

Kinetic Models Fitted to Nitrogen Mineralization Potential in Soils Amended with Municipal Compost and Urban Sewage Sludge

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ABSTRACT

An experimental incubation was conducted to study and describe the dynamics and kinetics of nitrogen (N) mineralization, using six different kinetic models, on two different soils, amended with municipal solid waste compost (MSWC) and sewage sludge (SS). For this purpose, a pot experiment was carried out, under semi-controlled conditions and without crop, in a complete randomised block design, with application of seven levels of organic amendments (0, 15, 30 and 60 t ha⁻¹ for both MSWC and SS). The two contrasting texture soils were an Haplic Podzol (PZha) and a Calcic Vertisol (VRcc). The soil samples were collected at the end of 1st, 2nd, 3th, 4th and 8th weeks and mineral N was measured. The kinetic models applied showed a lower fitting for the PZha soil than to the VRcc soil. However, for both soils the best determination coefficients were obtained with the simple and the double exponential models. The results suggested that to choose the model that better fits N mineralization data soil texture must be considered and soils should be modeled separately.

Keywords: Nitrogen mineralization, kinetic models, municipal solid waste compost, urban sewage sludge

INTRODUCTION

The determination of N mineralization potential in soils after organic amendments allows the evaluation of N dynamics in the soil and its true effectiveness in economic and ecological effects. The mathematical description of N mineralization in soils, showed at **Table 1**, is a possible approach to characterize and quantify the organic matter (OM) pool and mineralization constant rate. The single exponential model is the most widely used for soil N mineralization, although other types have also been tested (e.g., the zero-order kinetic equation, the parabolic model, the double exponential model, the exponential plus linear model and the hyperbolic model). Incubations under controlled conditions are the most widely procedures to develop these mathematical models.

MATERIALS AND METHODS

Both soils used in the present experiment were sampled at 0-20 cm depth at Pegões and Queluz (Portugal), respectively corresponding to an Haplic Podzol (PZha) and a Calcic Vertisol (VRcc) (FAO,

1998), and showing sandy and clay textures, pH 5.1 and 7.4, Kjeldahl N of 0.4 and 1.2 g kg⁻¹ and fulvic acids content of 325 and 630 mg kg⁻¹, respectively. The soil samples were air-dried, homogenized and sieved to <5 mm for the pot experiment. Sewage sludge (SS) sampled at Frielas Wastewater Treatment Plant, near Lisbon (Portugal) and a municipal solid waste compost (MSWC) produced at Amarsul MSW Composting Plant (Setúbal, Portugal) were used as amendments in the pot experiment. These amendments were air-dried, homogenized and sieved to <5 mm prior to mixing them with the soils. The pot experiment was carried out in a complete randomised block design, with seven treatments and three replicates, for both soils [PZha (A) and VRcc (B)], using the following rates (dry weight):

T0A and T0B – Control (unamended soil), respectively for soils A and B;

T1A and T1B – Application of 15 t ha⁻¹ of MSWC, respectively for soils A and B;

T2A and T2B – Application of 30 t ha⁻¹ of MSWC, respectively for soils A and B;

T3A and T3B – Application of 60 t ha⁻¹ of MSWC, respectively for soils A and B;

T4A and T4B – Application of 15 t ha⁻¹ of SS, respectively for

Table 1 Different kinetic models used to describe the N mineralization in soils.

Kinetic model	Equation	References
[1] Zero-order	$N_t = k \times t$	Addiscott 1983
[2] Parabolic	$N_t = N_0 \times t^k$	Broadbent 1986; Marion and Black 1987
[3] Single exponential	$N_t = N_0 \times (1 - e^{-k \times t})$	Stanford and Smith 1972
[4] Double exponential	$N_t = N_i \times (1 - e^{-k_i \times t}) + N_r \times (1 - e^{-k_r \times t})$	Molina <i>et al.</i> 1980
[5] Exponential plus linear	$N_t = N_i \times (1 - e^{-k_i \times t}) + C \times t$	Bonde and Roswall 1987
[6] Hyperbolic	$N_t = \frac{N_0 \times t}{(k \times N_0 + t)}$	Juma <i>et al.</i> 1984

N_t – amount of N mineralized (mg N kg⁻¹); N_0 – N mineralization potential at t_0 (mg N kg⁻¹); N_i – labile N pool (mg N kg⁻¹); N_r – resistant N pool (mg N kg⁻¹); k , k_i , k_r – mineralization constant rates; C – resistant N pool mineralization constant rate (week⁻¹); t – time (week).

soils A and B;

T5A and T5B – Application of 30 t ha⁻¹ of SS, respectively for soils A and B;

T6A and T6B – Application of 60 t ha⁻¹ of SS, respectively for soils A and B.

Soil samples were collected at the end of 1st, 2nd, 3th, 4th and 8th weeks, air-dried and sieved (<2 mm) for mineral N (NH₄⁺-N and NO₃⁻-N) determination. Kinetic models were fitted to the measured mineral N vs. length incubation set by using non-linear regression procedures in the Statgraphics plus 5.1 software package.

RESULTS AND DISCUSSION

VRcc soil presented a higher mineral N than the PZha soil, in all sampling date, since it showed more favorable physical and chemical characteristics for N mineralization.

The kinetic parameters values obtained are presented in **Tables 2** and **3** (PZha and VRcc soils, respectively). Better fitted models were found with the VRcc soil than with the PZha soil. The linear [1] and parabolic [2] models showed the poorest results for both soils, plus the hyperbolic model [6] for the PZha soil. With the exponential plus linear model [5], negative C values were obtained for six of the seven treatments in both soils. Since C cannot be negative, as it is given by the physical meaning of the resistant organic N

Table 2 Mineral N at the end of 8-weeks incubation period (N₁₈) and kinetic parameter values in unamended and amended PZha soil, by applying six different kinetic models.

Kinetic model	Parameter	Treatments ^a						
		T0A	T1A	T2A	T3A	T4A	T5A	T6A
	N ₁₈ measured ^b	16.3	17.5	17.5	24.5	31.5	30.3	30.3
[1]	k	5.16	6.54	8.72	8.63	8.71	10.3	12.3
	R ^{2c}	0.000 ^{(d)ns}	0.000 ^{ns}	0.000*	0.000**	0.000***	0.000 ^{ns}	0.000*
[2]	N ₀	23.2	30.7	31.8	28.3	34.9	49.5	73.6
	k	0.104	0.091	0.235	0.306	0.171	0.067	-0.055
	R ²	0.322*	0.0770 ^{ns}	0.398*	0.614***	0.732***	0.113 ^{ns}	0.0318 ^{ns}
[3]	N ₀	27.3	37.1	49.3	51.6	44.9	56.4	71.9
	k	1.58	1.19	0.751	0.590	1.43	1.50	1.95
	R ²	0.372*	0.310*	0.302 ^{ns}	0.745***	0.294 ^{ns}	0.380**	0.082 ^{ns}
[4]	N _i +N _r	27.7	37.2	49.4	51.5	46.3	42.9	-22.0
	N _i	13.3	14.8	62.9	32.7	99.1	129	161
	k _i	2.73	1.27	0.744	0.588	0.854	0.665	0.668
	N _r	14.4	22.4	-13.5	18.8	-52.8	-86.1	-183
	k _r	0.90	1.12	0.736	0.593	0.714	0.302	0.121
	R ²	0.389**	0.310*	0.302**	0.745***	0.163**	0.584***	0.783***
[5]	N _i	26.3	37.1	41.0	51.6	44.9	56.4	71.9
	k _i	1.74	1.19	0.988	0.590	1.43	1.50	1.95
	C	0.198	0.000	1.20	0.000	0.000	0.000	0.000
	R ²	0.382**	0.310*	0.317**	0.745***	0.294 ^{ns}	0.380**	0.0822 ^{ns}
[6]	N ₀	29.3	39.7	55.7	62.0	50.4	59.3	70.9
	k	0.011	0.011	0.016	0.024	0.010	0.004	0.001
	R ²	0.379**	0.196*	0.367**	0.706***	0.564***	0.261*	0.004 ^{ns}

^aTreatments: T0, Control; T1, T2, and T3 application of 15, 30 and 60 t ha⁻¹ of MSWC, respectively; T4, T5 and T6 application of 15, 30 and 60 t ha⁻¹ of SS, respectively. ^bmeasured mineral N (mg N kg⁻¹). ^cCoefficient of determination. ^(d) ns, ***, **, * non-significant and significant probability level at P ≤ 0.001, P ≤ 0.01 and P ≤ 0.05, respectively.

Table 3 Mineral N at the end of 8-weeks incubation period (N₁₈) and kinetic parameter values in unamended and amended VRcc soil, by applying six different kinetic models.

Kinetic model	Parameter	Experimental treatments ^a						
		T0B	T1B	T2B	T3B	T4B	T5B	T6B
	N ₁₈ measured ^b	112	115	128	125	117	134	135
[1]	k	17.2	18.0	17.9	18.4	18.3	20.5	21.8
	R ^{2c}	0.000 ^{(d)***}	0.000**	0.000*	0.000**	0.000**	0.000**	0.000**
[2]	N ₀	55.4	59.8	64.1	71.3	70.8	69.6	88.3
	k	0.317	0.298	0.254	0.199	0.203	0.285	0.173
	R ²	0.773***	0.733***	0.559**	0.769***	0.649***	0.714***	0.667***
[3]	N ₀	101	104	103	100	102	119	119
	k	0.616	0.661	0.744	0.958	0.886	0.669	1.06
	R ²	0.906***	0.906***	0.836***	0.932***	0.861***	0.894***	0.880***
[4]	N _i +N _r	101	104	103	102	93.0	91.0	119
	N _i	41.4	54.5	61.0	70.8	231	233	242
	k _i	0.616	0.658	0.744	0.750	0.544	0.413	0.918
	N _r	59.6	50.0	42.0	31.3	-138	-142	-123
	k _r	0.617	0.665	0.744	1.75	0.334	0.184	0.795
	R ²	0.906***	0.906***	0.836***	0.935***	0.878***	0.906***	0.880***
[5]	N _i	101	104	103	98.0	102	119	119
	k _i	0.616	0.661	0.744	1.00	0.886	0.669	1.06
	C	0.000	0.000	0.000	0.477	0.000	0.000	0.000
	R ²	0.906***	0.906***	0.836***	0.934***	0.861***	0.894***	0.880***
[6]	N ₀	122	126	121	115	116	142	133
	k	0.012	0.011	0.009	0.006	0.007	0.009	0.005
	R ²	0.880***	0.863***	0.737***	0.906***	0.802***	0.843***	0.824***

^aTreatments: T0, Control; T1, T2, and T3 application of 15, 30 and 60 t ha⁻¹ of MSWC, respectively; T4, T5 and T6 application of 15, 30 and 60 t ha⁻¹ of SS, respectively. ^b measured mineral N (mg N kg⁻¹). ^cCoefficient of determination. ^(d) ns, ***, **, * non-significant and significant probability level at P ≤ 0.001, P ≤ 0.01 and P ≤ 0.05, respectively.

pool multiplied by its mineralization constant rate, C was constrained to be equal to 0. With this constrain, the exponential plus linear model produced N mineralization potentials and the corresponding constant rate values similar to the results obtained with the single exponential model [3]. After 8-weeks incubation, N mineralization potential showed the same range of values by the simple and double exponential models. Both models [3 and 4] fitted well for both soils, and will be further discussed. Estimated N mineralization potential was smaller than the measured mineral N at the end of 8-weeks incubation period in PZha soil, whereas the mineral N measured in the VRcc soil was in the similar range of estimated N mineralization potential. The results of N_T+N_r in double exponential model [4] for both soils showed a tendency to be similar to N_0 data in simple exponential model [3]. In general, treatments presented higher N_T than N_r pools. On simple [3] and double [4] exponential models, most data in the PZha soil showed a tendency to decrease k values with higher rates of amendment, except for the SS treatment on simple exponential model [3]. VRcc soil showed an opposite behaviour, and k values increased with higher amounts of amendments applied, except for 30 t ha⁻¹ of SS. It was also observed, on the PZha soil, that the mineralization constant rate k_l was always higher than the k_r . However, on the VRcc soil amended with MSCW, the k_r was slightly higher than k_l .

In PZha soil, the light texture induced a weaker fitness of tested models (lower R^2) than in VRcc soil. Actually, some soil characteristics, such as pH and clay content, may influence the OM mineralization (Pedra *et al.* 2007) and consequently interfere with the kinetic model results. The good fitness obtained with the simple [3] and double [4] exponential models for both soils, indicated that the degradability of the organic N pools varied with the incubation length since OM is formed by heterogenic substances with diverse mineralization resistance degrees to microbial activity. The experimental data of mineral N on VRcc soil was very similar to the estimated N mineralization potential by both simple [3] and double [4] exponential models, confirming that these models were adequate to evaluate the N dynamics in this particular soil. The main identified errors in the remaining models were the overestimation of mineralized N in the last weeks of the incubation, indicating that some models cannot fit the data when a period of N loss exists (Plaza *et al.* 2005). The double exponential model [4] presented similar N_T+N_r to N_0 values in simple exponential model [3] for both soils, confirming that the parameter N_T+N_r had the same physical meaning that N_0 , i.e. added OM was mostly formed by labile N forms. Higher mineralization constant rates ($k_l > k_r$) in the PZha soil, showed that a greater aeration would improve microbe performance and activity to decompose the substrates. Similar k_l and k_r values in VRcc soil amended with 15 and 30 t ha⁻¹ of MSWC and the lower k_l value for 60 t ha⁻¹ of MSWC suggested that the clay particles protected some of the more easily decom-

posable organic compounds. The advantage on the use of the double exponential model [4] in relation to single model [3] is that it originates a better characterization of mineralization kinetic, through the quantification of active and resistant N pools. However, choice of the models should depend on the purpose of modeling, the accuracy desired, and the performance of other model components, such as the simulation of water dynamics (Dou *et al.* 1996) and soil texture.

CONCLUSIONS

The simple and the double exponential models fitted better with experimental data than the other models. A poorer fitting was obtained with the PZha soil than with VRcc soil, suggesting that the choice of proper model for N mineralization data is also dependent on soil texture. The different N mineralization potentials and kinetic constants for both soils confirmed the influence of soil physical (e.g., texture) and chemical (e.g., pH and initial OM) characteristics and showed the proper fit of double exponential model, especially on the VRcc soil, which presented more favourable conditions for N mineralization. Results emphasize the importance of continuing these studies for a better understanding on N mineralization mechanisms that take place in soils.

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