



# COMPARISON OF EMPIRICAL MODELS FOR ESTIMATING THE MINERALIZATION POTENTIAL OF SOIL ORGANIC NITROGEN

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## ABSTRACT

Modeling is an attempt to describe a natural event mathematically. The modeling of N mineralization process has a dual interest, agronomical and ecological. The objective of this study was to evaluate several mathematical models in order to describe the nitrogen mineralization process of soil samples. These samples were collected from 34 sites spatially distributed in the semi-arid region of *El-Madher (the Aures area, north-east of Algeria)*. Using an auger, the systematic surveys have been carried out also composite samples of soils were collected in the field, and subjected to physical and chemical analyzes. In order to track the kinetic organic nitrogen mineralization, similar samples were collected and taken into cool boxes, have been incubated in laboratory, sieved (2 mm) and stored at 4°C before used and then incubated at 28°C for 56 weeks. To facilitate comparison, all results have been statistically analyzed, by *nonlinear regression* and *analysis of variance* method. Four empirical models were tested to fit the value found experimentally. The linear kinetics model  $N_m = k t - N_i$ , the single first-order kinetics model (MI)  $N_m = N_i e^{-kt} + N_o (1 - e^{-kt})$ , the double first-order, the exponential kinetics model (MII)  $N_m = N_i e^{-kt} + N_o (1 - e^{-kt}) + e^{-ht}$  and the hyperbolic kinetics model (MH)  $N_m = N_o \frac{t}{T_c + t} - N_i$  were used to simulate the cumulative mineralized N ( $NH_4^+$ -N and  $NO_3^-$ -N) in the laboratory incubation. In order to test the performance and robustness of the different models three goodness of fit (coefficient of determination  $R^2$ , Root Mean Square RMS and Mean Relative Error RMSE) were used. Moreover, the parameters obtained by the different models determined the predictions of nitrogen mineralization. The best results were obtained using the double first-order and exponential kinetics model. The results showed no significant difference between nitrogen mineralized for 56 weeks and nitrogen predicted by various models. However, the N predicted by the MII appears to be the best compared to other models. Indeed, the overestimation of nitrogen potentially mineralizable ( $N_o$ ) obtained by this model was relatively lower than other models. This has been confirmed by the study of multiple correlations between net mineral nitrogen and nitrogen predicted by each model. Thus, the results obtained showed a strong positive correlation between mineralized nitrogen values and those of nitrogen predicted by the different models. The correlation coefficients values indicate the following order MII ( $R^2 = 0.878$ ) > MI ( $R^2 = 0.748$ ) > MH ( $R^2 = 0.709$ ). The MII model has, therefore, highlighted that two pools of organic matter, which are mineralized simultaneously. One pool is stable and the other one is labile. This labile pool evolves with first-order kinetics and the other with exponential kinetics.

**Keywords:** Soil, nitrogen, empirical model, fertilization, organic matter

## Academic Discipline And Sub-Disciplines

Agronomic and Soil sciences

## SUBJECT CLASSIFICATION

Agronomics Subject Classification

## TYPE (METHOD/APPROACH)

Modeling natural processes

## INTRODUCTION

Nitrogen (N) is an essential nutrient for plant growth, development and reproduction. Since this nutrient is a paramount element, for plants, more than any other nutrients such as carbon, oxygen and hydrogen. Also it is a fundamental component of many plant structures especially, for their metabolic processes [1]. Nitrogen (N) is, further more, one of the major yield-limiting nutrients for crop production around the world [2]. However, the high levels of nitrates and nitrites, which can be accumulated in the edible leafy crop plants [3] and can lead to serious problems of environmental pollution [4]. Among all nutrients in soil, nitrogen is undoubtedly the most problematic element for the management and monitoring fertilization [5]. Meanwhile, it is the most important nutrient for crop growth and yield levels [6]. It is indeed, the N which determines the development of the plant, roots and stimulates optimal absorption of other nutrients from the soil [7]. Without adequate amounts of N, other nutrients are therefore less absorbed [5]. Mineralization of this element is not only a fundamental step in the transformation of soil organic nitrogen, but it is also one of the most important processes in the soil nitrogen cycle [8]. In order to improve N management in agriculture, predicting the process of its mineralization *in-situ*, has become one of the biggest challenges facing scientists around the world in recent decades [9].

Modeling is an attempt to describe a natural event mathematically [10]. The modeling of N mineralization process has a dual interest, agronomic and ecologic. By taking into account potentially mineralizable quantities and the rate constant, modeling not only predicts the availability of N to crop at specific times [11], but also reduces the losses of mineral nitrogen [12] by rationalizing nitrogen fertilization. The main aim of modeling is, therefore, to obtain quantitative data to be



recommended when applying nitrogen fertilizer to the soil [13]. One of the major obstacles to limiting the modeling of the N mineralization process is that the organic pool is very important compared to the inorganic pool [14]. This reason causes large errors in estimating the amount of organic N available to crops [15].

Initially a simple model was proposed, where cumulative mineralized nitrogen for 30 weeks of incubation in the laboratory is described by first order kinetics [16]. It is a simple exponential model, considering the existence of a single form of potentially mineralizable nitrogen ( $N_0$ ) that decomposes at a rate proportional to its concentration [10]. This model assumes that the mineralized nitrogen comes from a single pool of organic nitrogen (ON). The biggest criticism of the Stanford and Smith model is that this exponential model is based on the assumption that there is only one form of potentially mineralizable nitrogen in the soil. Since that, most models consider the existence of at least two compartments of mineralizable N; one highly mineralizable more and other one recalcitrant. Because soil organic matter contains fraction with high turnover and slower turnover, they commonly called easily and less mineralizable N fractions [17] [18] [19].

Stanford and Smith [16] approach, has been criticized by many authors [18] [20] and [21]. Since nothing is perfect, the model has some negative aspects and raises certain weaknesses. These weaknesses are mainly related to description of mineralization curves. Thus, the work of [22] showed that the nitrogen release model in the laboratory would be similar to that in the field. On the other hand, [23] found that the results of disturbed sample incubations used to predict field mineralization overestimated nitrogen mineralization from 67 to 343%. This was thought to be due to the pretreatment effects of the samples including mixing, sieving, air drying and/or re-wetting of soil samples. It also thought that it was due to the conditions of incubation as well as to the soils properties and the chemical constitution of organic matters. The same observations were made by [24] and [25] who attributed this weakness to samples pretreatment before incubation in particular, air drying, which can cause a flush mineralization. Indeed, to solve this extra mineralization, which occurs during the first two weeks, [25] has made a gap of the origin of the curve. With the same idea, [26] deducted mineralized N during the first two weeks of the calculation of  $N_0$ , which will then be added to  $N_0$  thus determined. [18] and [21] suggested that the mineralization of the organic nitrogen is the result of two or several compartments. They proposed a bi-compartmental model that represents the sum of two first-order equations. These models suppose the existence of two fractions of  $N_0$ ; one highly mineralizable and the other one recalcitrant with a very low turnover. Although, several studies estimate that different results could be obtained from the comparison between the laboratory experiments and fields. Indeed, the incubation conditions of soils in laboratory are very different from those of fields [27]. Moreover, certain authors consider that long-term incubation, will lead to deteriorations of the quality of the soil organic matter and proportion of the various fractions present at the origin, so the incubated soil will be very different from the soil of fields [28] [29]. Despite the discrepancies between the results obtained *in situ* and those in laboratory, incubation methods still to be commonly used methods to explain both kinetics of carbon and of nitrogen mineralization. Indeed, these methods are simple, easily used and supply the least biased estimates possible [30]. Simard and N'Dayegamiye [31] Working under controlled conditions revealed a sigmoid trend in the N mineralization process at the beginning of incubation followed by relative linearity over time. While [32] showed that the mineralization of N can be described by a hyperbolic equation. Some authors report that N mineralization curves over time are linear (zero-order kinetics) [33] [34] [35]. On the other hand, [36] found that the exponential model did not conform to N mineralization and that the hypothesis of the existence of several mineralizable compartments could only be a wrong conception.

The purpose of this work is to compare the mathematical models described in the literature and the most used in the adjustments of experimental data for the description of nitrogen mineralization kinetics. The comparison will be carried out using experimental data on soil organic nitrogen mineralization from certain farmlands in Aurès, Algeria.

## MATERIALS AND METHODS

### SAMPLING AND SITE DESCRIPTION

Soils used in this study were collected from *El-Madher* plain with low slopes (1 – 2 %). This area has geographic coordinate's latitude of 35°37'00.75" N, a longitude of 6°22'00.13" S and an altitude of 1020 m, located in Aures province of Algéria. The region has a mediterranean semi-arid climate with a cold and rainy winter and a hot and dry summer, which begin, respectively, from November to June. The averages annual precipitation and temperature are respectively 350 to 450 mm and 21 °C. Based on the US Soil Classification system (USDA, 1995), most soils of this region are categorized as *Calcixerollic xerochrept mesic fine clay*. These soils are dominated by the characteristics with the following averages values, bulk density ( $\text{g cm}^{-3}$ )  $1.7 \pm 0.12$ , Clay (%)  $24.98 \pm 6.92$ , silts (%)  $33.21 \pm 10.99$ , sands (%)  $41.82 \pm 8.99$  and soil humidity ( $\text{mm.cm}^{-1}$ )  $1.36 \pm 0.02$ , total organic carbon (TOC)(%) ( $5.30 \pm 1.01$ ), total nitrogen (TN) (%) ( $0.38 \pm 0.09$ ),  $\text{pH}_{\text{H}_2\text{O}}$   $7.23 \pm 0.29$ , S ( $\text{cmol}+\text{kg}^{-1}$  s)  $9.93 \pm 2.27$ , CEC (T) ( $\text{cmol}+\text{kg}^{-1}$  s)  $13.42 \pm 3.57$  and V (%)  $75.09 \pm 100.48$  at depth 20 cm.

Soil samples, were taken in zigzag to cover the entire field. At a depth of at least 20 cm, 10 to 15 sub-samples are taken at random and mixed together to make a composite sample. After removing the pieces of gravel and visible debris, the samples were air dried and passed through a stainless steel sieve with 2mm diameter. Some of these soil samples were physically and chemically analyzed and others were incubated under controlled temperature and humidity conditions to monitor the kinetics of organic nitrogen mineralization.

## PHYSICAL AND CHEMICAL ANALYSIS OF SOIL SAMPLES



After sampling, the properties of the soil selected for analysis, on the 0-20 cm layer, are: Soil moisture determined by the gravimetric method [37] which consists of drying at 105 °C a soil sample and then knowing by final weighing (brought back to the initial weighing) the weight of the soil. Water contained by the sample. The  $pH_{H_2O}$  [38] soil was determined using a glass calomel electrode using a mixture of deionized water / sol = 1 / 2.5. Soil texture quantitatively determines the physical proportions of three soil particle sizes (sands, silts, and clays) taking into account their sedimentation rates in an aqueous solution using a hydrometer [39]. The bulk density ( $D_a$ ) was measured by the cylinder method. Using undisturbed soil samples, knowing the constant dry weight of the samples at 105 °C and the volume of the cylinders of the samples used [40]. The cation exchange capacity (CEC) was determined by the [41] method. Soil total organic carbon (TOC) and total soil nitrogen (NT) were determined, respectively, by [42] and Kjeldahl's potassium dichromate oxidation [43]. The mineral forms of carbon ( $C_m = C-CO_2$ ) and nitrogen ( $N_m = N-NH_4^+ + NO_3^-$ ), of 28 days, were determined, after incubation of the soil samples, at temperature (28°C) and optimum moisture levels (soils maintained at 2/3 of the water retention capacity).

The  $Ca^{++}$  and  $Mg^{++}$  cations were assayed by atomic absorption spectrophotometry, the  $Na^+$  and  $K^+$  cations were determined by flame emission spectrophotometry.  $S$  ( $cmol.kg^{-1}$ ) is the sum of all exchangeable bases =  $Ca^{++} + Mg^{++} + Na^+ + K^+ + NH_4^+$ , the saturation rate in bases is obtained by the relation  $V(\%) = S / CEC$ .

Physical and chemical analyzes of composite soil samples are reported in Table 1.

## INCUBATION METHODS FOR MONITORING THE KINETICS OF ORGANIC N MINERALISATION

Mineralization of organic nitrogen ( $N_{min}$ ) was determined by measuring the mineral N ( $NH_4^+$  and  $NO_3^-$ ) production during incubation. To monitor mineral nitrogen kinetics, soil samples were aerobically incubated [44] over a long period of time. Incubation was performed with 50 g (dry weight equivalent) of soil moistened with distilled water at 60% of the water holding capacity (WHC) and incubated at 28 °C for 56 weeks. The ammonium  $NH_4^+$  and nitric  $NO_3^-$  ions contained in the soil were determined, respectively, by the Nessler reagent method (iodo-mercurate solution in an alkaline medium) and with the phenol-disulphonic acid. For the determination of  $NH_4^+$ , a soil sample of 10 g (dry weight equivalent) was stirred with 50 ml KCl (2.0 M) for 30 minutes. Filtration was performed after centrifugation for 10 minutes at 5100 x g. After addition of 2 drops of stabilizer-disperser and 0.4 ml of Nessler's reagent to 10 ml of filtrate,  $NH_4^+$  was assayed using a spectrophotometer [45]. For the determination of  $NO_3^-$ , the sample of each soil weighing 10 g was stirred with 50 ml of  $CuSO_4$  (0.01 M) for 30 minutes. Filtration was carried out after addition of 0.2 g of  $Ca(OH)_2$  and  $MgCO_3$  powder to the suspension. Two milliliters of filtrate were evaporated at 80°C dry and then 2 ml of phenol-disulfonic acid, 20 ml of ultrapure distilled water and 10 ml of concentrated  $NH_4OH$  were added [46]. The color produced by the addition of phenol-disulphonic acid was measured with a spectrophotometer. The operation was the subject of 3 repetitions for each type of soil. The net rate of ammonification and nitrification was calculated by difference of  $N-NH_4^+$  and  $N-NO_3^-$  contained before and after incubation. The mineralization rate of the total organic nitrogen was estimated by summing the ammonification and nitrification rates ( $(N-NH_4^+ + N-NO_3^-) / NT * 100$ ).

## FIT MODELS AND DATA STATISTICAL ANALYSIS

The results obtained at the end of the incubation period were modeled. Experimental data modeling was performed using the nonlinear regression technique. To adopt a model on which we adjust our experimental data, we considered it useful to test the different models, the single-compartmental model proposed by [16], the bi-compartmental model proposed by [21], the linear model [47] and the hyperbolic model proposed by [32].

The differences in this incubation method and that used by [16] were taken into account. Indeed, this method consists of an incubation of soil samples, or periodically, the soil samples are leached so that the mineral nitrogen can not accumulate, therefore the curve passes through the origin. However, for our experimental conditions, the curve does not go through zero because at  $t = 0$ , the N-mineral ( $N_i$ ) remains in system all along the incubation. This is why some modifications considered relevant to the different mathematical models are made.

Thus the following differential equation is given:

$$dN/dt = -k(N - N_i) \quad (a)$$

After integrating the equation in the interval ( $N_i$ ,  $N_0$  and 0,  $t$ ) and taking the primitive, the solution of the differential equation (a) is:

$$Nt = N_0 e^{-kt} - N_i e^{-kt} \quad (b)$$

At time  $t$  ( $N_t$ ), the mineralized nitrogen is equal to:  $N_m = N_0 - N_t$

$$\text{Single-compartmented first-order model proposed by [16]} \quad N_m = N_i e^{-kt} + N_0 (1 - e^{-kt}) \quad (c)$$

$N_m$  is the mineralized nitrogen at time  $t$ ,  $N_i$  is the mineral nitrogen initially in the medium,  $N_0$  is potentially mineralizable N, and  $k$  is the mineralization rate constant of  $N_0$  ( $wk^{-1}$ ).

The same modifications are made to the other models namely the linear model, hyperbolic and double exponential, by subtracting the initial N-mineral ( $N_i$ ).

$$\text{Linear model proposed by [47]} \quad N_m = k t - N_i \quad (d)$$

$$\text{Hyperbolic model proposed by [32]} \quad N_m = N_0^H \cdot t / (b N_0^H + t) - N_i \quad (e)$$



$N_m$  represents the N mineralized at time  $t$ .  $N_0^H$  is defined as potentially mineralizable N and  $b$  is the constant [weeks. (mg N  $kg^{-1}$ .sol) $^{-1}$ ]. The constant  $b$  can be written as:  $b = T_c / N_0^H$

$$N_m = N_0^H \cdot t / (T_c + t) - N_i \quad (f)$$

$T_c$  is expressed in weeks and represents the time required for the mineralization of  $1/2 N_0^H$ .

Double compartmental model (double exponential) proposed by [18] and [21]

$$N_m = N_0 S (1 - e^{-kt}) + N_0 (1 - S) (1 - e^{-ht}) + N_i e^{-ht} \quad (g)$$

$N_m$ ,  $N_0$  and  $t$  are defined above.  $S$  represents the easily mineralizable fraction of  $N_0$  that mineralizes at a rate constant  $k$  ( $wk^{-1}$ ) and  $(1 - S)$  is the recalcitrant fraction of  $N_0$  that mineralizes at a rate constant  $h$  ( $wk^{-1}$ ).

By compiling the data on equation (g), it was found that the velocity constant  $h$  takes values that are 2 to 3 times larger than those found by [18] and [21], therefore the part of the equation with the constant  $h$  vanishes. This is why we have made modifications, considering that the mineralization of N is explained by the sum of two equations, one of first order and the other exponential.

Double compartmentalized first order and exponential model were proposed by [20]

$$N_m = N_i e^{-ht} + N_0 (1 - e^{-kt}) + e^{-ht} \quad (h)$$

## CALCULATION TECHNIQUE

Initially [16] used the graphical method (linear regression) to estimate kinetic parameters ( $N_0$  and  $k$ ). This method was criticized by [49] [24] [11] and [50]. The weaknesses reproached of this method that it uses the logarithmic transformation of the data, therefore the error is log-transformed. This leads to an overstated weighting of small values versus high values, causing a smoothing factor, which is responsible for the low variability of the rate constant  $k$  [24] [11]. These authors suggest the *Non-Linear Least Squares* fit (NLLS) by Newton's iterative method. This method consists of minimizing the sum of the squares (SS) of the deviation between the model and the experimental data.

According to these considerations, the NLLS fit by iteration is used according to Newton's method. This technique has the advantage of giving the same weighting for all points. The kinetic parameters of nitrogen mineralization ( $N_0$  and  $k$ ) that will be retained correspond to the two consecutive iterations of less than  $10^{-5}$  value [51].

## CRITERIA USED FOR THE BEST FIT MODEL

The model that will be retained is the one that offers the best description of the data and leaves the smallest value of the *Root Mean Square* (RMS) unexplained by the model [52]. In addition to the coefficient of determination  $R^2$ , another more empirical approach to the accuracy of fit will be used, which is given by the calculation of the *Mean Relative Error* (MRE) (Edwards and Wilke, 1968 *in* [53]). In the same vein, [54] mentioned the effectiveness of this measure for model validation. In addition, [55] recommend this method for testing the performance of models. It is therefore, computed in order to determine the goodness of fit.

$$MRE (\%) = \frac{100}{n} \sum_{i=1}^n \left| \frac{C_i - E_i}{E_i} \right| \quad [9]$$

$C$  = calculated value by the model

$E$  = experimental value

$n$  = number of experimental points.

The determination of differences between RMS and MRE from different models, an F test has been performed (Robinson, 1985). To conclude, the parameters that determine the final choice of the model are:  $R^2$ , RMS and MRE.

The software used to realize NLLS is [56].

## RESULTS AND DISCUSSION

### NITROGEN ADJUSTMENT MODEL

This study, only deals with the comparative aspect of the models. It also should be noted that the data relating to the linear model proposed by [47] is presented only for illustrative purposes and will not be compared to other data, since the coefficients of determination are relatively small compared to the found values of other models (Table 2). Similarly, the RMS values, generated by this model are relatively very high. They can in some cases, reach 7 times the values obtained by the other models (Table 2).



## COMPARISON BETWEEN MI AND MII MODELS

Firstly, it is observed that all the experimental data relating to the mineralization of the nitrogen were adjusted on the model I (*MI*), while for the model II (*MII*), only some data, in particular those of the sites 10, 11, 15, 22 and 33 are not adjusted to this model (Table 3).

## COMPARISON OF MODEL SELECTION CRITERIA

The coefficients of determination  $R^2$  are very significant and substantially identical for both models and provide information on the correct fit. In fact, the  $R^2$  vary from 0.880 to 0.994 and from 0.856 to 0.995 respectively for *MI* and *MII* (Table 3). It should be noted that for *MII*, 19 values of  $R^2$  have higher values than 0.9, whereas for *MI*, 22, the values are higher than 0.9 (Table 3). It is also important to note that in general, RMS and MRE in *MII* seem to be inferior to *MI* (Table 3). This suggests a difference between the two models. Indeed, variance analysis between the different RMS and RME from *MI* and *MII* models has revealed high significant differences (Tables 4 and 5). Indeed, at the low significance level of 5 %,  $F = 14.53$  with  $p < 0.0003$  and  $F = 32.78$  with  $p < 0.0003$ , respectively for RMS and RME.

## COMPARISON BETWEEN PARAMETERS OF MI AND THOSE OF MII MODEL

The comparison of the parameters calculated from *MI* and *MII* (Table 3) showed that unlike the *MII*, the *MI* overestimated the  $N_0$  and underestimated the rate constant  $k$ . These results show compensation relationships between  $N_0$  and its rate constant  $k$ , which makes the choice difficult between the models. Moreover, [26] found that the [16] model (equivalent to *MI*) overestimates the potentially mineralizable  $N_0$  from 15 to 20 mg kg<sup>-1</sup>. These authors attribute these overestimates of  $N_0$  to N mineralized from stable soil organic matter. However, taking into account other explanatory elements and arguments that make it easier to choose the right model becomes indispensable. Indeed, by evoking the notion of potentially mineralizable N, we refer to N easily mineralizable (labile) [52]. However, it has been observed during the monitoring of the process that, from the 15th to the 32nd week of incubation, depending on the soil, the mean weekly mineralization of N is relatively low. While it is very high, sometimes 5 times higher, during the period from the 1st to the 15th week.

These findings allow us to deduce that the mineralized N during the period between 25 or 32 to 56 weeks cannot be accounted for in  $N_0$  as *MI* does. For these reasons, it seems clear that the *MI* does not better describe the mineralization of N. Nevertheless, this model remains valid since it generates parameters ( $N_0$  and  $k$ ) close to those generated by *MII*. However, if precision is sought in the  $N_0$  determination, the *MII* seems better to describe the mineralization kinetics of N while generating a  $N_0$  is consistent with the notion of easily mineralizable N. These results have been able to elucidate the compensatory effect due to the interdependence between  $k$  and  $N_0$  recently underlined by [57].

## COMPARISON BETWEEN THE MH AND MII MODELS

### COMPARISON OF MODEL SELECTION CRITERIA

A same observation was made and as above for the comparison between the hyperbolic model (*MH*) and the model II (*MII*). Indeed, the *MH* model fitted to all experimental data relating to the mineralization of nitrogen. The coefficients of determination  $R^2$  are very high. In fact, just like *MII*, the mineral nitrogen values of the soils fitted to the *MH* model, generated 19  $R^2$  higher than 0.9 (Tables 2 and 3). While RMS and MRE of *MII* seem to be significantly lower than those of *MII* (Tables 2 and 3). As a result, a variance analysis is conducted. Thus, the results obtained show highly significant differences at a low significance level of 5% ( $F = 10.47$ ,  $p = 0.0019$  and  $F = 99.9$ ,  $p = 0.0001$ , respectively, for RMS and MRE).

### COMPARISON BETWEEN PARAMETERS OF MII AND THOSE OF MH MODEL

The analysis of the variance between the parameters shows a very significant difference between the different  $N_0$  from the two models (*MH* and *MII*) ( $F = 12.29$ ,  $p < 0.005$ ). The *MH* generates  $N_0$  values are significantly higher than the mineralized N during the 56 weeks of incubation, whereas the  $N_0$  values obtained by *MII* are generally lower than the mineralized N. In addition, a match is noted between  $N_0$  and half-life time (*HLT*). Indeed, if we exclude the *HLT* of  $N_0$ , soils of sites S6, S10, S12, S15, S18, S21, S25, S26, S27 which are between 27.24 and 32 weeks and seems consistent with the contents of  $N_0$ . Soil *HLT* from other sites range from 6.86 to 15.40 weeks, indicate that  $N_0$  is depleted between 5 and 15 weeks of incubation.  $N_0$  is significantly higher than mineralized N during 56 weeks. Indeed, variance analysis indicates a highly significant difference between mineral nitrogen ( $N_m$ ) and potentially mineralizable nitrogen ( $N_0$ ) ( $F = 26.83$ ,  $p < 0.005$ ). This allows us to conclude that the *MH* overestimates the  $N_0$ .

In addition, significant differences between the  $N_0$  values generated by *MH* (standard deviation = 22.83) are observed, while the standard deviation between the  $N_0$  values of the *MII* is 48.21, according to the soils (Tables 2 and 3). Moreover, [32] reported significant differences between the  $N_0$  generated by the exponential model and the hyperbolic model. [58] Observed a slight stall of the curve when the experimental data approached the asymptote. This suggests substantial differences between the parameters calculated by the two models. Moreover, from the parameters obtained by the different models, we have determined the predictions of nitrogen mineralization by the models (Table 4). Thus, the results show no significant difference between the nitrogen mineralized for 56 weeks and N predicted by *MI*, *MII* and *MH* ( $F = 2.3$ ,  $p = 0.133$ ,  $F = 1.19$ ,  $p = 0.105$  and  $F = 0.13$ ,  $p = 0.149$ , respectively). However, the N predicted by *MII* seems to be the best compared to other models. In fact, the overestimation of N by *MII* is 5 mg kg<sup>-1</sup>, whereas for *MI* and *MH*, the overestimation is respectively 9 and 21 mg kg<sup>-1</sup>, (Table 4). This is confirmed by the study of multiple correlations between  $N_m$  net and Nitrogen predicted by each model. Thus, the results obtained show a strong positive correlation between the



mineralized N values and the N values predicted by the different models (Table 5). Indeed, the correlation coefficients obtained are respectively in the order 0.878, 0.748 and 0.709 for the models *MII*, *MI* and *MH*. As a result, the relationship between N mineralized and N predicted by the different models is in the following order: *MII* > *MI* > *MH*.

## CONCLUSION

The aim of this study was to compare several models (first order model, hyperbolic and first order-exponential model). The results thus obtained clearly show, based on several selection criteria (the coefficient of determination  $R^2$ , the RMS and MRE) that the first order model does not seem to be adequate with the given data. In deed, it is especially noticed that the type of model, evoked by some authors seems to be unrealistic when the rate of transformation is unaffected by the nature and concentration of the substrate. Whereas, in reality there are constraints that can limit the mineralization of N, including the nature of the soil organic matter. The *MII* model however, represents two simultaneous kinetic, one is the first order and the other is exponential and seems to better describe the kinetic. It is the same for the hyperbolic model. This last one does not generate a rate constant of mineralization, which makes a difficult task for a possible estimate of the mineralized nitrogen when planning nitrogen fertilization.

The *MII* model as first order and as an exponential  $Nm = N_i e^{-kt} + N_o (1 - e^{-kt}) + e^{-ht}$ , revealed two pools of soil organic matter that mineralize simultaneously. The stable one is intimately related to secondary minerals of the soil, which seems to mineralize very slowly. While the other, represents the easily mineralizable pool of soil organic matter. This pool is included essentially the microbial biomass, the light fraction of OM as well as soluble organic matter. In addition, this fraction constitutes a potential nutrient that can be released after mineralization and cannot be neglected during fertilization.

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**Table N ° 1: Soils physical and chemical properties of El-Madher (Aures, Algéria)**

Sites for sampling composite soil	Total silt (%)	Total sand (%)	Soil Humidity (mm.cm <sup>-1</sup> )	Bulk density Da (g.cm <sup>3</sup> )	N-NH <sub>4</sub> <sup>+</sup> (mg.kg <sup>-1</sup> s)	N-NO <sub>3</sub> <sup>-</sup> (mg.kg <sup>-1</sup> s)	Nmineral at 28 days (%)	Soil Total Organic Carbon (COT) (mg.kg <sup>-1</sup> s)	Soil Total Nitrogen (NT) (mg.kg <sup>-1</sup> s)	pH <sub>H2O</sub>	Sum Exchangeable Cation S (cmol.kg <sup>-1</sup> s)	Cationic Exchange Capacity CEC : T (cmol.kg <sup>-1</sup> s)	Rate Saturation Cations V (%) = S/T
1	22.33	44.65	1.38	1.8	65.67	160	225.67	66600	5550	7.6	15.59	28.63	54.45
2	49	39	1.35	1.65	43.21	110	153.21	33600	2563	7.5	11.71	14	83.64
3	9	51.99	1.36	1.7	20.34	130.25	150.59	69500	5452	7.8	10.63	12	88.58
4	37.85	33.9	1.38	1.8	18.86	160.68	179.54	59500	4231	6.95	9.98	14.85	67.21
5	30	56.88	1.32	1.5	40.74	134.64	175.38	36200	2010	7.01	8.69	13.25	65.58
6	36.04	42.01	1.38	1.8	46.26	137.62	183.88	48600	3500	7.55	10.33	12.86	80.33
7	29.03	46.02	1.32	1.5	76.01	156.25	232.26	52600	4010	7.25	8.78	12.56	69.9
8	28.26	46.69	1.32	1.5	81.88	165.33	247.21	53500	3010	7.69	8.55	14.85	57.58
9	40.04	23.01	1.38	1.8	49.73	135.33	185.06	58110	4100	6.85	7.37	10.25	71.9
10	41.96	34.81	1.38	1.8	45.85	133.84	179.69	49988	3990	6.99	9.78	13.85	70.61
11	28.89	48.15	1.32	1.5	96.8	163.65	260.45	50612	4210	7.25	9.19	10.22	89.92
12	26.05	49.03	1.32	1.5	24.36	128.36	152.72	54612	4400	7.45	7.91	10.65	74.27
13	29.46	36.25	1.38	1.8	91.44	160.33	251.77	67500	5456	7.5	13.34	15.36	86.85
14	21.02	46.01	1.38	1.8	33.73	137.63	171.36	66311	5010	6.95	12.28	15.95	76.99
15	10	58.99	1.36	1.7	50.84	152.33	203.17	63200	4011	7.25	12.65	17.59	71.92
16	34.26	35.72	1.38	1.8	49.75	143.44	193.19	61898	4210	6.85	8.28	12.55	65.98
17	19.66	53.02	1.38	1.8	35.52	138.22	173.74	57233	4011	7.15	8.82	10.72	82.28
18	33.04	40.01	1.38	1.8	26.3	122.33	148.63	56322	4023	7.25	14.53	17.53	82.89
19	27.87	49.64	1.32	1.5	38.32	136.25	174.57	48902	3450	7.55	11.6	16.41	70.69
20	47.24	25.18	1.38	1.8	43.28	138.25	181.53	57601	3912	6.95	12.79	14.88	85.95
21	29.87	45.57	1.36	1.7	30.34	128.26	158.6	53204	4123	7.25	12.83	15.33	83.69
22	36.89	32.24	1.38	1.8	85.33	155.33	240.66	63333	4889	7	9.03	10.74	84.08
23	32.65	45.23	1.38	1.8	70.59	163.54	234.13	48912	3333	6.85	8.03	11.4	70.44
24	46	30.5	1.38	1.8	39.54	136.45	175.99	50233	3750	7.1	11.89	14	84.93
25	45.36	31.51	1.38	1.8	51.99	144.29	196.28	49956	3451	7.25	7.75	13.54	57.24
26	49.27	39.73	1.35	1.65	38.37	132.22	170.59	23666	1633	6.8	8.58	12.11	70.85
27	45.23	43.11	1.35	1.65	45.31	140.3	185.61	32654	2199	6.9	12.07	13.6	88.75
28	43.02	33.08	1.38	1.8	24.24	122.23	146.47	51230	4563	7.1	6.42	8.7	73.79
29	10	60.98	1.36	1.7	41.83	138.38	180.21	60523	5011	7.75	7.22	8.29	87.09
30	36.5	36.25	1.38	1.8	29.34	126.33	155.67	57123	4611	7	8.9	9.72	91.56



31	30.44	44.68	1.32	1.5	23.76	120.2	143.96	53698	4452	7.5	7.05	9.17	76.88
32	33.05	38.72	1.38	1.8	62.62	152.52	215.14	58655	3301	7.65	8.79	12.03	73.07
33	48.98	38.52	1.35	1.65	53.42	143.44	196.86	45621	2820	7.4	8.99	12.82	70.12
34	30	47.99	1.32	1.5	48.15	143.23	191.38	48000	3123	6.9	8.29	15.25	54.36
35	44	34.5	1.38	1.8	61.02	154.02	215.04	47800	3310	7.3	9.04	14.2	63.66
Mean	33.21	41.82	1.36	1.70	48.14	141.30	189.43	53057.06	3876.51	7.23	9.93	13.42	75.09
Standard Deviation	10.99	8.99	0.02	0.12	20.35	14.00	32.28	10130.53	947.11	0.29	2.27	3.57	10.48



**Table 2 : Comparison of parameters relating to linear and hyperbolic models**

Site	Linear model				Hyperbolic model (MH)					
	$N_m$ <i>mg.kg<sup>-1</sup></i>	$k$ <i>sem</i>	$R^2$	RMS	$N_0$ <i>mg. kg<sup>-1</sup> sol</i>	$N_m$	$T_0^H$ <i>sem.</i>	$R^2$	RMS	RME %
1	122,51	1,64	0,908	<b>16,13</b>	177,30	122,56	11,17	0,954	5,90	<b>8,53</b>
2	167,51	1,67	0,938	<b>15,05</b>	177,30	124,63	12,73	0,950	8,80	<b>24,3</b>
3	152,17	1,75	0,912	<b>19,58</b>	195,82	125,63	11,02	0,961	4,00	<b>7,63</b>
4	199,26	1,94	0,914	<b>19,60</b>	191,35	130,45	9,70	0,970	8,40	<b>9,08</b>
5	222,16	1,72	0,884	<b>21,91</b>	239,95	200,25	6,86	0,970	8,90	<b>11,3</b>
6	200,65	2,02	0,875	<b>39,42</b>	205,72	170,36	28,56	0,911	5,10	<b>30,8</b>
7	175,93	1,68	0,826	<b>23,65</b>	203,73	186,23	8,92	0,880	7,50	<b>17,4</b>
8	190,03	1,87	0,894	<b>20,22</b>	231,88	200,23	14,22	0,926	7,70	<b>14,6</b>
9	228,26	1,68	0,862	<b>18,74</b>	171,38	145,25	12,73	0,902	5,30	<b>10,9</b>
10	152,53	1,31	0,899	<b>12,98</b>	283,37	150,36	30,68	0,919	4,60	<b>12,3</b>
11	217,03	1,39	0,821	<b>21,57</b>	283,88	151,56	8,02	0,897	11,20	<b>20,1</b>
12	138,77	1,73	0,901	<b>17,10</b>	171,56	140,36	29,53	5,433	5,60	<b>10,0</b>
13	158,92	1,72	0,809	<b>23,97</b>	281,25	150,23	8,27	0,871	12,50	<b>14,3</b>
14	178,50	1,54	0,904	<b>16,81</b>	281,25	150,33	8,17	0,881	5,30	<b>8,27</b>
15	163,83	1,40	0,857	<b>16,59</b>	281,25	151,33	30,22	0,881	3,70	<b>14,7</b>
16	143,56	1,46	0,864	<b>18,72</b>	205,62	170,89	12,30	0,902	6,20	<b>14,2</b>
17	199,76	1,40	0,582	<b>20,37</b>	172,12	165,36	11,08	0,899	7,20	<b>17,6</b>
18	168,89	1,77	0,848	<b>17,73</b>	177,18	168,25	27,84	0,882	5,90	<b>15,2</b>
19	126,36	1,67	0,823	<b>22,40</b>	181,92	150,36	8,65	0,877	5,70	<b>16,1</b>
20	152,19	1,54	0,814	<b>22,57</b>	208,55	75,36	8,30	0,962	5,90	<b>9,18</b>
21	198,08	1,18	0,924	<b>29,37</b>	181,92	145,45	29,56	0,879	3,40	<b>15,6</b>
22	146,21	1,15	0,850	<b>18,25</b>	199,99	163,23	15,40	0,921	2,40	<b>13,8</b>
23	214,43	1,16	0,899	<b>14,44</b>	206,00	185,23	10,62	0,948	5,70	<b>9,57</b>
24	189,61	0,71	0,822	<b>15,84</b>	186,62	155,45	13,58	0,859	3,40	<b>15,6</b>
25	175,99	0,93	0,929	<b>10,75</b>	194,39	137,26	29,56	0,958	3,40	<b>9,75</b>
26	218,77	1,51	0,902	<b>13,38</b>	182,80	136,85	31,56	0,920	3,90	<b>12,1</b>
27	156,73	1,52	0,905	<b>17,40</b>	230,36	205,00	32,00	0,946	2,50	<b>10,0</b>
28	148,23	1,05	0,915	<b>12,62</b>	201,70	222,26	9,78	0,965	4,30	<b>8,12</b>
29	215,80	0,81	0,821	<b>14,51</b>	170,22	145,15	13,49	0,855	3,30	<b>12,4</b>
30	214,28	1,13	0,888	<b>14,56</b>	197,60	145,23	11,57	0,935	2,50	<b>8,91</b>
31	195,20	0,92	0,857	<b>45,22</b>	263,36	133,26	7,85	0,962	3,70	<b>7,99</b>
32	212,08	0,84	0,862	<b>14,34</b>	182,07	158,14	9,18	0,912	3,30	<b>12,7</b>
33	188,65	0,81	0,904	<b>11,44</b>	182,34	153,25	9,82	0,951	3,90	<b>9,21</b>
34	176,79	1,18	0,891	<b>26,89</b>	210,30	200,03	9,57	0,940	3,70	<b>20,9</b>
35	202,75	1,29	0,893	<b>22,38</b>	170,35	145,69	9,66	0,948	3,50	<b>16,2</b>

Linear model :  $N_m = k N - N_i$  proposed by Houot et al. (1989)

Hyperbolique model (MH) :  $N_m = N_0.t / (T_0^H + t) - N_i$  proposed by Juma et al. (1984)

$N_m$  : Mineral Nitrogen N at time  $t = 0$

$N_0$  : Proportion of potentially minéralizable N

$T_0^H$  : exprimed in weeks et corresponds to Half-life time of  $N_0^H$

RMS : Root Mean Square

MRE : Mean Relative Error



**Table 3 : Comparaison of parameters of non linear regression relating models II (MII) and I (MI)**

Site	First-order and exponential MII							First-order MI					
	N <sub>m</sub>	N <sub>o</sub>	k	h	R <sup>2</sup>	RMS	MRE	N <sub>m</sub>	N <sub>o</sub>	k	R <sup>2</sup>	MRE	
	mg.kg <sup>-1</sup> sol		sem. <sup>-1</sup>				(%)	mg.kg <sup>-1</sup>		sem. <sup>-1</sup>		(%)	
1	225,67	122	0,061	0,062	0,95	4,30	5,8	250	217	0,07	0,951	6,10	6,00
2	153,21	121	0,057	0,041	0,95	6,20	9,5	210	219	0,04	0,949	8,90	10,70
3	150,59	165	0,061	0,098	0,96	3,90	3,7	228	226	0,04	0,961	4,60	4,10
4	179,54	125	0,069	0,018	0,96	4,50	7,5	245	229	0,04	0,994	6,60	7,50
5	175,38	145	0,085	0,060	0,95	6,25	10	221	212	0,08	0,907	8,00	9,90
6	183,88	178	0,051	0,014	0,88	2,22	3,7	238	236	0,06	0,880	3,60	3,60
7	232,26	174	0,069	0,041	0,92	6,23	11,1	210	231	0,05	0,917	8,70	11,60
8	247,21	158	0,057	0,041	0,90	2,40	8,9	221	219	0,04	0,897	8,60	9,70
9	185,06	131	0,057	0,031	0,92	2,85	5,1	219	256	0,04	0,912	4,70	4,70
10	179,69						ND	163	202	0,03	0,907	4,60	9,20
11	260,45						ND	158	186	0,03	0,933	8,90	17,10
12	152,72	201	0,058	0,043	0,88	3,53	7,8	215	214	0,03	0,880	5,50	7,20
13	251,77	180	0,075	0,047	0,87	8,25	16,02	215	207	0,03	0,870	12,50	18,90
14	171,36	170	0,071	0,047	0,88	3,25	3,9	210	207	0,03	0,877	7,10	4,50
15	203,17						ND	185	201	0,04	0,880	3,60	9,20
16	193,19	222	0,055	0,037	0,87	5,00	7,5	190	228	0,07	0,886	7,10	9,10
17	173,74	278	0,064	0,012	0,86	4,90	12,8	165	181	0,05	0,863	6,60	13,40
18	148,63	333	0,035	0,028	0,89	4,33	10,9	223	240	0,09	0,886	6,10	11,60
19	174,57	201	0,072	0,042	0,88	4,35	9,5	215	205	0,07	0,879	6,70	6,30
20	181,53	165	0,075	0,036	0,96	3,75	6,9	195	234	0,06	0,956	5,20	4,80
21	158,60	205	0,053	0,035	0,88	2,1	6,5	147	178	0,05	0,881	3,20	5,70
22	240,66						ND	148	178	0,04	0,937	3,00	9,50
23	234,13	155	0,062	0,030	0,85	4,58	5,9	159	174	0,08	0,851	6,40	5,70
24	175,99	245	0,053	0,038	0,95	2,22	7,9	99	160	0,04	0,946	3,80	8,10
25	196,28	135	0,043	0,034	0,92	2,56	7,4	115	173	0,04	0,936	3,20	9,80
26	170,59	180	0,033	0,027	0,94	3,53	8,9	175	280	0,02	0,937	4,00	5,00
27	185,61	165	0,053	0,058	0,96	3,71	3,5	185	238	0,06	0,964	4,70	5,40
28	146,47	153	0,064	0,031	0,85	4,42	5,8	148	208	0,10	0,852	6,00	5,40
29	180,21	160	0,053	0,037	0,93	3,65	6,5	119	221	0,04	0,927	5,65	4,65
30	155,67	122	0,06	0,045	0,96	2,2	3,2	145	200	0,05	0,952	2,70	4,90
31	143,96	145	0,077	0,025	0,91	2,3	5,5	128	163	0,08	0,916	3,60	7,90
32	215,14	123	0,068	0,039	0,95	3,8	8,3	125	163	0,05	0,946	5,70	6,70
33	196,86						ND	112	181	0,05	0,935	4,40	6,90
34	191,38	132	0,065	0,056	0,94	2,7	3,6	136	167	0,07	0,941	5,00	6,10
35	215,04	130	0,067	0,053	0,94	3,1	4,7	145	174	0,06	0,943	4,45	4,60

N<sub>m</sub> = N mineralized at 56 weeks, N<sub>p</sub> = N potentially mineralizable (mg.kg soil).

k et h represent the constants of speed and are expressed in week<sup>-1</sup>

MODEL II  $N_m = N_i e^{-kt} + N_o (1 - e^{-kt}) + e^{-ht}$  First-order and exponential (bi-compartmentalized model) proposed by Bonde et al. (1988)

Modèle Mode I  $N_m = N_i e^{-kt} + N_o (1 - e^{-kt})$  First-order (single-compartment model) proposed by Stanford and Smith (1972)

RMS : Root Mean Square

MRE : Mean Relative Error.

ND : Non Determined



**Table 4 : Experimental and Predicted data from different models for nitrogen mineralization**

<i>Mineralized N (mg.kg<sup>-1</sup> s) after 56 weeks</i>				
Sites	N <sub>m</sub> net	Predict <i>MI</i>	Predict <i>MII</i>	Prédit <i>MH</i>
----- mg kg <sup>-1</sup> -----				
1	175	122,51	170,44	135,56
2	160	167,51	165,14	174,63
3	140	152,17	150,25	165,63
4	198	199,26	188,26	200,45
5	200	222,16	223,23	180,25
6	200	222,65	183,88	190,36
7	202	225,93	232,26	256,23
8	241	199,03	275,26	273,23
9	188	208,26	185,06	199,23
10	153	152,53		165,36
11	230	247,03		251,56
12	140	148,77	144,25	164,36
13	200	258,92	225,25	250,23
14	160	178,50	170,53	153,33
15	170	183,83		202,33
16	183	193,56	193,19	193,89
17	170	189,76	173,74	185,36
18	158	168,89	148,63	178,25
19	150	126,36	170,69	155,36
20	140	152,19	155,86	65,36
21	160	188,08	158,60	155,45
22	180	186,21		203,23
23	220	214,43	234,13	255,23
24	183	189,61	174,25	255,45
25	165	175,99	200,28	167,26
26	180	208,77	185,59	206,85
27	185	206,73	195,61	189,00
28	155	168,23	166,47	165,26
29	215	215,80	190,21	145,15
30	190	214,28	185,67	215,23
31	150	195,20	144,96	183,26
32	200	212,08	220,14	218,14
33	180	188,65		215,25
34	185	176,79	198,38	195,03
35	200	202,75	225,04	215,69

$MI$  : Modèle I  $N_m = N_1 e^{-kt} + N_0 (1 - e^{-kt})$   
 $MII$  : Modèle II  $N_m = N_0 (1 - e^{-kt}) + e^{-ht} + N_i e^{-kt}$   
 $MH$  : Modèle hyperbolique :  $N_m = N_0.t / (T_C^H + t) + N_1$



**Table 5 : Multiple correlation between N mineralized and N predicted by MI, MII and MH models**

	net Nm	Nm predict MI	Nm predict MII	Nm predict MH
Nm net	1			
Nm predict MI	0,748	1		
Nm predict MII	0,878	0,604	1	
Nm predict MH	0,709	0,656	0,688	1

*Significance : P < 0.05*