

Supplementary material for

Nitrogen mineralisation in sugarcane soils in Queensland, Australia: I. evaluation of soil tests for predicting nitrogen mineralisation

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Table S1 Soil sample details for the samples of the 301-day laboratory incubation

Samples used for long-term incubation of potentially mineralisable N. The particle size data (%) are as measured for the 15 samples, while the dominant soil orders are as extracted from the ASRIS 250-m Australian Soil Classification map [Isbell, R., 2002. 'The Australian Soil Classification.' (CSIRO Publishing: Melbourne)].

Unique identifier	Coarse Sand	Fine Sand	Silt	Clay	Dominant soil order
1	54.2	36.1	6.3	4.6	Kandosol
5	26.4	41.0	20.7	14.2	Sodosol
6-1	14.8	40.7	23.0	21.4	Chromosol
6-2	27.5	37.7	21.3	14.7	Chromosol
8	6.8	20.3	28.2	47.6	Vertosol
12	28.2	35.5	23.0	18.1	Sodosol
13	2.5	30.2	24.9	47.3	Vertosol
17	16.6	57.4	12.9	14.5	Dermosol
19	7.4	30.4	33.1	28.1	Vertosol

21	4.5	11.0	38.0	46.9	Dermosol
24	20.5	26.5	19.1	35.2	Dermosol
26	1.6	24.9	39.6	38.5	Dermosol
28	4.9	17.2	29.5	48.5	Dermosol
30	0.7	26.1	36.1	38.3	Dermosol
33-1	9.0	30.0	21.6	37.1	Dermosol

Text S2 Equivalence of the two-pool exponential model and a generalised exponential model

We begin by defining the function $g_i(t)$ as:

$$g_i(t) = -\ln\left(\frac{N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}}{N_{a,i} + N_{s,i}}\right) \quad (\text{S1})$$

The chain rule of differentiation can be applied to give:

$$\frac{dg_i(t)}{dt} = \frac{N_{a,i}k_{a,i} \exp\{-k_{a,i}t\} + N_{s,i}k_{s,i} \exp\{-k_{s,i}t\}}{N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}} \quad (\text{S2})$$

With $f_i(\tau)$ defined through Equation 7, we have:

$$\int_0^t f_i(\tau) d\tau = \int_0^t \frac{N_{a,i}k_{a,i} \exp\{-k_{a,i}\tau\} + N_{s,i}k_{s,i} \exp\{-k_{s,i}\tau\}}{N_{a,i} \exp\{-k_{a,i}\tau\} + N_{s,i} \exp\{-k_{s,i}\tau\}} d\tau \quad (\text{S3})$$

Therefore, Equations S1 and S2 can be used to write:

$$\begin{aligned} \int_0^t f_i(\tau) d\tau &= \left[-\ln\left(\frac{N_{a,i} \exp\{-k_{a,i}\tau\} + N_{s,i} \exp\{-k_{s,i}\tau\}}{N_{a,i} + N_{s,i}}\right) \right]_{\tau=0}^{\tau=t} \\ &= -\ln\left(\frac{N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}}{N_{a,i} + N_{s,i}}\right) + \ln\left(\frac{N_{a,i} \exp\{0\} + N_{s,i} \exp\{0\}}{N_{a,i} + N_{s,i}}\right) \\ &= -\ln(N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}) + \ln(N_{a,i} + N_{s,i}) \end{aligned}$$

$$= -\ln\left(\frac{N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}}{N_{a,i} + N_{s,i}}\right) \quad (\text{S4})$$

Substituting Equations S4 and 6 into Equation 3 (the generalised exponential model; Rovira and Rovira, 2010) and simplifying gives:

$$\begin{aligned} N_L(t; i) &= N_{0,i} \left(1 - \exp\left\{-\int_0^t f_i(\tau) d\tau\right\}\right) \\ &= (N_{a,i} + N_{s,i}) \left(1 - \exp\left\{\ln\left(\frac{N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}}{N_{a,i} + N_{s,i}}\right)\right\}\right) \\ &= (N_{a,i} + N_{s,i}) \left(1 - \frac{N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}}{N_{a,i} + N_{s,i}} \right) \\ &= N_{a,i} + N_{s,i} - (N_{a,i} \exp\{-k_{a,i}t\} + N_{s,i} \exp\{-k_{s,i}t\}) \\ &= N_{a,i}(1 - \exp\{-k_{a,i}t\}) + N_{s,i}(1 - \exp\{-k_{s,i}t\}) \end{aligned} \quad (\text{S5})$$

This is exactly the form of the double exponential model, Equation 3.

Text S3 Formulation of the mixed-effects model

A standard matrix notation for a mixed-effects model (Pinheiro and Bates, 2004) for data, \mathbf{y}_i is:

$$\mathbf{y}_i = \mathbf{X}_i \boldsymbol{\beta} + \mathbf{Z}_i \mathbf{b}_i + \boldsymbol{\varepsilon}_i \quad (\text{S6})$$

In our case, the data \mathbf{y}_i , $i = 1, \dots, 15$, represent the vector of cumulative mineralised N of soil sample i for the $T = 14$ measurement times $t = t_1, \dots, t_T$. The terms $\mathbf{X}_i \boldsymbol{\beta}$ and $\mathbf{Z}_i \mathbf{b}_i$ represent the fixed effects and random effects, respectively, and $\boldsymbol{\varepsilon}_i$ the vector of residuals with t th element ε_{it} , assumed to be identically and independently normally distributed for all soil samples i and times t with mean 0 and variance σ^2 .

Suppose for simplicity of presentation that we have exactly one covariate, W_a (with measured value w_{ai} in soil sample i), used for modelling the active pool, and exactly one, W_s , for the slow pool.

Further suppose (as was the case with our data) that each soil sample was measured at the same T time-points, t_1, \dots, t_T . Then the fixed-effects design matrix \mathbf{X}_i is defined as a $T \times 4$ matrix:

$$\mathbf{X}_i = \begin{bmatrix} (1 - \exp\{-k_a t_1\}) & (1 - \exp\{-k_a t_1\})w_{ai} & (1 - \exp\{-k_s t_1\}) & (1 - \exp\{-k_s t_1\})w_{si} \\ \vdots & \vdots & \vdots & \vdots \\ (1 - \exp\{-k_a t_T\}) & (1 - \exp\{-k_a t_T\})w_{ai} & (1 - \exp\{-k_s t_T\}) & (1 - \exp\{-k_s t_T\})w_{si} \end{bmatrix}$$

The vector $\boldsymbol{\beta}$ (of length 4 in this case) contains the fixed-effects parameters.

The random-effects design matrix, \mathbf{Z}_i , is defined by the first and third columns of \mathbf{X}_i . As noted in the main manuscript, the length-2 vector $\mathbf{b}_i = [\varepsilon_{ai}, \varepsilon_{si}]^T$ is assumed to follow a bivariate normal distribution with mean $\mathbf{0}$ and 2×2 covariance matrix $\boldsymbol{\Psi}$, and is considered to be independent between different soils.

Table S2. Fitted regression statistics based on the archived soil samples

Shows the relationship between 14-day mineralised N and soil properties for sugarcane sites from archived projects, ranked in order of level of significance (p values adjusted for multiple comparisons using Benjamini and Hockberg 1995; *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$, $P < 0.1$). Column (a) represents analytical results combined from numerous laboratories; column (b) represents analytical results from the same archived soils, re-analysed using one laboratory, to minimise sources of errors.

(a) Regression of PMN (301 days at 35°C) with soil properties							(b) Regression of PMN (14 days at 35°C) with soil properties						
Soil property	Year of measurement	n	slope	int	R ²	Sig	Soil property	Year of measurement	n	R ²	slope	int	Sig
WB_C_CSRlab	2006	54	10.528	4.229	0.563	***	FieldCapacity	2016	90	0.401	1.208	-1.177	***
CaCl2	2006	112	0.255	9.638	0.224	***	TN	2016	90	0.396	157.518	5.460	***
H2SO4	2006	112	0.019	10.638	0.206	***	KOC	2016	90	0.386	14.817	6.385	***
Zn	2006	113	1.770	12.980	0.193	***	moisture	2016	90	0.380	6.880	7.809	***
P	2006	68	0.007	11.501	0.277	***	MIR_HOC	2016	89	0.366	18.214	4.848	***
TN	2006	113	89.653	8.163	0.133	***	TC	2016	90	0.354	10.080	6.648	***
Mn	2006	113	0.089	11.966	0.133	***	WB_C	2016	90	0.282	11.401	5.497	***
S	2006	68	0.032	11.051	0.211	***	Clay	2006	69	0.337	0.479	7.724	***
CEC	2006	113	0.493	12.043	0.126	***	Heanes_C	2016	90	0.223	8.972	6.268	***
Delta pH	2006	79	-15.505	10.713	0.161	**	MIR_TOC	2016	90	0.208	6.528	10.506	***
Denitrification capacity	2006	57	0.155	9.913	0.200	**	CoarseSand	2006	69	0.226	-0.255	24.917	***
1/3_Bar	2006	73	0.416	7.857	0.153	**	Silt	2006	69	0.150	0.365	11.552	**
15_Bar	2006	94	0.511	10.120	0.119	**	MIR_ROC	2016	90	0.089	16.218	14.009	**
CoarseSand	2006	94	-0.173	19.700	0.111	**	pH _{CaCl2}	2006	90	0.085	6.274	-9.764	**
Clay	2006	94	0.219	10.484	0.109	**	MIR_POC	2016	90	0.081	30.835	15.365	**
Cu	2006	110	2.368	12.455	0.090	**	ADMC	2016	34	0.162	1.678	14.893	*
Exch_K	2006	113	19.378	11.472	0.077	**	Delta pH	2006	55	0.078	-20.401	14.395	*
PBI	2006	113	0.031	11.890	0.076	**	pH _{Water}	2006	90	0.037	3.861	-1.968	.
TC	2006	113	3.296	10.571	0.066	*	pHKCl	2006	90	0.035	3.828	2.121	.
KOC_lab1	2006	113	4.334	10.870	0.063	*							
ExtrctMn	2006	113	0.136	13.216	0.063	*							

CECclayRatio	2006	73	18.184	11.453	0.080	*							
Silt	2006	94	0.224	11.215	0.060	*							
KOC_lab2	2006	62	1.109	12.147	0.079	.							
Na	2006	112	-0.542	17.176	0.039	.							
Lime_requirement_p H 6.0 ^A	2006	52	1.133	12.205	0.082	.							
C:N	2006	113	-0.408	22.567	0.037	.							
Lime_requirement_p H 5.0 ^A	2006	52	1.705	12.816	0.074	.							
Initial mineral N	2006	102	0.189	12.694	0.037	.							
Lime_requirement_p H 6.5 ^A	2006	52	0.798	11.931	0.073	.							

^ARayment and Lyons (2011) method 16C1.