal et al., 1998) but no clear relationship was found. Compo b and Compo + (mixture of

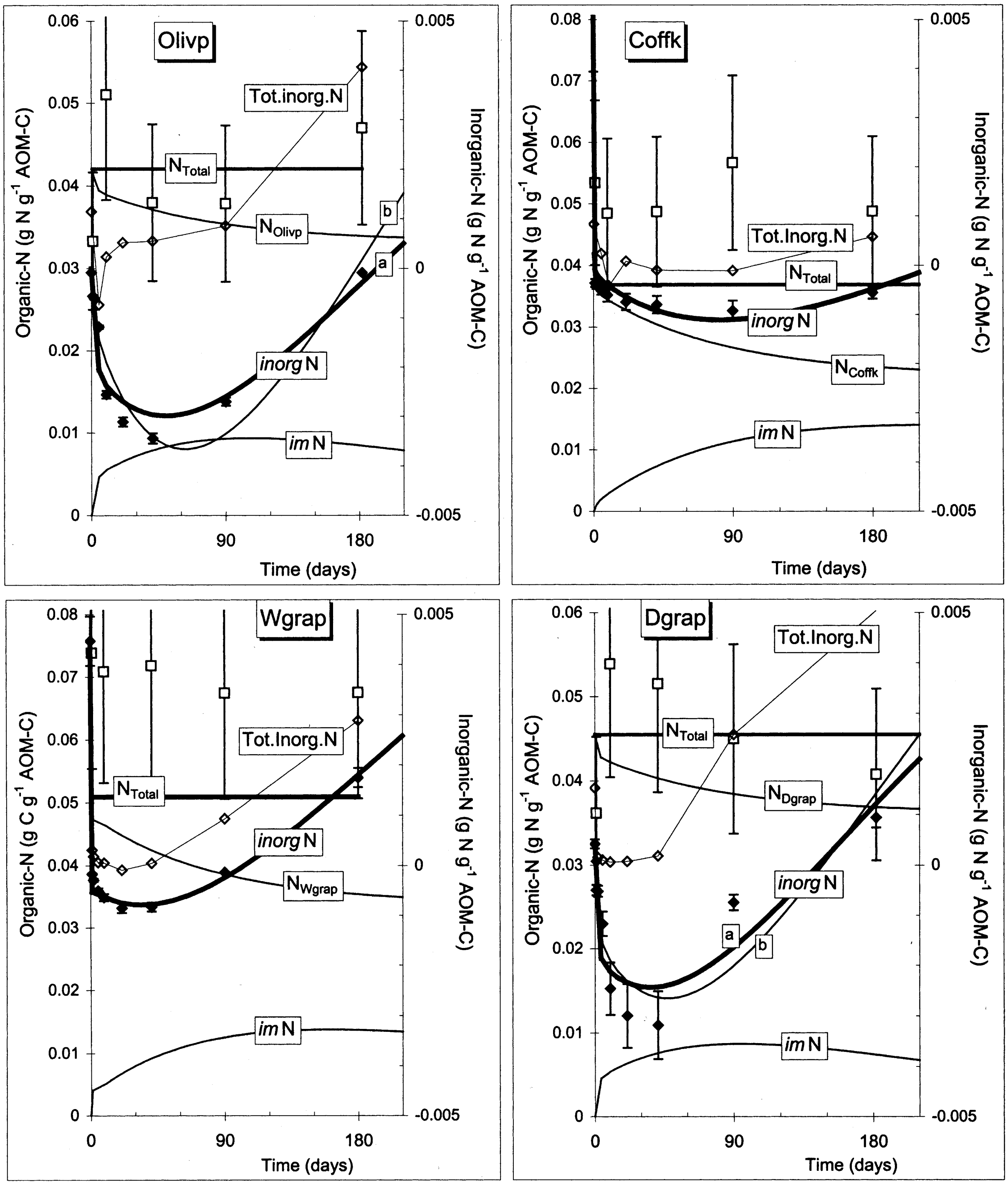

Fig. 3. Mineralization and immobilization of nitrogen from plant-originated AOM: olive pulp (Olivp), coffee cake (Coffk), wet grape berry pellicle cake (Wgrap) and dry grape berry pellicle cake (Dgrap). Points = experimental data with 95% confidence intervals (◆, inorgN from AOM; ◇, total (soil + AOM) inorganic N; □, total N from AOM) continuous lines = TAO predictions of inorgN (bold lines: a, prediction with C-to-N of fractions; b, predictions with C-to-N_{AOM}), immobilized N (imN) and remaining N_{AOM} (thin lines).

75% Compo e and 25% Dgrap, curve not shown) induced an inorgN immobilization during the first two months followed by a net inorgN production.

Fig. 5 shows the inorgN curves of three N-rich animal AOM (Guano, Featm and Chicm), and an atypical N-rich plant residue (Kokoa) which could have lost gaseous N during the experiment. Estimated gaseous losses were particularly evident for Guano: 30% of its N mineralized during the first month of incubation, with only 1% remaining as inorganic N after 6 months (Fig. 5). Rubins and Bear

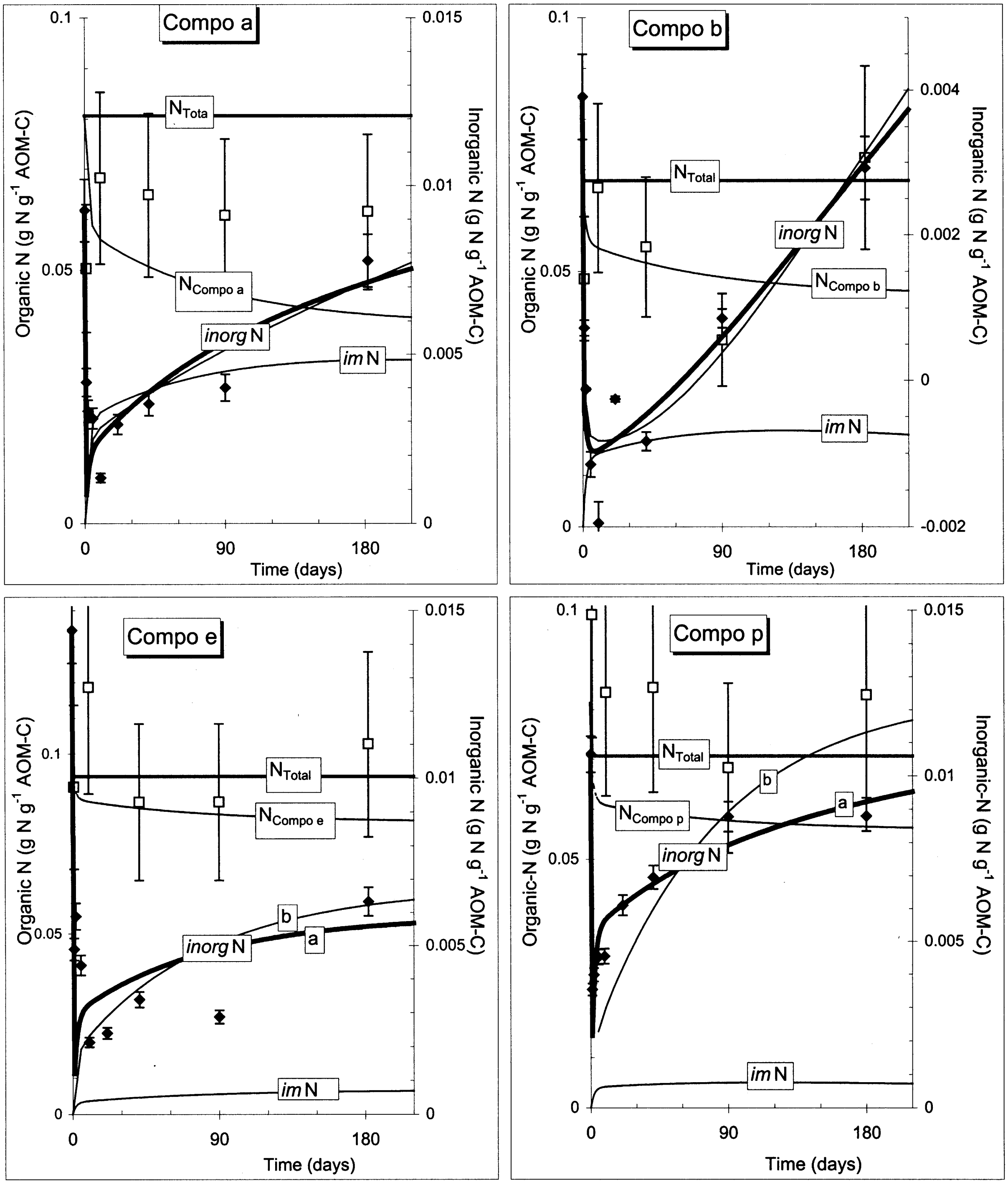

Fig. 4. Mineralization and immobilization of N from composts. Points = experimental data with 95% confidence intervals (◆, inorgN; □, total N from AOM) continuous lines = TAO predictions of inorgN (bold lines: a, prediction with C-to-N of fractions; b, predictions with C-to-N_{AOM}), immobilized N (imN) and remaining N_{AOM} (thin lines).

(1942) and Leclerc (1990) showed that 80 and 60–93% guano-N, respectively, were transformed in NO_3-N in leachates. The removal of NO_3 by leaching was not studied in this experimental design. Total gaseous losses estimated by difference from N_{Total} analyses were about 90% of added N for Guano, and 30% for Chicm. Similar losses for chicken manure were observed by Mahimairaja et al. (1994) and Gagnon and Simard (1999). Gaseous N loss was not demonstrated for Kokoa (quantified to about 10%, i.e. within experimental error) and Featm (about 20%). This experiment highlighted the stabilization effect of the industrial process used to produce the organic fertilizer Gnofer (Fig. 2) by

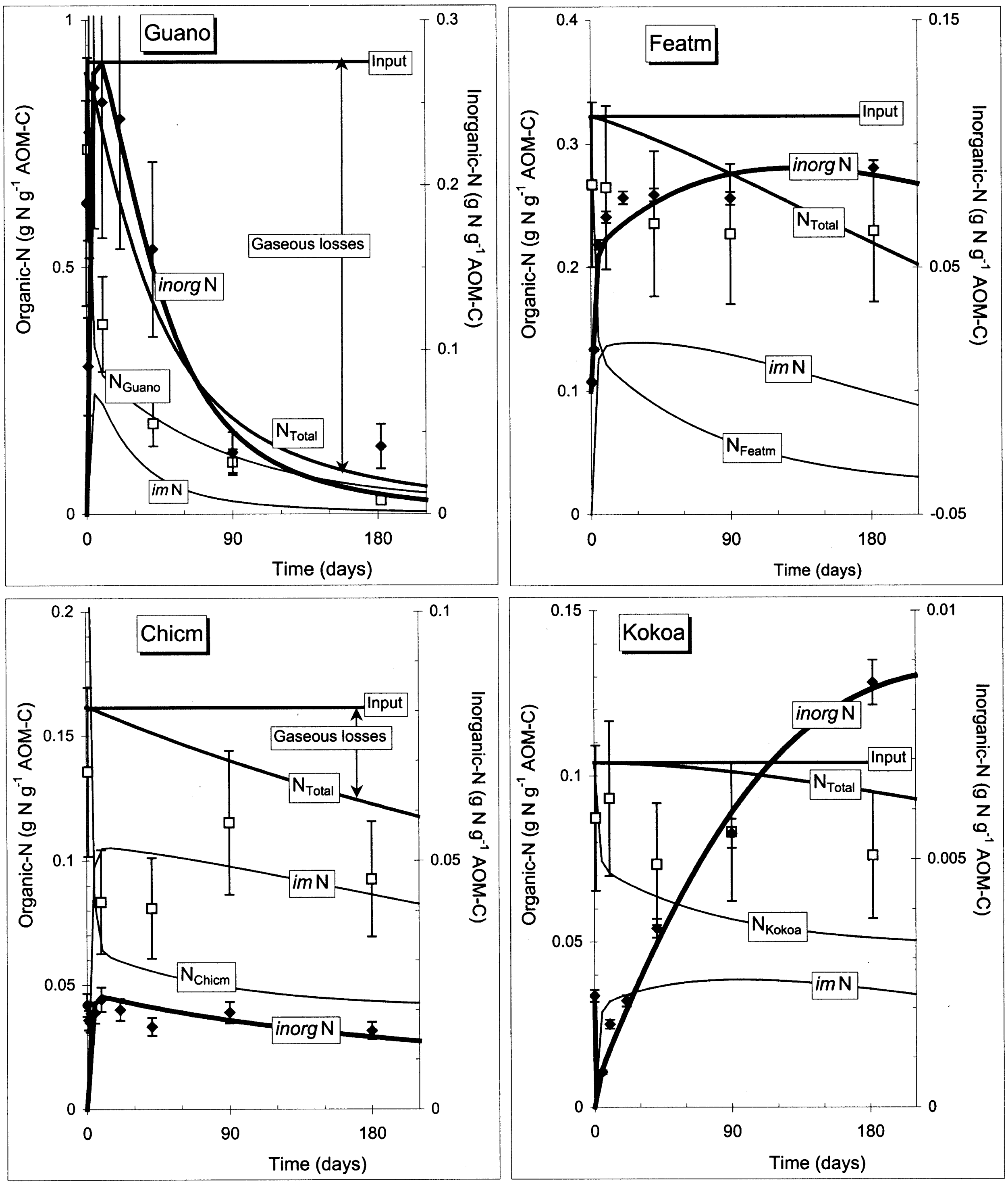

Fig. 5. Mineralization, immobilization and gaseous losses of N from (i) animal-originated AOM: guano (Guano), feather meal (Featm), chicken manure (Chicm), and (ii) plant-originated AOM: cocoa cake (Kokoa). Points = experimental data with 95% confidence intervals (◆, inorgN; □, total N from AOM) continuous lines = TAO predictions of inorgN (bold lines), remaining N_{AOM}, immobilized N (imN) and N_{Total} from AOM (thin lines).

the addition of N-poor plant residues (Wgrap and Olivp) to Guano. The same effect was observed by Mahimairaja et al. (1994) when mixing chicken manure with wheat straw. These are usefull processes for avoiding N volatilization (compare Gnofer, Fig. 2, and Guano, Fig. 5).

3.2. Predictions made with C-to-N ratios of biochemical fractions

All the TAO-inorgN predictions were in good accordance with the data (Figs. 2–5). AOM-N transformations could be predicted for 4 materials using P_{im} only (Table 1): Shepm, Gnofer, Compo e, Compo p. Let $\mathrm{N_{AOM}}$ be the remaining untransformed N in AOM ($\mathrm{N_{Nfeat}}$ and $\mathrm{N_{Shepm}}$ in Fig. 2, $\mathrm{N_{Compo\ e}}$ and $\mathrm{N_{Compo\ p}}$ in Fig. 4) and $\mathrm{N_{Total}}$ the N input from AOM, at any incubation time the curves were plotted in accordance with the balance equation:

$$\mathrm{N_{Total}} - \mathrm{N_{AOM}} = \mathrm{inorgN} + \mathrm{imN} \tag{12}$$

N transformations were predicted for 9 AOM, only with the two N-parameters P_{im} and k_{remin} (Table 1): four plant residues (Fig. 3), the animal residue Nfeat, the fertilizer Comfer (Fig. 2) and three composts (Fig. 4). In these cases, the slope of imN decreased when k_{remin} increased. In this experiment, the highest k_{remin} value was found for Nfeat which explained the strong decrease of imN for this AOM (Fig. 2); after three months of incubation, the balance relationship (Eq. (12)) became: $\mathrm{inorgN} = \mathrm{N_{Total}} - \mathrm{N_{Nfeat}}$. All transformed N was mineralized.

The four other AOM required the three TAO parameters P_{im}, k_{remin} and k_v: three animal N-rich residues Guano, Featm and Chicm, and the atypical plant residue Kokoa (Fig. 5). The highest k_v value was found for Guano with also a high k_{remin} value. Guano presented the highest fraction of very labile compounds and a small fraction of stable compounds (see P'_{L} and P_{S} values, Table 1). It was thus rapidly decomposed (see $\mathrm{N_{Guano}}$ in Fig. 5) into unstable N forms. Important gaseous N-losses occurred from inorgN, this compartment being supplied by further mineralization of imN. By these transfer processes, almost all N was lost under gaseous forms at the end of the incubation (Fig. 5), although Guano represented the highest N-input.

3.3. Predictions using C-to-N ratios of AOM

For 13 of the 17 AOM tested, F tests (Table 1, Eqs. (11) and (11a)) showed $\mathrm{RSS}_{10} > \mathrm{RSS}_4$. The predictions with C-to-N ratios of biochemical fractions thus tended to be better than predictions made with C-to-$\mathrm{N_{AOM}}$ solely, the difference being significant for Nfeat only. In the four other cases ($\mathrm{RSS}_4 > \mathrm{RSS}_{10}$), there were no significant differences. The inorgN predictions by the two methods were plotted in Figs. 2–5. The two simulations were almost similar for Comfer and for Shepm, but slightly different for Gnofer and for Nfeat (Fig. 2). There was only a significant difference for Nfeat because the predictions with biochemical fractions were very close to the data. The two simulations were identical for Coffk and for Wgrap and slightly different for Olivp and for Dgrap (Fig. 3), but the differences were not significant and did not modify the predicted duration and amounts of inorgN immobilization. As for composts, the two methods gave almost the same predictions except for Compo p (Fig. 4), but the difference was not significant. For the four AOM with N-losses, the predictions made with the two methods were identical (Fig. 5).

4. Discussion

4.1. Decomposition and immobilization

Decomposition of AOM was based on C evolution (Eqs. 3 and 4): P_{S} (Table 1) defined the stable non-transformed $\mathrm{N_{AOM}}$, the rate of transformation (slope of $\mathrm{N_{AOM}}$ curve) was related to P'_{L} and P_{R} (Table 1, $P'_{\mathrm{R}} = 1 - P'_{\mathrm{L}} - P_S$). The lowest P_{S} values, for Featm, Guano and Gnofer, showed the lowest remaining $\mathrm{N_{AOM}}$ and a high value of imN (only during the first stage, before volatilization for Guano). Most AOM from plant origin, composts and Nfeat displayed high P_{S} values together with high remaining $\mathrm{N_{AOM}}$ levels and low N immobilization. Compo e and Compo p, with the longest composting times, presented the highest P_{S} value, high $\mathrm{N_{AOM}}$ and low imN levels. The fertilizer Gnofer mineralized more rapidly than Comfer during the early stages ($P'_{\mathrm{L}} = 0.39$ and 0.26, respectively). During the later stages, further Gnofer mineralization and immobilization occurred, resulting from the decomposition of the $\mathrm{N_{Gnofer}}$ resistant compounds ($P'_{\mathrm{R}} = 0.49$, $k_{\mathrm{remin}} = 0$). A more constant mineralization of Comfer from imN ($P'_{\mathrm{R}} = 0.12$, $k_{\mathrm{remin}} = 0.0048$) displayed a more regular pattern.

4.2. C-to-N ratios and transformations of AOM

Predictions made with η_{L}, η_{R} and η_{S} of the first hypothesis (Eq. (4)) were close to those made with η_{AOM} of the second hypothesis (Eq. (10)). This represented a technical advantage since the later required C-to-$\mathrm{N_{AOM}}$ ratios only. Significant correlations were often reported between mineralized-N and C-to-$\mathrm{N_{AOM}}$ ratios (Frankenberger and Abdelmagid, 1985; Quemada and Cabrera, 1995; Trinsoutrot et al., 2000a). The model proposed by Nicolardot et al. (2001) was also based on C-to-$\mathrm{N_{AOM}}$ data. Although the first hypothesis was more logical (Eq. (4)), the correspondences between theoretical and measured fractions (labile-soluble, resistant-holocellulosic, stable-ligneous) remained to be proved. Chesson (1997) considered the soluble fraction as a sum of polysaccharides (poor in N) plus soluble proteins of low molecular weight (very rich in N). On the other hand, as lignin is known to be the least biodegradable plant polymer (Melillo et al., 1982; Heal et al., 1997), ligno-protein N should represent the most recalcitrant part of $\mathrm{N_{AOM}}$.

In order to explain how the two hypotheses were linked (Eqs. (4) and (10)), one should consider the relationships existing between all the C-to-N values. First, these values were linked by the balance Eq. (7). Three significant relationships were computed from Table 1: $\eta_{\mathrm{Sol}} \cong 0.05 \times \eta^2_{\mathrm{AOM}}$, $\eta_{\mathrm{Hol}} \cong 2\eta_{\mathrm{AOM}}$, $\eta_{\mathrm{Lig}} \cong 1.8\eta_{\mathrm{AOM}} - 0.04\,\eta^2_{\mathrm{AOM}}$. From these relationships (curves not shown), $\eta_{\mathrm{Sol}} < \eta_{\mathrm{AOM}}$ for $\eta_{\mathrm{AOM}} < 20$ ($\eta_{\mathrm{Sol}} \le 5$ for $\eta_{\mathrm{AOM}} \le 10$, $\eta_{\mathrm{Sol}} \le 10$ for $\eta_{\mathrm{AOM}} \le 20$), otherwise $\eta_{\mathrm{Sol}} > \eta_{\mathrm{AOM}}$ for $\eta_{\mathrm{AOM}} > 20$. Most soluble compounds were probably proteinaceous molecules for N-rich AOM, and polysaccharides for N-poor ones.

The curvature of η_{Lig} predictions was inverse to that of η_{Sol} (not shown). For $\eta_{AOM} < 15$, $\eta_{Lig} \cong \eta_{AOM}$ otherwise for $\eta_{AOM} > 15$, the slope of η_{Lig} predictions decreased, and η_{Lig} tended to $\cong 18$. This maximum value occurred with plant-originated AOM of C-to-N $\cong$ 19–27. It could be indicative of the minimum N content required for stabilizing ligno-proteinaceous macromolecules. Trinsoutrot et al. (2000b) reported a lignin C-to-N $\cong 21$ for C-to-$N_{AOM} \cong 22$–26. The η_{Hol} values showed the greatest variability but were generally higher than η_{Sol} and η_{Lig}, in accordance with their hemicellulose- and cellulose-like molecular structures.

For the calculation of the stable N fraction, the two predictive methods (Eqs. (4) and (10)) used P_S (Eq. (3)) first. The stable fractions were P_S/η_{Lig} and P_S/η_{AOM} in Eqs. (4) and (10), respectively. Since these two fractions were not very different, the predicted level of TAONF was similar with the two methods. The main differences concerned the slopes of the predictive curves governed by the relative values of P'_L/η_L and P'_L/η_{AOM} on one hand, P'_R/η_R and P'_R/η_{AOM} on the other hand. Although the F-test (Eqs. (11) and (11a)) was only significant for Nfeat (Table 1), Figs. 2–5 showed a good agreement with the shape of measured data by the first method (‘a’ in Figs. 2–4) for some AOM: Gnofer, Nfeat, Olivp, Dgrap, Compo p. The first hypothesis was therefore validated and the second hypothesis was a good approximation of the former one in all the cases tested.

4.3. Conclusions

The TAO (Transformation of Added Organics) model was proposed in this paper as a predictive tool for C mineralization, N mineralization, N immobilization, and N volatilization from added AOM, without taking into account the native SOM. The interest of this work was to relate the TAO-N version to the TAO-C one, which employs the C-to-N ratio of the AOM. The transformed N_{AOM} fraction (TAONF) was higher than the mineralized AOM. In TAO, the split parameter P_{im} allowed us to partition TAONF between mineralized N and immobilized N. A value $P_{im} > 1$ indicated a total immobilization of TAONF, plus a further immobilization ($P_{im} - 1$) of soil inorganic N. The first order kinetic parameter k_{remin} was used according to the AOM type, for regulating a further mineralization from immobilized N. The two parameters P_{im} and k_{remin} were sufficient for predicting various properties of a large range of organic fertilizers. For some AOM with high N content (animal wastes), another first order kinetic parameter k_v was sometimes introduced for predicting a volatilization from N_{AOM}. All the predictions were in good agreement with the data collected from very different AOM: plant residues, manures, animal wastes, organic fertilizers, and amendments.

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