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Determination of potentially mineralizable nitrogen in agricultural soil

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Abstract Potentially mineralizable soil N was determined after incubation for 2, 4, 8, 12, 16, 22, and 30 weeks, according to the Stanford and Smith method. A first-order kinetics model was used, and a simulation study was performed using three different statistical methods to estimate potentially mineralizable N and the rate constant k . The first method was based on the maximum-likelihood approach. The second one relied on non-linear least square data fitting. The third method was based on linear or logarithmically transformed data. The results of the simulation study suggested that the non-linear least square method was preferable to the others. This method was then applied to real data from 30 different Italian soils. The values obtained for potentially mineralizable N were, on average, 10% of total N (mean standard error = 0.9). The estimated value of k was 0.050 (mean standard error = 0.005). Finally, from the values obtained for k and the results of the simulation, the results indicated that significantly less reliable estimates of potentially mineralizable N were obtained by using data for up to only 22 weeks of incubation.

Key words Statistical methods · Mineralization · Nitrogen · First-order kinetics · Incubation experiment · Model for N mineralization

Introduction

N mineralization makes a key contribution to the amount of available N in soil. However, no fast, accurate, and seri-

al methods are available to determine mineralizable N, especially in field conditions (Skjemstad et al. 1988). The numerous references in the literature on this topic distinguish between chemical and biological determinations. The chemical methods are based on the extraction of mineral N using different extractants such as boiling water (Jenkinson 1968; Stanford 1969; Verstraeten et al. 1970), acid, alkaline, and salt solution (e.g., 0.01 M CaCl₂), or by determination of the NH₄⁺ released during alkaline permanganate oxidation (Trough 1954; Stanford 1978; Richter et al. 1994). The biological methods make use of soil incubation under controlled conditions of moisture and temperature for a length of time ranging from one to many weeks (Delphin 1986; Catroux et al. 1987; Tabatabai and Al-Khafaji 1988). The results of these methods are difficult to interpret and show their limitations when transferred to open field conditions.

In 1972 decisive progress was made by Stanford and Smith with their method based on leaching, at predetermined times, the N mineralized at 35 °C, to simulate plant uptake. They described N mineralization by a first-order kinetics model according to the following equation (1):

$$N_t = N_0(1 - e^{-kt}) \quad (1)$$

where N_t is N mineralized in the time considered, N_0 the potentially mineralizable N in the soil (i.e., the maximum quantity of N that the soil can mineralize), and k the rate constant expressed week⁻¹. Stanford and Smith (1972) estimated k by using the maximum likelihood method and obtained the value 0.054 ± 0.009 week⁻¹. Subsequently, many authors have studied the adequacy of first-order kinetics to describe the N mineralization rate (Juma et al. 1984; Dendooven et al. 1991) and this is considered to represent a correct description of the mineralization course (Bonde and Roswall 1987). Recent studies have shown that when Stanford and Smith's method is used in a controlled environment the values obtained are too high (Cabrera and Kissel 1988), due to many factors, including the use in the laboratory of disturbed soil samples (Stanford and Epstein 1974; Smith et al. 1977; Smith et al. 1980; Smith et al. 1982; Griffin and Laine 1983;

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Frankenberger and Abkelmagid 1985). In particular, Hadas et al. (1989) pointed out that the mineralization in the field is 13–26% lower than the calculated values.

The objectives of the present study were (1) to assess by a simulation approach, the goodness of three different statistical methods for estimating N_0 and k in a first-order kinetics model for a special case of correlated errors; (2) to check the adequacy of a first-order kinetics model to describe N mineralization data from 30 Italian soils by applying the best method to the real data, and obtain a mean value for the estimate of the constant rate k together with an interval of variation; and (3) to study the possibility of achieving reductions in the maximum incubation time because the length of time necessary to carry out the determinations represents the main difficulty in the serial use of this technique (Menasseri et al. 1994).

Materials and methods

The research was carried out using 30 soils sampled from the arable layer (0–40 cm) of experimental fields of the Institute for Plant Nutrition (ISNP) located in central and northern Italy. These soils are of alluvial, volcanic, and volcanic cyneritic origin and were sampled during the uncultivated period between two crops.

The chemical and physical properties of the soils (Table 1) were determined by Italian Society of Soil Science (1985) methods. Potentially mineralizable N data (Table 2) were measured following the

method proposed by Stanford and Smith (1972), partially modified by Benedetti (1983). In this measurement 50 g of soil, air-dried and sieved through a 2-mm screen, was mixed with quartz sand in a 1:1 ratio (sand particle size, 0.2–0.8 mm) and incubated in a Buchner funnel (outer diameter 13 cm), at 60% water-holding capacity and at 30 °C for 30 weeks. The mineral N in the soil was leached before incubation by adding 900 ml CaSO_4 solution and 100 ml nutrient solution without N (0.002 M $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, 0.005 M $\text{Ca}(\text{H}_2\text{PO}_4)$, 0.0025 M K_2SO_4 , 0.002 M MgSO_4). NO_3^- -N and NH_4^+ -N concentrations were measured periodically (after 2, 4, 8, 12, 16, 22, and 30 weeks) using an Autoanalyzer Techniton II. At the end of the incubation period, exchangeable NH_4^+ -N was extracted, using a 2 N KCl solution following the Bremner procedure (1965). All analyses were carried out in triplicate.

Statistical analysis

With $t_1 = 2$, $t_2 = 4$, $t_3 = 8$, $t_4 = 12$, $t_5 = 16$, $t_6 = 22$, $t_7 = 30$ representing the (cumulative) incubation times in weeks, the experimental (cumulative) value N_i for the N mineralized during time $0-t_i$ was obtained as the sum of the i values y_1, \dots, y_i for the N mineralized during the first i consecutive incubations, that is (2):

$$N_i = \sum_{j=1}^i y_j \quad (2)$$

The variables $y_j, j = 1, \dots, 7$ are affected by errors, and we assumed the errors $e_j, j = 1, \dots, 7$ to be uncorrelated and Gaussian-distributed, with mean zero and variance σ^2 . Therefore (3):

$$N_i = N_0(1 - e^{-kt_i}) + \tilde{e}_i \quad (3)$$

Table 1 Some physical and chemical properties of soils tested (total N, organic C, and humus calculated on dry-weight basis; 105 °C). RM, Roma; FR, Frosinone

Sample	Location	Texture	pH (1:2.5)	Field capacity (%)	Total N (Kjeldahl) (%)	Organic C (Springer- Klee) (%)	C:N	Humus (organic C × 1.724) (%)
1	Mantova	Silty loam	8.1	24.5	0.08	1.20	15	2.10
2	Città Castello	Sandy silty clay	7.9	34.5	0.13	1.18	9	2.03
3	Mazzano (RM)	Sandy	7.5	18.0	0.18	2.44	14	4.21
4	Settecamini (RM)	Sandy loam	7.8	17.4	0.05	0.50	13	0.86
5	Celimontana (RM)	Sandy loam	7.2	24.0	0.15	1.91	13	3.29
6	Colleferro (FR)	Sandy silty clay	5.8	40.3	0.04	0.27	7	0.46
7	Anagni (FR)	Clay loam	5.9	27.6	0.12	1.07	9	1.85
8	Paliano (FR)	Clay	5.8	28.5	0.08	0.09	8	1.35
11	Frosinone	Sandy	7.8	20.0	0.11	0.92	8	1.59
12	Frosinone	Silty loam	6.9	23.9	0.11	1.05	9	1.81
13	Frosinone	Sandy silty loam	7.8	22.2	0.14	1.26	9	2.17
14	Paliano (FR)	Loam	7.2	24.2	0.11	1.18	11	2.03
15	Anagni (FR)	Loam	6.8	20.0	0.07	0.73	10	1.26
16	Anagni (FR)	Loam	6.8	25.9	0.13	1.26	10	2.17
17	Ferentino (FR)	Loam	7.1	22.6	0.19	2.32	12	3.99
18	Paliano (FR)	Clay	6.2	30.9	0.12	1.20	10	2.06
19	Anagni (FR)	Clay	6.5	34.6	0.19	1.76	9	3.03
20	Anagni (FR)	Clay	7.0	41.5	0.09	1.00	11	1.72
21	Paliano (FR)	Clay	5.5	25.7	0.15	1.42	9	2.44
22	Anagni (FR)	Sandy loam	7.6	19.9	0.10	1.16	12	2.00
23	Anagni (FR)	Clay	6.6	33.3	0.10	0.94	9	1.62
24	Paliano (FR)	Clay	6.8	33.9	0.08	0.86	11	1.48
25	Anagni (FR)	Sandy loam	7.6	19.9	0.11	1.20	11	2.06
26	Anagni (FR)	Sandy loam	7.1	20.8	0.10	1.07	11	2.06
27	Anagni (FR)	Sandy loam	6.6	13.4	0.05	0.44	8	0.76
28	Ferentino (FR)	Sandy loam	7.6	17.6	0.11	1.04	9	1.79
29	Ferentino (FR)	Silty loam	6.2	45.9	0.28	3.06	11	5.26
30	Torice (FR)	Silty loam	7.9	22.0	0.11	1.12	10	1.93
31	Paliano (FR)	Silty clay loam	5.7	34.8	0.06	0.57	9	0.198
32	Ferentino (FR)	Loam	6.7	18.3	0.09	0.85	9	1.46

Table 2 Potentially mineralizable N (mg kg⁻¹ dry weight); cumulative experimental values

	Weeks							
	0	2	4	8	12	16	22	30
1	12.5	7.0	14.5	22.8	26.0	53.0	63.3	70.8
2	66.0	19.0	26.0	35.0	35.0	35.0	35.0	35.0
3	80.0	41.0	59.0	75.0	95.0	115.0	133.0	155.0
4	8.0	7.4	16.4	20.6	22.8	28.7	35.0	41.0
5	80.0	80.0	135.0	204.0	256.0	304.0	344.0	386.0
6	25.0	0.0	11.0	20.0	20.0	20.0	20.0	20.0
7	15.0	2.0	13.8	19.6	25.0	35.0	47.6	83.8
8	48.0	14.2	37.6	53.9	67.7	76.1	86.9	98.7
11	17.5	21.3	39.4	44.0	53.6	64.3	76.0	92.0
12	19.2	21.0	29.8	33.3	41.1	50.6	66.7	77.5
13	8.7	13.7	22.1	27.2	37.3	48.1	58.8	77.7
14	13.0	8.0	14.4	21.4	24.7	34.7	42.4	52.3
15	9.8	11.5	18.0	23.4	30.6	39.4	48.4	58.0
16	12.5	15.6	21.1	26.0	33.8	42.3	50.6	63.0
17	42.8	19.9	30.0	34.9	42.0	58.7	71.1	102.2
18	26.6	8.5	14.3	22.8	26.0	36.1	44.3	53.3
19	10.4	18.6	25.3	30.0	37.9	47.3	61.8	95.2
20	15.3	7.8	15.3	23.1	27.1	39.1	46.0	55.2
21	34.6	11.4	17.3	26.6	30.4	39.5	47.0	56.2
22	12.7	10.7	18.3	26.6	33.3	40.3	50.0	62.3
23	14.8	6.4	13.4	22.6	28.9	36.2	46.2	62.4
24	9.9	10.1	15.7	25.0	29.0	39.0	49.3	64.1
25	41.6	6.0	12.4	19.9	26.5	33.3	44.5	56.3
26	10.9	8.3	15.0	22.5	28.8	36.0	44.7	58.6
27	20.2	7.8	14.9	23.5	30.0	36.6	45.9	59.0
28	10.5	6.2	12.2	20.2	26.7	33.5	42.0	58.0
29	90.8	122.3	129.5	172.6	198.0	238.6	302.1	346.8
30	27.9	11.6	17.2	27.7	32.1	42.2	50.5	74.7
31	7.3	5.7	11.4	18.8	23.9	29.4	37.1	47.5
32	9.2	9.2	15.0	22.7	27.5	37.5	44.7	54.1

where $\tilde{e}_i = \sum_{j=1}^i e_j$, k is the rate constant expressed per week, and t_i the incubation time in weeks. Then, the variables \tilde{e}_i , $i = 1, \dots, 7$ will also be Gaussian-distributed, with mean zero and covariance matrix C (Johnson and Wichern 1988) given by (4):

$$C = \sigma^2 \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 2 & 2 & 2 & 2 & 2 & 2 \\ 1 & 2 & 3 & 3 & 3 & 3 & 3 \\ 1 & 2 & 3 & 4 & 4 & 4 & 4 \\ 1 & 2 & 3 & 4 & 5 & 5 & 5 \\ 1 & 2 & 3 & 4 & 5 & 6 & 6 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 \end{pmatrix} \quad (4)$$

The joint distribution $f(N_1, \dots, N_7)$ for the variables N_i , $i = 1, \dots, 7$ will then be given by (5):

$$f(N_1, \dots, N_7) = \frac{1}{(2\pi)^{7/2} |C|^{1/2}} \exp \left[-\frac{1}{2} \sum_{i,j=1}^7 [N_i - N_0(1 - e^{-kt_i})] \cdot C_{ij}^{-1} [N_j - N_0(1 - e^{-kt_j})] \right] \quad (5)$$

where C_{ij}^{-1} is the element (i, j) of the inverse of the matrix C , and $||$ indicates the determinant of a matrix. In the maximum likelihood method, N_0 and k are estimated by maximizing the likelihood function f with respect to N_0 and k . This is equivalent to minimizing the function $F(N_0, k)$ (6):

$$F(N_0, k) = \sum_{i,j=1}^7 [N_i - N_0(1 - e^{-kt_i})] C_{ij}^{-1} [N_j - N_0(1 - e^{-kt_j})] \quad (6)$$

For a fixed k , the minimum of $F(N_0, k)$ is found by imposing the derivative $\frac{\partial N_0}{\partial F(N_0, k)} = 0$. This equation is solved as (7):

$$N_0 = \frac{\sum_{i,j=1}^7 [N_i C_{ij}^{-1} (1 - e^{-kt_i}) + (1 - e^{-kt_i}) C_{ij}^{-1} N_j]}{2 \sum_{i,j=1}^7 [(1 - e^{-kt_i}) C_{ij}^{-1} (1 - e^{-kt_j})]} \quad (7)$$

In the last equation, N_0 is a function of k alone, since both N_i and t_i , $i = 1, \dots, 7$ are known; thus, by introducing Eq. 7 into Eq. 6, F can be minimized as a function of k alone. This is done by the iterative Newton method (Wolfe 1978), which was stopped when the percentage difference of the values for F , N_0 , and k corresponding to two consecutive iterations was less than 10^{-4} .

The non-linear least square method (Smith et al. 1980) is based on minimizing the sum of the square of the deviations between the experimental data N_i and the corresponding model prevision $N_0(1 - e^{-kt_i})$, that is (8):

$$\bar{F}(N_0, k) = \sum_{i=1}^7 [N_i - N_0(1 - e^{-kt_i})]^2 \quad (8)$$

Since the functions F and \bar{F} have a similar structure, the same kind of procedure described for F was used to minimize \bar{F} .

Finally, the log-transformed linear least square method, proposed by Stanford and Smith (1972), is based on the equation $N_i = N_0(1 - e^{-kt_i})$ expressed in logarithmic form (9):

$$\log(N_0 - N_i) = \log(N_0) - kt_i/2.303 \quad (9)$$

By fixing a value of N_0 in the left side of this equation, a linear regression between the variables $\log(N_0 - N_i)$ and t_i can be performed to estimate k . An "optimal" value for N_0 is found by using an iterative procedure which involves repeated regressions based on different choices of N_0 . The best value of N_0 and k is the one that produces a regression with the greatest coefficient of determination r^2 .

Results and discussion

We present here the results from a simulation study used to assess the goodness of using different methods to estimate the parameters N_0 and k of a first-order kinetics model. The results obtained using the best of the three methods on data from 30 soils are also shown.

In the simulation study, we used samples from the statistical distribution of Eq. 5. The value chosen for N_0 was 100, while three different values for k were used, $k = 0.03, 0.05, 0.07$ week⁻¹. The value used for σ^2 was (4 ppm)². The three methods were applied to each sample replication by applying each of the three values of k ; thus estimates of N_0 and k were obtained. The sample average and standard deviation of the estimated quantities were computed for each value of k and for each of the three methods (Table 3). The number of replications used was 20000, and no significant changes in the averages or standard deviations appeared with only 10000 replications or with different samples. Table 3 also shows

Table 3 Estimates (means \pm SD) of N_0 and k obtained by using the maximum likelihood (ML), non-linear least square (NLLS), and log-transformed linear least square (LTLS) methods on simulated data. The values of the root mean square (RMS) deviations between the data and the model prediction are also shown

Methods	30 weeks			22 weeks		
	N_0 (ppm)	k (week $^{-1}$)	RMS (ppm)	N_0 (ppm)	k (week $^{-1}$)	RMS (ppm)
Total N = 100 ($1 - e^{-0.03t}$)						
ML	108 \pm 32	0.03 \pm 0.01	1.5 \pm 1.0	115 \pm 53	0.03 \pm 0.01	1.4 \pm 0.7
NLLS	108 \pm 34	0.03 \pm 0.01	1.2 \pm 0.5	115 \pm 53	0.03 \pm 0.01	1.1 \pm 0.5
LTLS	112 \pm 43	0.03 \pm 0.01	1.9 \pm 1.0	129 \pm 73	0.03 \pm 0.02	1.9 \pm 1.0
Total N = 100 ($1 - e^{-0.05t}$)						
ML	101 \pm 11	0.050 \pm 0.009	1.3 \pm 0.5	104 \pm 19	0.05 \pm 0.01	1.2 \pm 0.5
NLLS	102 \pm 12	0.05 \pm 0.01	1.2 \pm 0.4	106 \pm 24	0.05 \pm 0.01	1.1 \pm 0.4
LTLS	102 \pm 12	0.05 \pm 0.01	1.9 \pm 1.0	106 \pm 26	0.05 \pm 0.02	1.8 \pm 1.0
Total N = 100 ($1 - e^{-0.07t}$)						
ML	101 \pm 7	0.070 \pm 0.008	1.4 \pm 0.5	101 \pm 10	0.07 \pm 0.01	1.2 \pm 0.5
NLLS	101 \pm 8	0.070 \pm 0.009	1.2 \pm 0.4	101 \pm 11	0.07 \pm 0.01	1.0 \pm 0.4
LTLS	101 \pm 8	0.07 \pm 0.01	2.0 \pm 1.0	102 \pm 12	0.07 \pm 0.01	1.8 \pm 1.0

the results obtained using only the time parameter (up to 22 weeks). These results show that the maximum likelihood method performed better than the other two. The average N_0 and k values obtained with the maximum likelihood method were always the closest, or as close as the others, to the true values, and the standard deviations of N_0 and k were always the smallest, or as small as the others. However, the differences between the results of the maximum likelihood and the non-linear least square methods were small and the non-linear least square method consistently gave the best agreement between data and the prediction by the model. This is coherent with the results obtained by Smith et al. (1980), Molina et al. (1980), and Talpaz et al. (1981).

Furthermore, the non-linear least square method has less computation complexity. We therefore prefer this method over the other two for estimating the parameters N_0 and k . We applied it to data from 30 Italian soils.

In Fig. 1, the experimental values of N mineralization for some soils (1–8) are compared to those of a first-order kinetics model with parameters estimated by the non-linear least square method. There was generally good agreement between the experimental data and the model for all the soils except soil 7. In this case each of the three methods failed to estimate N_0 and k closely. Though a common pattern in the data suggested the use of a more refined model to allow changes in convexity, we believe that a first-order kinetics model was sufficient to describe these data.

The values of N_0 and k obtained by applying the non-linear least square method to these data are shown in Table 4. The values obtained for N_0 varied from 21 to 405 ppm, and k ranged from 0.011 to 0.370 week $^{-1}$. When the three soils for which $k < 0.02$ week $^{-1}$ or $k > 0.1$ week $^{-1}$ were excluded, the range was reduced to 0.022–0.093 week $^{-1}$, with an average of 0.050 week $^{-1}$ and a mean standard error of 0.005 week $^{-1}$. Further investigations are needed to quantify the variability of the estimates for k for a single soil. This will allow us to determine whether the variability of the k values obtained here was a result of sampling variation or not.

Using the $N_{(30)}$ and N_0 values in Table 4, we observed that in about 25% of the samples examined N_0 50% higher than the experimental data ($N_{(30)}$). However, another 25% of the samples presented the same value for N_0 and $N_{(30)}$. In the remaining samples, N_0 ranged from 30% to 10% higher than $N_{(30)}$. For the highest k values

Table 4 Values of potentially mineralizable N (N_0) and rate constant (k) estimated by applying the non-linear least square method to the data from the incubated soils. The values of the root mean square (RMS) deviations between the data and the prediction are also shown

Soil no.	$N_{(30)}$ (ppm)	N_0 (ppm)	Total N: N_0 ratio	k (week $^{-1}$)	RMS (ppm)
1	70.8	151	5.3	0.022	5.1
2	35.0	35	37.1	0.370	0.8
3	155.0	160	11.3	0.086	9.0
4	41.0	44	11.4	0.076	2.5
5	386.0	405	3.7	0.089	9.2
6	20.0	21	19.0	0.177	2.9
7	83.8	nd	nd	nd	nd
8	98.7	102	7.8	0.093	3.1
11	92.0	93	11.8	0.085	6.6
12	77.5	87	12.6	0.064	6.4
13	77.7	116	12.1	0.035	4.0
14	52.3	73	15.1	0.041	2.1
15	58.0	72	9.7	0.051	2.7
16	63.0	73	17.8	0.059	4.1
17	102.2	186	10.2	0.025	7.4
18	53.3	71	16.9	0.045	2.0
19	95.2	316	6.0	0.011	7.3
20	55.2	73	12.3	0.046	2.0
21	56.2	64	23.4	0.063	2.5
22	62.3	77	13.0	0.050	2.5
23	62.4	121	8.3	0.023	1.8
24	64.1	102	7.8	0.032	2.7
25	56.3	106	10.4	0.025	1.2
26	58.6	87	11.5	0.035	2.1
27	59.0	84	6.0	0.038	1.8
28	58.0	118	9.3	0.022	1.7
29	346.8	352	8.0	0.087	32.0
30	74.7	143	7.7	0.023	4.2
31	47.5	73	8.2	0.034	1.2
32	54.1	70	12.9	0.048	1.9

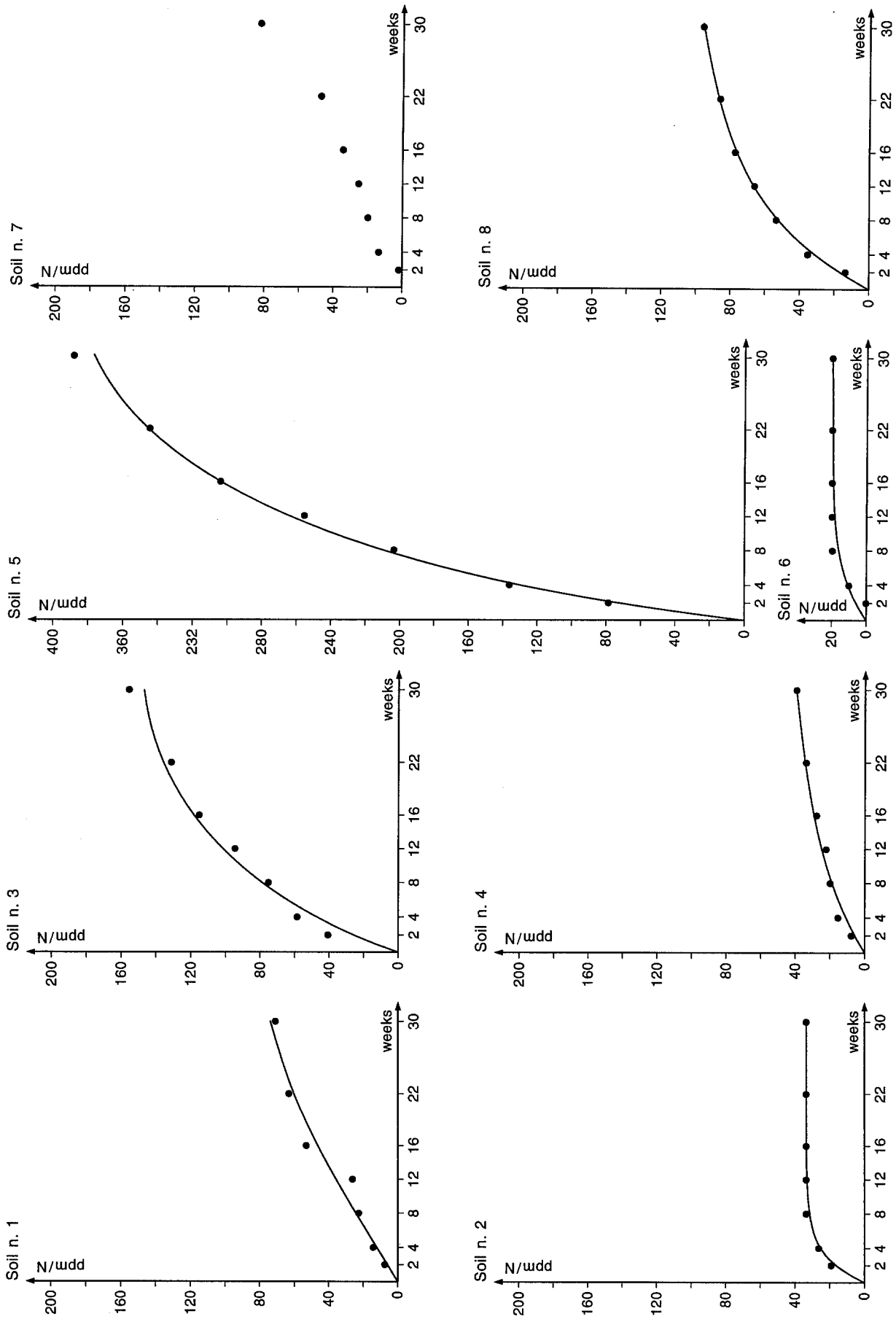


Fig. 1 Mineralization curves for soils 1-8

Table 5 Values of NH_4^+ -N determined after extraction in 2 M KCl at the end of the incubation period (30 weeks)

Soil no.	NH_4^+ -N (ppm)	Soil no.	NH_4^+ -N (ppm)
1	13.6	18	3.5
2	tr	19	4.7
3	8.8	20	3.2
4	2.0	21	2.7
5	9.5	22	8.5
6	2.0	23	10.9
7	2.6	24	2.8
8	2.0	25	7.3
11	6.0	26	7.3
12	3.4	27	5.1
13	5.9	28	3.9
14	5.6	29	2.2
15	3.2	30	1.7
16	5.1	31	8.3
17	8.0	32	1.6

we obtained the maximum of variability between N_0 and $N_{(30)}$. These results suggest that statistical analysis is required for a correct evaluation of N_0 (Stanford and Smith 1972). In addition, Table 4 shows that the ratio between total N and N_0 was characterized, in more than 65% of the samples, by values ranging from 7 to 13. Only three samples were largely outside this range (37, 23, and 19). This result is important because this ratio might be suitable as a rapid index of potentially mineralizable N obtained by measuring only the total N content.

These results were independent of the organic matter content of the soils. In fact, we did not find the highest values of N_0 in soils with the highest humus contents.

Finally, the possibility of reducing the incubation time was examined, by simulation as described above, using the data up to 22 weeks. The results are shown in Table 3. Significantly less reliable estimates of N_0 were obtained using 22 weeks of data. In fact, in some cases, the standard deviation of N_0 was twice the value obtained using 30 weeks of data. Furthermore, with a "low" value of k , i.e. $k = 0.03 \text{ week}^{-1}$, even using 30 weeks of data, the standard deviation of N_0 was about three times higher than those corresponding to $k = 0.05$ or 0.07 week^{-1} . In this case, a maximum incubation time greater than 30 weeks should be used. This is in agreement with the work of Mary and Remy (1979) and Menasseri et al. (1994).

The NH_4^+ -N values determined in a 30-day incubation period with 2 M KCl are reported in Table 5. Since all values were very low (< 14 ppm), we concluded that all the available N had been extracted during the experiment.

Conclusions

The results reported in this paper show that a first-order kinetics model can be successfully used to describe N mineralization in agricultural soils in equilibrium conditions, i.e. when there is no influence from farming activities, because in this second case the first-order kinetics

model failed (Alianiello and Benedetti 1994). According to Dendooven et al. (1991), this failure can be explained by the fact that the effects of growing plants, organic matter amendments, or N-fertilizer dressing on N-mineralization capacity were not taken into account and cannot be described by a first-order kinetics model.

The results from the simulation study suggest that the non-linear least square method is preferable to the maximum likelihood and the log-transformed linear least square methods for estimating the parameters N_0 and k of the first-order model.

The value of k estimated by using data from 30 Italian soils was 0.050 (mean standard error = 0.005). The present results confirm that it is not possible to obtain reliable values of N_0 if the maximum incubation time is shorter than 30 weeks, and in some cases a maximum incubation time of longer than 30 weeks is necessary. Finally, the N_0 parameter is a measure of potentially mineralizable N and can give useful information on biological activity in soil (Brookes 1992). However, further work is necessary to analyse the N_0 parameter with a forecasting mathematical model structured on the pedoclimatic environment, in order to obtain practical information on rationalization of N fertilization (Stanford and Epstein 1974; Cabrera and Kissel 1988; Hadas et al. 1989).

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