

Limitations of a calculated N mineralization potential in studies of the N mineralization process

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Abstract

Soil is often incubated under controlled conditions to assess its capacity to mineralize nitrogen and to define the N mineralization potential (N_o) by fitting a negative exponential curve to N mineralization data. The specificity of N_o for a given soil and its relevance in N mineralization studies was examined as part of an overall study of the N mineralization process. Soil mixed with an equal amount of sand was aerobically incubated at 35 °C and leached at specific time intervals. Upon leaching, ammonium and nitrate were measured in the extract.

It was found that N mineralization data did not always follow first-order kinetics making it difficult to calculate N_o . The computed N_o value was influenced by the shape of the curve, the duration of the incubation experiment and was reciprocally related to the N mineralization constant (k_{exp}). N_o did not always give an adequate indication of the amount of N mineralized and was not soil specific as the time of sampling largely affected its size. The usefulness of N_o in the simulation of the N mineralization process with a k_{exp} value valid for all soils was limited and a k_{exp} value specific for each soil was required. A value combining the soil specific N_o and k_{exp} values and reflecting the amount of N mineralized over one year was proposed as a suitable alternative to the use of N_o in comparative studies of the N mineralization process. It was concluded that a calculated N_o could not be used in studies comparing the N mineralization of different soils. In addition, the simulation of the N mineralization required the use of the soil specific k_{exp} and could not be carried out with a k_{exp} valid for all soils.

Introduction

The release of inorganic nitrogen through the decomposition of organic matter (N mineralization) is an important process in the study of nitrogen dynamics in the field. Laboratory incubation experiments are thought to be a convenient way of quantifying and studying the N mineralization process (Bremner, 1965; Keeney, 1982).

Stanford and Smith (1972) proposed a straightforward method to quantify the N mineralization capacity of a soil. An equal amount of soil is mixed with coarse sand, placed in a filter tube, moistened, incubated and mineralized N is periodically removed by leaching. A

single negative exponential function:

$$\log(N_o - N_t) = \log N_o - \frac{k_{exp} \times t}{2.303} \quad (1)$$

where:

N_t = cumulative mineralized nitrogen (mg N kg⁻¹)

N_o = nitrogen mineralization potential (mg N kg⁻¹)

k_{exp} = N mineralization constant (day⁻¹)

t = time (day)

is fitted to the N mineralization data and a hypothesized N mineralization potential (N_o) calculated (Stanford and Smith, 1972). It has been suggested that N_o is soil specific, whereas a N mineralization constant (k_{exp}), valid for all soils, can be found (Richter et al., 1982; Stanford and Smith, 1972).

In our study, the Stanford and Smith method (1972) was used to quantify the N mineralization of different soils, to calculate N_o and to study factors affecting it. It

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became apparent, however, throughout our study that N_0 was sometimes difficult to define in relation to the amount of N mineralized. Some of the problems in calculating N_0 , its relation to the amount of N mineralized and its limited value in simulation models are discussed.

Materials and methods

Experimental soils

As part of a previous study of factors affecting the N mineralization process, soil samples were collected from 17 sites and more than 100 incubation experiments were set up. These were selected to represent a range in textures, crop rotations or organic matter applications, and their potential to mineralize N was assessed (Dendooven, 1990). The sites used in the present experiment were selected from the initial study.

Soil samples were collected from the 0–30 cm layer of an experimental site at Zevenbergse hoek (NL) on 26 February 1985 [ZEV1], 21 May 1985 [ZEV2], and 12 June 1985 [ZEV3]; at Neerhespen (B) on 20 May 1986 [NEE1], on 3 June 1986 [NEE2], on 23 June 1986 [NEE3] and on 7 July 1986 [NEE4]; and from different sites around Watervliet (B) [WAT1, WAT2, WAT3, WAT4 and WAT5] on 2 February 1985. Wheat was cultivated on the Neerhespen and the Zevenbergse hoek plots on collection while the plots around Watervliet were fallow. Soil characteristics of the experimental sites are given in Table 1.

Aerobic incubation

Soil samples were moist-sieved (3 mm). The soil was not dried as specified in the original Stanford and Smith (1972) method as desiccation enhances the N mineralization in a rewetted soil (Seneviratne and Wild, 1985; Van Gestel et al., 1991). Fifty g of soil was mixed with 50 g of quartz sand (20 mesh) and added to a filter tube containing a layer of 5 cm glass-wool at the bottom. A layer of 5 cm glass-wool was placed on top of the soil-sand column to avoid disaggregation of the soil and silting up of the soil pores on leaching. Four replicates were prepared for each incubation experiment. At the outset of the incubation, the soil-sand mixture was leached with a 10 mM CaCl_2 solution added in 10 mL portions until a leachate of 250 mL was obtained. The extract was stored at -20°C pending analysis.

The soil-sand mixture was then leached with 100 mL of a nutrient solution containing 2 mM $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 2 mM MgSO_4 , 5 mM $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ and 2.5 mM K_2SO_4 , again added in 10 mL portions. After suction (-80 kPa) to drain excess water, the incubation tubes were sealed at the top with a rubber stopper. The small opening at the bottom of the filter tube was assumed to provide sufficient aeration during the incubation whilst preventing desiccation of the soil-sand mixture. The tubes were then stored at 35°C for at least 84 days and the procedure of leaching with 10 mM CaCl_2 and the nutrient solution was repeated at specific time-intervals. As the amount of N mineralized was highly variable in time, the interval between each leaching was not constant but adjusted to the amount of inorganic N measured in the extracts after the previous leaching. The period between two leaching procedures was prolonged when the concentrations of inorganic N in the extracts dropped to near undetectable concentrations of NH_4^+ -N or NO_3^- -N (below 0.1 mg N L^{-1}). It was assumed that a variation in the incubation interval had no effect on the calculated N mineralization parameters (N_0 and k_{exp}).

Chemical analysis

NH_4^+ -N and NO_3^- -N in the extracts were measured by continuous flow analysis on an automatic analyser (Skalar, NL). Nitrate was enzymatically reduced to nitrite and photometrically determined by the Griess reaction while ammonium was photometrically determined with a modified Berthelot reaction (Keeney and Nelson, 1982).

Calculation of nitrogen mineralization coefficients

N_0 and k_{exp} were calculated with the SAS statistical package (SAS Institute, 1988) using a non linear least square curve-fitting technique (Proc NLIN, method Marquardt). The values of N_0 and k_{exp} that gave the smallest residual sum of squares were retained with the only restriction that N_0 had to be larger than the total cumulative mineralized nitrogen.

Results and discussion

Nitrogen mineralization curves

N mineralization data gave different types of curves (Figs. 1, 2 and 3). They followed negative exponential

Table 1. Soil characteristics of the experimental sites

6-8 Soil	pH H ₂ O	Total		Texture			Class ^a
		C (g kg ⁻¹)	N (g kg ⁻¹)	Clay	Loam (g kg ⁻¹)	Sand	
Watervliet 1	7.75	24.6	2.7	143	297	560	Sandy loam
Watervliet 2	7.75	18.7	2.2	142	329	529	Sandy loam
Watervliet 3	8.25	12.0	1.5	210	345	445	Loam
Watervliet 4	8.20	9.4	1.2	131	474	395	Loam
Watervliet 5	8.00	8.2	1.1	203	356	441	Loam
Zevenbergse hoek	8.04	14.5	1.5	130	536	334	Silt loam
Neerhespen	6.85	10.6	1.1	96	125	790	Sandy loam

^a USDA soil classification.

(ZEV1, WAT1, WAT2, WAT3, WAT4, and WAT5), near linear (NEE1, NEE2, ZEV2, and ZEV3) or sigmoid curves (NEE3 and NEE4). Zero-order kinetics for N mineralization were reported by Tabatabai and Al-Khafaji (1980) and Addiscott (1983), first-order kinetics by Kirkham and Bartholomew (1955), Stanford and Smith (1972) and Cabrera and Kissel (1988) while sigmoid curves were found by Haque and Walmley (1972) and Chae and Tabatabai (1986). The function described by N mineralization data was sometimes related to the C-to-N ratio of the organic material applied (Dendooven, 1990). Negative exponential curves were often obtained when organic materials with a small C-to-N ratio were applied to a soil, e.g. bean leaves with a C-to-N ratio of 13.4. Sigmoid curves were often obtained in soils amended with organic material with a large C-to-N ratio, e.g. bean roots with a C-to-N ratio of 43.5. Near linear curves were found in soils from different texture, irrespective of their organic matter content and addition of organic materials.

As the N mineralization data did not always obey first-order kinetics, fitting a negative exponential function to those data is questionable. The computation of a N_0 value from such sigmoid curves is doubtful as indicated by Bonde and Lindberg (1988).

Time of sampling

The time of sampling had an important impact on the amount of N mineralized, the N mineralization curves and consequently on the calculated N_0 . N mineralization in soil from the experimental site at Zevenbergse hoek decreased from February to June (Fig. 1). Bonde and Rosswall (1987) found that mineralized N

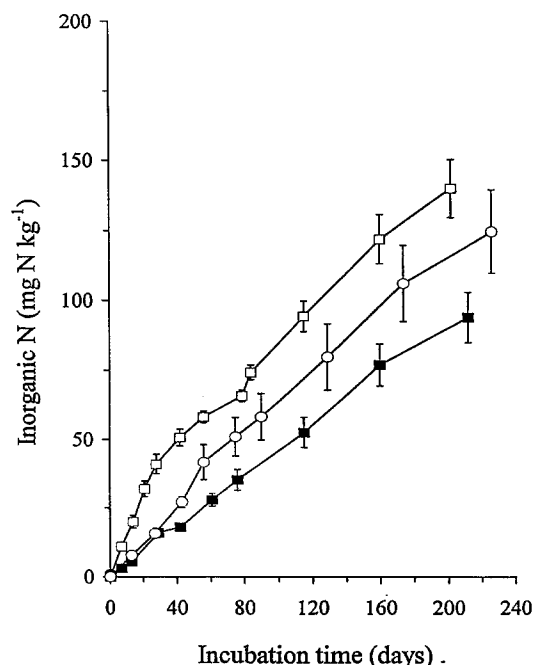


Fig. 1. Cumulative mineralized nitrogen (mg N kg⁻¹) from the Zevenbergse hoek soil for samples collected on 26.02.1985 (□) ZEV1, on 21.05.1985 (○) ZEV2, and on day 12.06.1985 (■) ZEV3. Aerobic incubation for 200 days at 35 °C. Bars indicate plus and minus standard deviation.

decreased in samples taken from April to August. This could be due to a decrease in readily decomposable organic material, i.e. crop residues from the previous season. The size of N_0 in our samples, however, increased with time (Table 2) and can be related to the shape of the N mineralization curves. A nearly straight curve (ZEV3) gave a greater N_0 value than a curve

Table 2. N_{exp} values (mg N kg^{-1}) calculated with an overall k_{exp} and a sample specific k_{exp} (day^{-1}). Aerobic incubation for 200 days at 35°C

Soil	Sampling time	k_{exp}		N_0		
		$(10^{-3} \text{ day}^{-1})$	$k_{\text{exp}}^{\text{a}}$	$N_{\text{exp}}^{\text{b}}$	$N_{\text{exp}}^{\text{c}}$	N_{exp}^*
ZEV1	Feb. 26, 1985	2.44	8.91	187	103	32
ZEV2	May 21, 1985	1.80	8.91	338	115	25
ZEV3	June 12, 1985	1.05	8.91	481	163	23
WAT2	Feb.02, 1985	10.52	8.91	205	70	79

^a Average value of 102N mineralization constants (Dendooven, 1990) obtained through a non-linear least square curve-fitting of N mineralization data.

^b $N_{\text{exp}} = N_0 \times (1 - e(0.00891 \times 365/7.86))$ where 7.81 is a temperature reduction factor converting the N mineralization constant from an incubation at 35°C to an annual average field temperature of 10°C (Dendooven et al., 1987) and 365 is a period of 1 y.

^c $N_{\text{exp}} = N_0 \times (1 - e(-k_{\text{exp}} / 7.86 \times 365))$ where k_{exp} is the soil specific N mineralization constant.

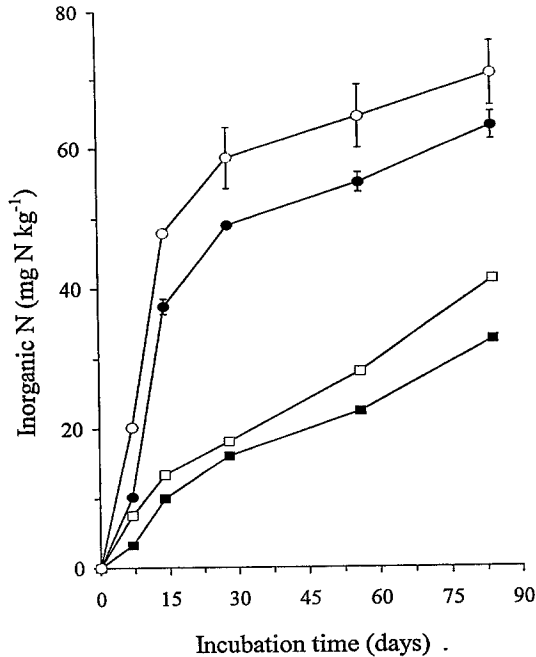


Fig. 2. Cumulative mineralized nitrogen (mg N kg^{-1}) from the Neerhespen hoek soil for samples collected on 20.05.1986 (\square) NEE1, on 03.06.1986 (\blacksquare) NEE2, on day 23.06.1986 (\circ) NEE3 and on day 07.07.1986 (\bullet) NEE4. Aerobic incubation for 84 days at 35°C . Bars indicate plus and minus standard deviation.

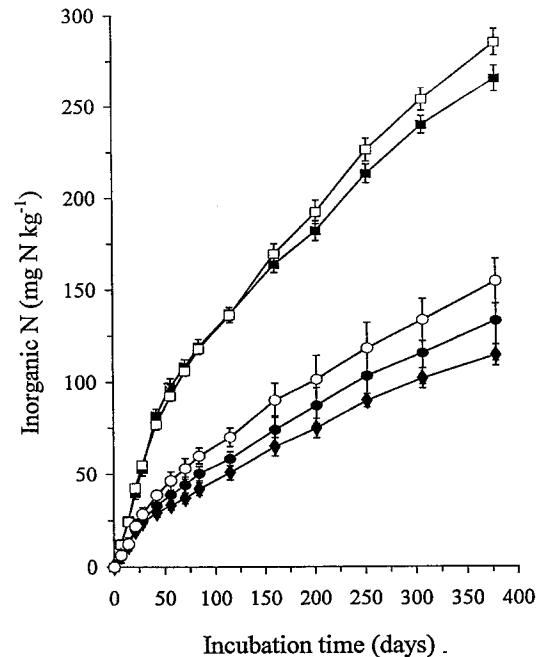


Fig. 3. Cumulative mineralized nitrogen (mg N kg^{-1}) from the Neerhespen hoek soil for samples collected from the Watervliet region with (\square) WAT1, (\blacksquare) WAT2, (\circ) WAT3, (\bullet) from WAT4, and (\blacklozenge) from WAT5. Aerobic incubation for 379 days at 35°C . Bars indicate plus and minus standard deviation.

following a negative exponential function (ZEV1): N_0 is the asymptotic limit of the curve.

N mineralization in the Neerhespen soil increased from May to July (Fig. 2). Samples collected later in the summer (NEE3 and NEE4) mineralized nearly twice as much as those collected earlier (NEE1 and NEE2). This

difference was probably due to the application of $40 \text{ kg fertilizer N ha}^{-1}$ on 12.06.86. The fertilizer N could induce a bigger root system or one with a lower C-to-N ratio and part of the fertilizer N could be immobilized into the microbial biomass (Jenkinson et al., 1985). A subsequent incubation with soil sampled later in the

year could thus give higher amounts of N mineralized as compared to soil sampled before the application of fertilizer N. More root material or root material with a lower C-to-N ratio would be mineralized and immobilized N would be re-mineralized.

Incubation time

The calculated value of the N mineralization potential depended largely on the duration of the incubation. An example of the variations in N_0 with length of incubation is given in Table 3. N_0 for the WAT1 soil was large when calculated after 28 days, i.e. 7380 mg N kg⁻¹ but dropped to a more acceptable value of 173 mg N kg⁻¹ after 115 days and then increased with prolonged incubation and to a value of 310 mg N kg⁻¹ after 379 days. A similar variation in N_0 values, although less extreme, was found when soil samples from the other experimental sites in the Watervliet region were incubated. Paustian (1987) stated that the length of incubation together with the treatment of the initial mineralization phase appeared to be the most important factors determining estimates of k_{exp} and N_0 .

Reciprocal relation between N_0 and k_{exp}

The variation in N_0 with prolonged incubation can be partly ascribed to the calculation of two unknown reciprocally related parameters (N_0 and k_{exp}) (Table 3). Inverse relationships between N_0 and k_{exp} were also found by Mary and Rémy (1978), Paustian (1987) and Bonde and Rosswall (1987). To overcome variation in the N_0 value and to incorporate its reciprocal relation with k_{exp} , Mary and Rémy (1978) proposed the use of the product of N_0 and k_{exp} as an indication of the N mineralization capacity of soil. This function, i.e. $N_0 \times k_{exp}$ is more constant than N_0 (Table 3) but is not applicable as it has no direct biological meaning. A new expression ' N_{texp} ' was proposed, combining the computed N_0 and k_{exp} values which reflects the amount of N mineralized over 1 year, assuming an average annual temperature of 10 °C to approximate that in Western Europe. N_{texp} was calculated in the following way :

$$N_{texp} = N_0 \times (1 - e(-k_{exp}^{10^\circ C} \times 365)) \quad (2)$$

$$k_{exp}^{10^\circ C} = k_{exp}/7.86 \quad (3)$$

where: 7.86 = is a temperature reduction factor converting the N mineralization constant from an incubation at 35 °C to a annual average field temperature of 10 °C (Dendooven et al., 1987)

$$k_{exp}^{10^\circ C} = \text{N mineralization constant at } 10^\circ \text{C} \quad (\text{day}^{-1})$$

365 = number of days

The postulated N_{texp} values are more constant within a particular soil and less dependent on the duration of the incubation (Table 3).

N_0 and amounts N mineralized

The usefulness of N_0 values in comparative studies of N mineralization was limited. First of all, N_0 did not reflect the changes in time in the amounts of N mineralized for a given soil. Thus N_0 for ZEV3 (481 mg N kg⁻¹) was greater than the N_0 for ZEV1 (187 mg N kg⁻¹) (Table 2) even though ZEV1 mineralized more than ZEV3 (Fig. 1). The N_{texp} values (32 mg N kg⁻¹ for ZEV1 and 23 mg N kg⁻¹ for ZEV3) gave a better indication of the N mineralization potential than the N_0 values.

Secondly, N_0 values could not be used to compare the N mineralization capacity of different soils. The N_0 value for the WAT2 soil (205 mg N kg⁻¹) was smaller than that for ZEV3 (481 mg N kg⁻¹), although that the amount of N mineralized was greater in the WAT2 soil (Fig. 3) than in ZEV3 soil (Fig.1). The N_{texp} values (79 mg N kg⁻¹ for WAT2 and 23 mg N kg⁻¹ for ZEV3) (Table 2), gave a better indication of the N mineralization capacity than the N_0 values.

The limited use of N_0 was related to the shape of the N mineralization curves obtained. A N_0 value derived from a near straight line overestimated the N mineralization potential. The asymptotic limit of the curve (or N_0) was much greater than the amounts of N mineralized.

The use of N_0 in simulation models

The simulation of the N mineralization with a k_{exp} value valid for all soils and a N_0 specific for a given soil has to be carried out with care. If the N_{texp} value was calculated with the soil specific N_0 and k_{exp} values (Eq. 2) and compared with a N_{texp} value calculated with the soil specific N_0 value but with an overall k_{exp} , e.g. the mean of 102 k_{exp} values (Dendooven, 1990) i.e.:

$$N_{texp}^* = N_0 \times (1 - e(0.00891/7.81 \times 365)) \quad (4)$$

Table 3. k_{exp} , N_0 , N_{texp} and $N_0 \times k_{\text{exp}}$ values for the Watervliet 1 soil calculated after different periods of incubation and that from 28 days onwards. Aerobic incubation for 379 days at 35 °C

Incubation time (days)	k_{exp} (day ⁻¹)	N_0 N_{texp}^a		$N_0 \times k_{\text{exp}}$ (mg N kg ⁻¹ day ⁻¹)
		(mg N kg ⁻¹)		
28	0.0002	7380	68	1.5
42	0.0021	852	79	1.8
56	0.0085	250	81	2.1
70	0.0110	202	81	2.2
84	0.0126	181	80	2.3
115	0.0135	173	80	2.3
160	0.0111	197	80	2.2
202	0.0100	210	78	2.1
252	0.0082	239	76	2.0
307	0.0065	275	72	1.8
379	0.0054	310	69	1.7

^a $N_{\text{texp}} = N_0 \times (1 - e^{-(k_{\text{exp}} / 7.86 \times 365)})$ where k_{exp} is the soil specific N mineralization constant, 7.81 a temperature reduction factor converting the N mineralization constant from an incubation at 35 °C to an annual average field temperature of 10 °C (Dendooven et al., 1987) and 365 is a period of 1y.

where: 0.00891 = the mean of 102 k_{exp} values obtained through a non-linear least square curve-fitting of N mineralization data (Dendooven, 1990)

an over- or under-estimation of N_{texp} for the present soils was often observed. For example, an underestimation was observed for the WAT2 soil as N_{texp} (79 mg N kg⁻¹) was greater than the N_{texp}^* value (70 mg N kg⁻¹) (Table 2). A large over-estimation was found for the ZEV3 soil because N_{texp} was only 23 mg N kg⁻¹ but N_{texp}^* was 163 mg N kg⁻¹.

It was concluded that N_0 was of limited value in defining the N mineralization capacity of a soil and should be used with care when comparing the N mineralization of different soils. N_0 was influenced by the duration of the incubation, its reciprocal relationship with k_{exp} and the shape of the N mineralization curve. The N_{texp} value, i.e. or the amount of N mineralized over a period of one year for a soil with an average annual temperature of 10 °C, was less dependent on the duration of the incubation and the shape of the N mineralization curve. It appeared therefore to be more suitable for use in comparative studies of the N mineralization process than N_0 .

The simulation of the N mineralization should be carried out with a plot or field specific k_{exp} and not with an averaged one valid for all soils. However, factors affecting the N mineralization potential of a soil,

such as growing plants, organic material applications or N fertilizer dressings, are not taken into account in relatively straightforward models. Including these factors in the simulation of the N mineralization requires a more mechanistic approach of the N mineralization process.

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