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Net mineralization and nitrification rates in a clay soil measured and predicted in permanent grassland from soil temperature and moisture content

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Summary Net mineralization of N and net nitrification in field-moist clay soils (Evesham-Kingston series) from arable and grassland sites were measured in laboratory incubation experiments at 4, 10 and 20°C. Three depth fractions to 30 cm were used. Nitrate accumulated at all temperatures except when the soil was very dry (θ = 0.13 cm^3 cm^{-3}). Exchangeable NH_4-ions declined during the first 24 h and thereafter remained low. Net mineralization and net nitrification approximated to zero-order reactions after 24 h, with Q_{10} values generally < 1.6. The effect of temperature on both processes was linear although some results conformed to an Arrhenius-type relationship. The dependence of net mineralization and net nitrification in the field soil on soil temperature (10 cm depth) and moisture (0–15, 15–25, 25–35 cm depths) was modelled using the laboratory incubation data. An annual net mineralization of 350 kg N ha^{-1} and net nitrification of 346 kg N ha^{-1} were predicted between September 1980 and August 1981. The model probably overstressed the effect of soil moisture relative to soil temperature.

Introduction

In many terrestrial ecosystems N released by mineralization constitutes a large fraction of the total annual flux of mineral N through the plant available pool of soil N. An understanding of the dynamics of mineralization and nitrification is important to the prudent management of the N cycle in agricultural systems.

A study[32] of the dynamics of mineral N in clay soils of a small agricultural catchment (9.1 ha) at Wytham, Oxford, UK, suggested that mineralization and nitrification were prominent in determining seasonal changes in the profile distribution of mineral N. It was expected that soil temperature and moisture content would affect the rate of these processes and there was evidence that both processes occurred at a measurable rate during winter.

Numerous studies have demonstrated the effects of temperature[1,14,17,42,43,50,55] or soil moisture[15,34,39,45,47] on mineralization

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and nitrification. In some[10,23,27,30,38] both these factors have been varied and a significant interactive effect upon ammonification and nitrification has been reported[27]. In relatively few cases[1,27,44,47,50,51] have quantitative data been obtained on the kinetics of mineralization and nitrification or on the relationship between kinetics and soil temperature and soil moisture. In very few cases have expressions predicting mineralization in terms of temperature and soil moisture inputs been applied to field behaviour[11,49].

It is well known that the results of any short-term incubation will be influenced by sample treatment and handling[7,12,18,24]. The use of structurally undistributed soil cores in studies of soil N transformations has been advocated[26] although spatial variability may demand unmanageable replication. Incubation procedures often involve air drying, mixing with sand or vermiculite, leaching, rewetting and adding nutrient solutions. These operations may reduce variability. It has been argued that a leaching and incubation technique simulates the uptake of mineral N by plants and leaching under field conditions[53]. Continuous culture methods have also been advocated[33,36]. In the experiments we report, sample treatment prior to incubation was minimized. Apart from physical disturbance of soil structure there was continuity of state between field site and laboratory incubation. This countered criticisms concerning the validity of results obtained during the first week of incubation[48] and we believe made the results more appropriate than otherwise to prediction of behaviour in field soils.

Six experiments were carried out on soils from 3 sites, repacked into small cores, to measure the effects of soil temperature, depth and soil moisture upon net mineralization (mineralization less immobilization and denitrification) and net nitrification (nitrification less denitrification). Results were used to construct a simple model to predict the weekly net mineralization and net nitrification in the grassland soil at Wytham between September 1980 and August 1981, with environmental inputs of weekly mean soil temperatures (10 cm depth) and volumetric moisture fractions at 0–15, 15–25 and 25–35 cm depths.

Materials and methods

Soils and sampling

The soils of the Wytham catchment have been described elsewhere[25,57]. Soil samples were taken at intervals between March and May 1982 from 3 sites (X, Y, Z) each 4 m^2 (Table 1). Sites X and Z were 100 m apart in permanent grassland established for over 30 years (dominant species *Lolium perenne* L.). Site Y was in a neighbouring arable field, on the same soil type as X, fallowed after winter wheat. Sampling depths and details of each of the 6 experiments are given in Table 2. The top 2 cm of grassland soil was excluded from sampling due to

Table 1. Characteristics of Wytham soils used in incubation experiments

Site and land use	Soil series	Sampling depth (cm)	Texture	pH (1:2.5 v/w H_2O)	Total N (%)	Organic C (%)
X (grassland)	Evesham	2–10	Clay	7.8	0.94	7.5
Y (arable)	Evesham	0–10	Clay	8.0	0.46	3.1
Z (grassland)	Evesham/ Kingston	2–10	Sandy clay loam	7.8	0.57	–
		15–20	Sandy clay loam	7.9	0.43	–
		25–30	Sandy clay loam	8.1	0.26	2.2

Table 2. Depth of soil sampled and moisture content, temperature and duration of incubation experiments

Expt.	Sampling date	Site	Profile depth (cm)	Volumetric moisture fraction θ ($cm^3\ cm^{-3}$)	Dry bulk density ($g\ cm^{-3}$)	Period of incubation (h)	Temperatures (°C)
1	220382	X	2–10	0.60	0.89	164	10, 20
2	260382	X	2–10	0.60	0.90	281	10, 20
3	300382	X	2–10	0.67	0.82	340	10, 20
		Y	0–10	0.33	1.17	340	4, 10, 20
4	050482	Y	0–2	0.13	1.37	361	4
						509	10, 20
5	160482	Z	2–10	0.50	1.00	335	10
			15–20	0.44	1.06	314	10
			25–30	0.40	1.09	335	10, 20
6	260482	X	2–10	0.64	0.86	195	4, 10, 20

the high content of plant material. Site Z was chosen in experiment 5 because soil from site X at depths greater than 15 cm could not be sieved in a field-moist state. The moisture content range of soil samples was limiting to that occurring in the field between March and May 1982.

Core construction and incubation

The preparation of soil cores for each experiment took one hour from sampling in the field to the start of incubation. 5 kg samples of field moist soil were shaken through a sieve (2.4 mm aperture) and the first 500 g were collected and mixed. Cores were made by packing 87 g of sieved soil into a perspex cylinder (internal diameter 5.1 cm) to a height of 2.85 cm, giving a moist bulk density of 1.5 g cm^{-3}. Batches of 8 to 12 cores were prepared at one time. Cores were extruded into aluminium containers with lids (not airtight) and grouped randomly for subsequent incubation at 4, 10 or 20°C (± 0.5°C). At each temperature samples were sealed in a polythene bag containing a moistened filter paper. Aeration was daily by opening the bags and containers for one minute. Incubations lasted 164–509 hours (Table 2), depending upon the pattern of sampling during incubation and the number of cores available.

Additional samples of sieved soil were removed during the procedure, triplicate samples (20 g) for gravimetric moisture content at 105°C, duplicate samples (2.0 g) for total N by the Kjeldahl method, 30 g for air-dry moisture content and determination of organic C[4,54], five samples (10 g) for extraction (1 h) in 50 ml 2*M* KCl and determination of NO_3^-, NO_2^- and NH_4^+ ions at time 0 using a Technicon Autoanalyser, Series 2[13,29].

Sampling during incubation

Cores were sampled to follow changes in concentrations of mineral N during incubation. At intervals one core at each temperature was removed and cut in half. One half was returned to incubation and the other (43 g) crumbled, mixed and duplicate subsamples (15 g) extracted in 75 ml 2*M* KCl for determination of NO_3^-, NO_2^- and NH_4^+ ions as above. Total mineral N was calculated as NO_3 + NO_2 + exchangeable NH_4-N. On the next occasion the remaining half-core was extracted. Coefficients of variation for concentrations of NO_3-N and exchangeable NH_4-N measured on several replicate cores incubated for the same time were 4–5% and 15–18% respectively.

Results and discussion

Net mineralization and net nitrification of soil organic N

Concentrations of N were expressed in $\mu g\ g^{-1}$ dry soil. In the concentration time-courses each point is the mean of duplicate analyses on a half-core and sequential pairs of points, excluding zero-time, originate from the same core. In general the 2–10 cm depth of the grassland soil, site X (Figs. 1, 2 and 3), behaved similarly to the 0–10 cm depth of arable soil, site Y (Fig. 4), with respect to the effect of temperature on net mineralization and net nitrification. However, in the dry top 2 cm of the arable soil (θ = 0.13, experiment 4) all forms of mineral N were unchanged throughout incubation, irrespective of temperature. The rate of accumulation of total mineral N and NO_3-N declined sharply with increasing depth in the grassland soil from site Z (Fig. 5).

Rates of net production of total mineral N and NO_3-N were usually highest during the first 24–50 hours. This ephameral enhancement probably reflected the effect of redistribution of substrate and microbial populations during the sieving of the soil. Thereafter net

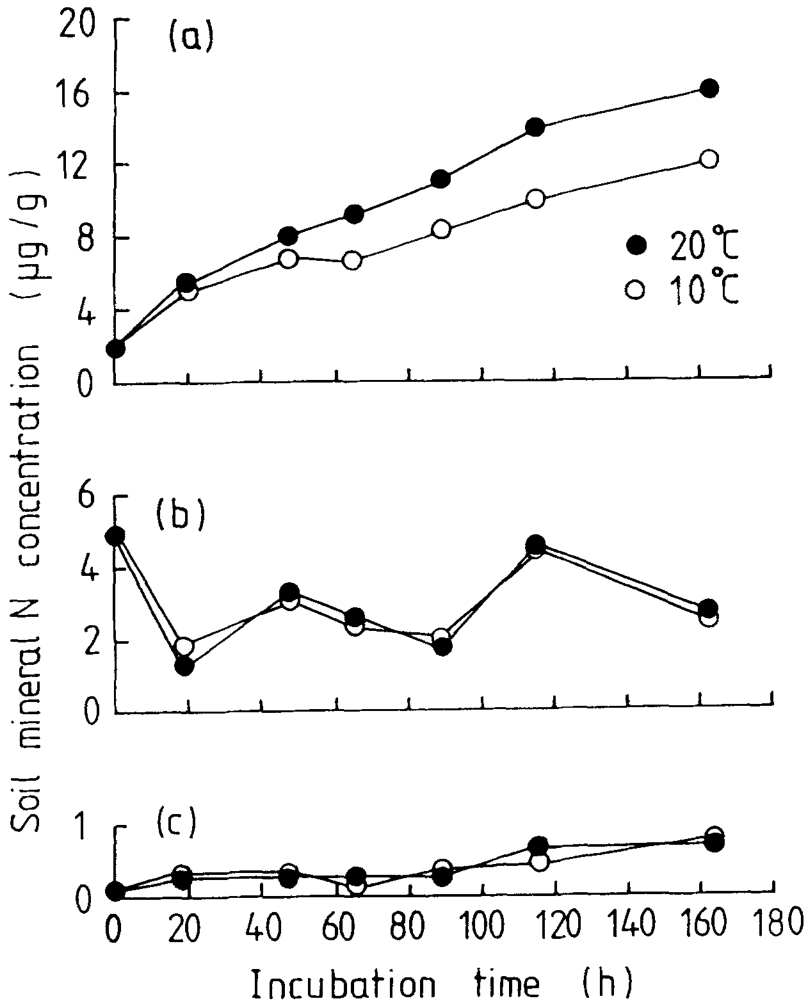

Fig. 1.*Experiment 1.* (a) NO_3-N, (b) exchangeable NH_4-N and (c) NO_2-N in grassland soil, site X, 2–10 cm depth, during incubation at 10 or 20°C.

mineralization and net nitrification appeared to obey zero-order kinetics, according to the equations:

$$N_t = k_1 t \quad (1)$$

and

$$(NO_3)_t = k_2 t \quad (2)$$

where N_t and $(NO_3)_t$ were the net amounts of N mineralized and nitrified ($\mu g\ g^{-1}$) in time t (h). The coefficients k_1 and k_2 which

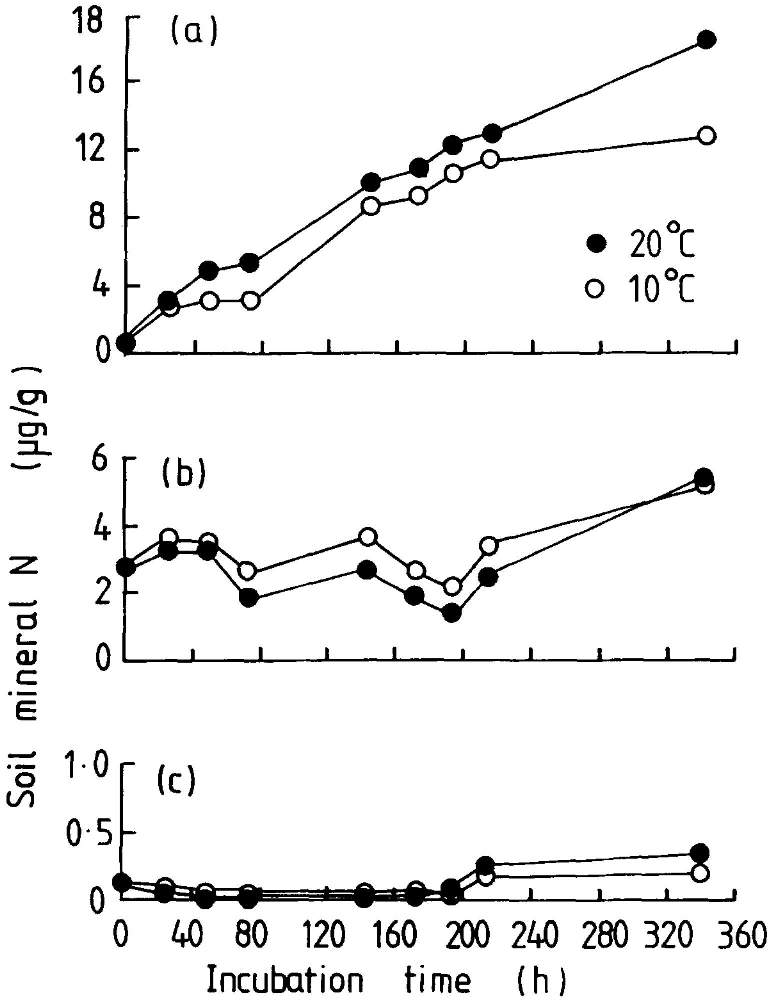

Fig. 2. *Experiment 3.* (a) NO_3-N, (b) exchangeable NH_4-N and (c) NO_2-N in grassland soil, site X, 2–10 cm depth, during incubation at 10 or 20°C.

are estimates of the rate of net mineralization and net nitrification ($\mu g\ g^{-1}\ h^{-1}$), were derived from the slopes of linear regressions fitted to the data between 24 and 168 h incubation (Table 3). Data from the 0–24 h were excluded for the reason given above. The upper limit of 168 h was the shortest total length of incubation in any experiment. Values of k_1 were generally 2–10 times greater than reported by other workers[1,53].

Q_{10} values for net mineralization and net nitrification were calculated from the ratio of the rate at 20°C to the rate at 10°C. Values were usually below 1.6 (Table 4) compared to > 2 reported elsewhere[1,50,53,55]. However, Q_{10} may change with temperature[1,37] and

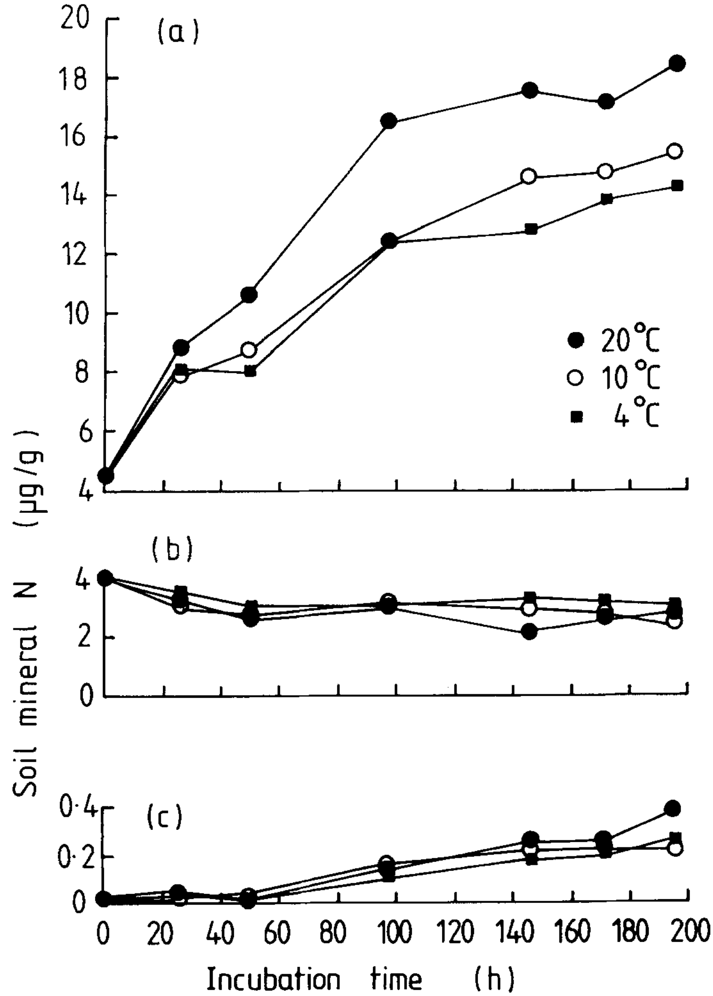

Fig. 3. *Experiment 6.* (a) NO_3-N, (b) exchangeable NH_4-N and (c) NO_2-N in grassland soil, site X, 2–10 cm depth, during incubation at 4, 10 or 20°C.

in the soils used here the availability of substrate may have limited the response to temperature. The available data (Figs. 3 and 4) suggest that mineralization and nitrification were nearly as rapid at 4°C as at 10°C. Other workers have reported substantial mineralization and nitrification activity at low temperatures[2,14,17,30].

Values of k_1 and k_2 for 4, 10 and 20°C, taken from experiments 3 and 6 were used to test whether the relationship between rate of mineralization or nitrification and absolute temperature (T_1) followed the Arrhenius relationship.

$$\ln k = \ln A - (B/T_1) \qquad (3)$$

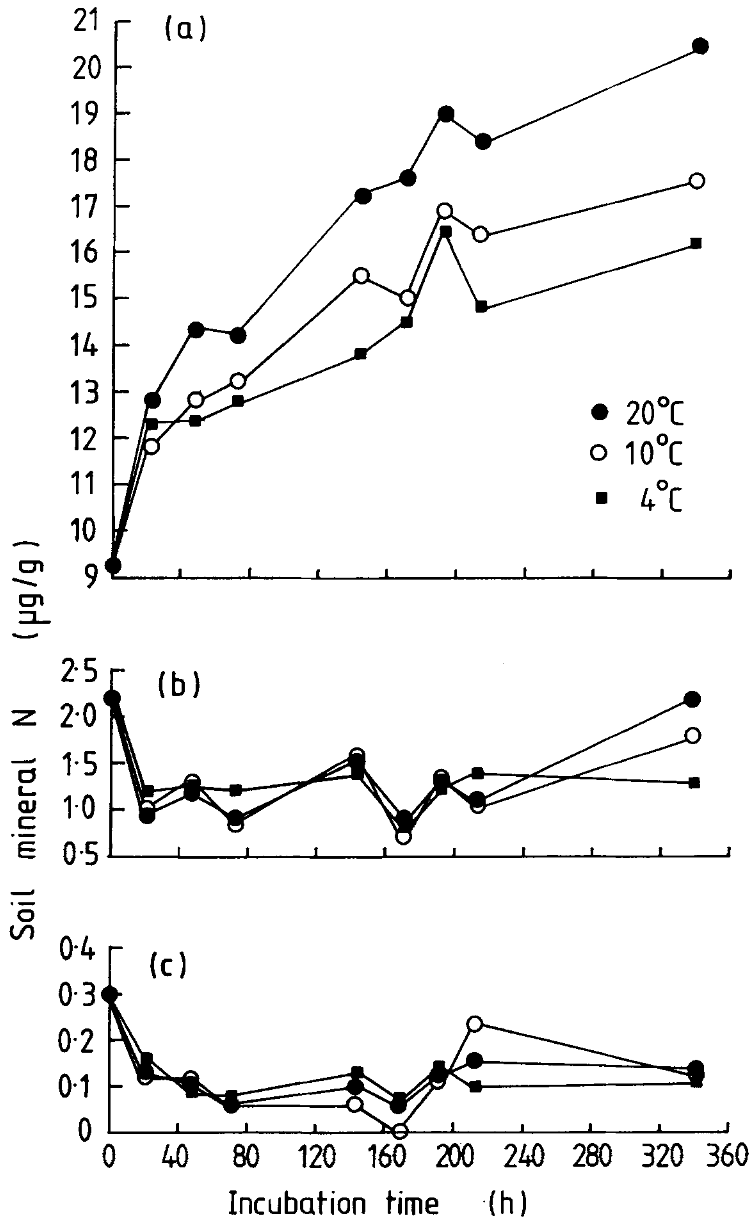

Fig. 4. *Experiment 3.* (a) NO_3-N, (b) exchangeable NH_4-N and (c) NO_2-N in arable soil, site Y, 0–10 cm depth, during incubation at 4, 10 or 20°C.

where A and B are coefficients, the later being a measure of the temperature sensitivity of the process. Regressions of ln k_1 and ln k_2 on T_1 are shown in Table 5 and must be regarded with caution in view of the single degree of freedom for error. Arrhenius B-coefficients

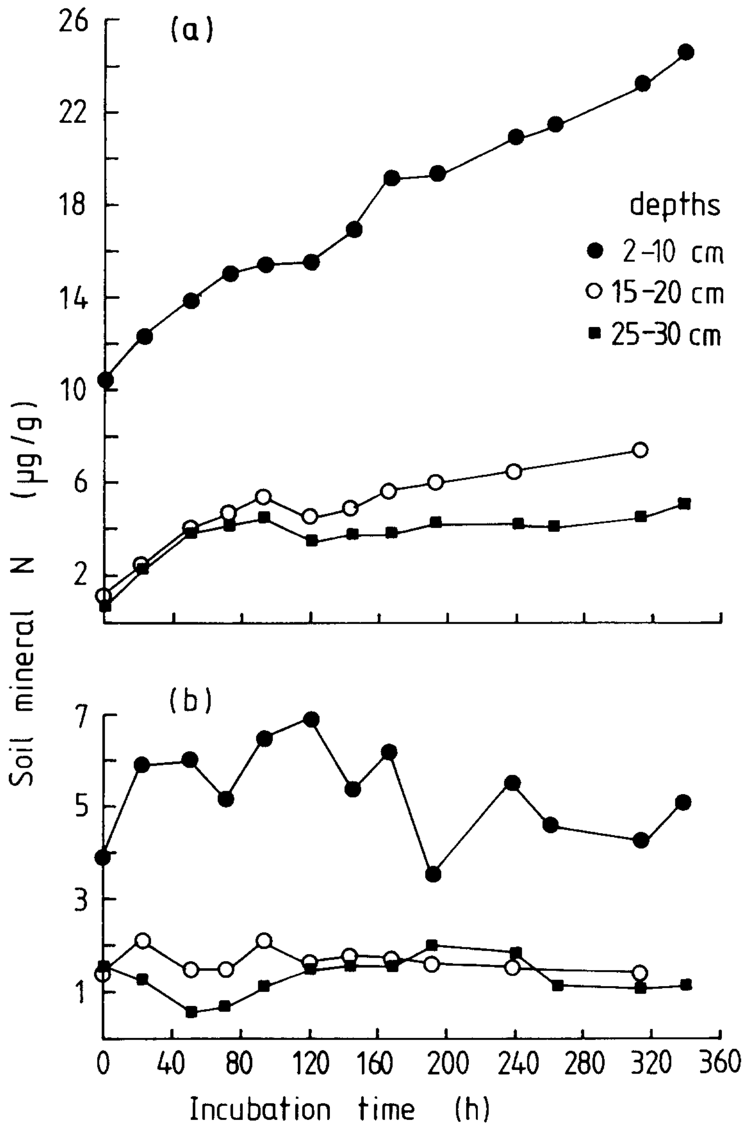

Fig. 5. *Experiment 5.* (a) NO_3-N and (b) exchangeable NH_4-N in three profile depth fractions of grassland soil, site Z, during incubation at 10°C.

for mineralization have been reported[1] in the range 5732–10700°K and inferred from other data[51,53] as 5294–8871, but no B-coefficients for nitrification have been recorded[1]. In this study significant B-coefficients were found for mineralization and nitrification for the grassland soil, experiment 6 only (Table 5).

Levels of exchangeable NH_4-N measured at 4, 10 and 20°C were similar for a given experiment, suggesting that the responses of

Table 3. Linear regressions of N concentration on time for data from the 24–168 h period of incubation. The slopes, b, for NO_3-N on time and total mineral N on time estimate the rates of net nitrification and net mineralization respectively

					Linear regression of N concentration on time		
Expt.	Soil site	Sample depth (cm)	Temperature (°C)	Process**	b (μg Ng^{-1}	SE_b* dry soil h^{-1})	r^2
1	grassland	2–10	10	NN	0.047	0.003	0.98
	(X)			NM	0.056	0.011	0.87
			20	NN	0.073	0.005	0.98
				NM	0.085	0.015	0.89
2	grassland	2–10	10	NN	0.049	0.011	0.90
	(X)			NM	0.033	0.009	0.88
			20	NN	0.064	0.010	0.96
				NM	0.054	0.006	0.98
3	arable	0–10	4	NN	0.015	0.001	0.98
	(Y)			NM	0.013	0.001	0.97
			10	NN	0.024	0.004	0.92
				NM	0.023	0.007	0.79
			20	NN	0.033	0.004	0.96
				NM	0.033	0.006	0.92
	grassland	2–10	10	NN	0.047	0.009	0.89
	(X)			NM	0.043	0.013	0.77
			20	NN	0.054	0.004	0.98
				NM	0.047	0.009	0.90
5	grassland	2–10	10	NN	0.042	0.005	0.94
				NM	0.044	0.006	0.91
	(Z)	15–20	10	NN	0.017	0.005	0.66
				NM	0.016	0.005	0.64
		25–30	10	NN	0.006	0.005	0.23
				NM	0.012	0.003	0.71
			20	NN	0.016	0.003	0.88
				NM	0.025	0.002	0.96
6	grassland	2–10	4	NN	0.043	0.008	0.90
	(X)			NM	0.045	0.009	0.89
			10	NN	0.051	0.004	0.96
				NM	0.051	0.007	0.95
			20	NN	0.062	0.014	0.86
				NM	0.060	0.015	0.84

* Standard error of b

**NN = Net nitrification, NM = net mineralization

ammonification and nitrification to temperature were similar. Apparently the rate of nitrification was never less than the rate of ammonification. Irrespective of temperature nitrification was limited by the supply of NH_4.

Justice and Smith[23] reported that high (35°C) and low (2°C) temperatures had a greater inhibitory effect upon nitrite oxidizers than

Table 4. Average daily rates of net mineralization (ADRNM) and average daily rates of net nitrification (ADRNN) calculated from the slopes of linear regressions of data from the 24–168 h period of incubations, at different soil temperatures, volumetric moisture fractions (θ) and depths

				ADRNM (kg N ha^{-1} day^{-1} cm^{-1} depth)				ADRNN (kg N ha^{-1} day^{-1} cm^{-1} depth)			
				Temperature (°C)				Temperature (°C)			
Expt.	Soil site**	Depth (cm)	θ (cm^3 cm^{-3})	4	10	20	Q_{10}	4	10	20	Q_{10}*
1	X	2–10	0.60		0.120	0.182	1.5		0.100	0.156	1.6
2	X	2–10	0.60		0.070	0.117	1.6		0.106	0.138	1.3
3	X	2–10	0.67		0.085	0.092	1.1		0.092	0.106	1.3
6	X	2–10	0.64	0.093	0.105	0.124	1.2	0.089	0.105	0.128	1.2
Mean (1, 2, 3, 6)			0.63		0.095	0.129	1.4		0.101	0.132	1.3
5	Z	2–10	0.50		0.106				0.101		
		15–20	0.44		0.041				0.043		
		25–30	0.33		0.031	0.065	2.1		0.016	0.042	2.6
3	Y	0–10	0.33	0.037	0.065	0.092	1.5	0.042	0.067	0.093	1.4
4	Y	0–2	0.13	0	0	0		0	0	0	
6	Y	0–10	0.23			0.042				0.123	

* Rate at 20°C/rate at 10°C.
** X grassland, Y arable, Z grass.

Table 5. Arrhenius linear regressions of ln k on 1/T

Expt.	Soil	Rate constant	Intercept	Slope (B-coefficient) (°K)	% variation accounted for
3	arable (0–10 cm)	k_1	15.26 ± 3.97 NS	−4529 ± 1130 NS	88.3
		k_2	12.90 ± 3.10 NS	− 384 ± 881 NS	90.3
6	grassland (2–10 cm)	k_1	5.25 ± 0.20*	−1432 ± 57*	99.7
		k_2	6.59 ± 0.49*	−1814 ± 138*	98.8

* denotes significance at $P < 0.05$, NS is not significant.

ammonium oxidizers. Our results showed that NO_2-ions did not accumulate and no temperature effect on NO_2-ion accumulation was detectable. NO_2-ion oxidation always proceeded as fast as NH_4-ion oxidation.

Rates of mineralization and net nitrification decreased with increasing depth in the profile (Fig. 5 and Table 3), probably due to decreasing microbial populations and substrate concentration. The higher rates of net mineralization and net nitrification at 20°C compared to 10°C (Q_{10} = 2.6) in the 25–35 cm layer suggest that the low rates were primarily caused by low microbial activities.

Modelling net mineralization and net nitrification in the field

Concepts. The laboratory incubations of repacked cores of field moist soil suggested that the net mineralization of organic N in this soil, and its subsequent net nitrification, were linearly related to time. These data could then be used to predict the rate of net mineralization and net nitrification in the field soil, provided allowance was made for the effects of temperature, moisture content and the change in microbial activity with soil depth. Data from the grassland sites X and Z were used to develop a first approximation model for the grassland fields at Wytham (4.92 ha) for the period 1 September 1980 to 31 August 1981.

Measured values of k_1 and k_2 (μg N g^{-1} h^{-1}) were multiplied by a conversion factor of 2.4 p, where p was the dry bulk density of repacked cores (g cm^{-3}), to give estimates of the average daily rate of net mineralization (ADRNM) and net nitrification (ADRNN) respectively, in kg N ha^{-1} day^{-1} cm^{-1} (Table 4). The principle adopted was to use the values of ADRNM and ADRNN for the 2–10 cm layer at optimal moisture and to adjust these for temperature change. The soil profile was then subdivided into a number of depth intervals and the assumption made that ADRNM and ADRNN decreased approximately

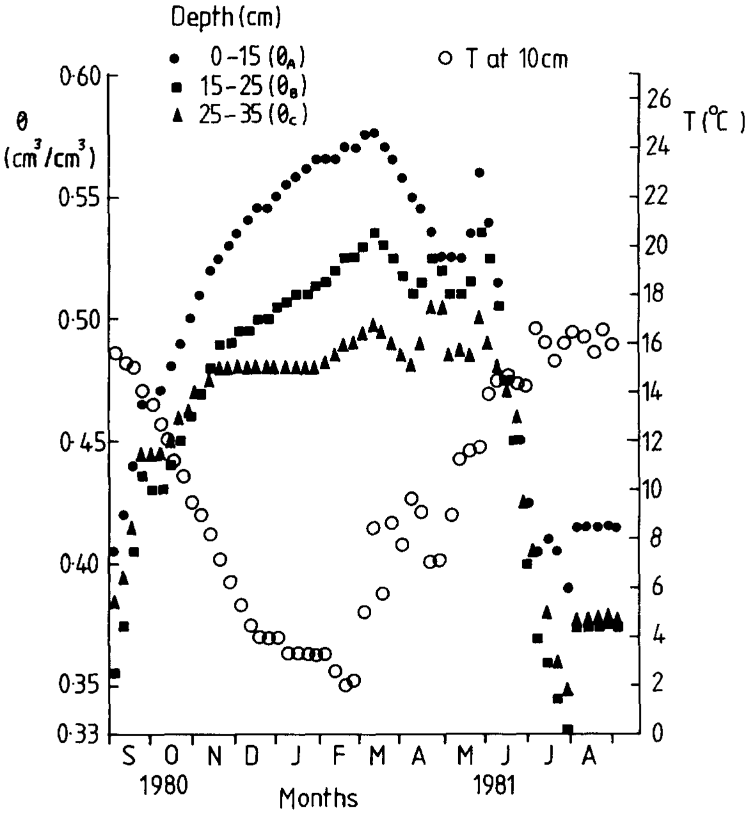

Fig. 6. Weekly mean soil temperatures at 10 cm depth (T) and weekly mean volumetric moisture fractions (θ) in the 0–15 cm (θA), 15–25 cm (θB) and 25–35 cm (θC) profile layers of the Wytham grassland soil, for the period 1 September 1980 to 31 August 1981.

linearly with depth from a maximum in the surface (0–2 cm layer) to zero at depths > 35 cm. This was justified on the evidence of experiment 5, the sharp decline in total soil N with depth and the heavy clay texture of the subsoil. Furthermore, ADRNM and ADRNN were adjusted for changes in moisture content with time in the 0–15, 15–25 and 25–35 cm depth intervals, on the basis of changes in the volumetric moisture fraction, θ, measured by neutron probe (Fig. 6)[25,57]. Soil temperature data, as weekly means at 10 cm depth under grass, were obtained from two sources. For the period to January 1981 they were estimated from areal averages in UK agroclimatic areas 26 and 31 N[35], and from February 1981 onwards from continuous measurements at 10 cm depth some 20 m from site X in the grassland[31] (Fig. 6). A more elaborate input of temperature data, for example as daily values at a range of profile depths, was inappropriate

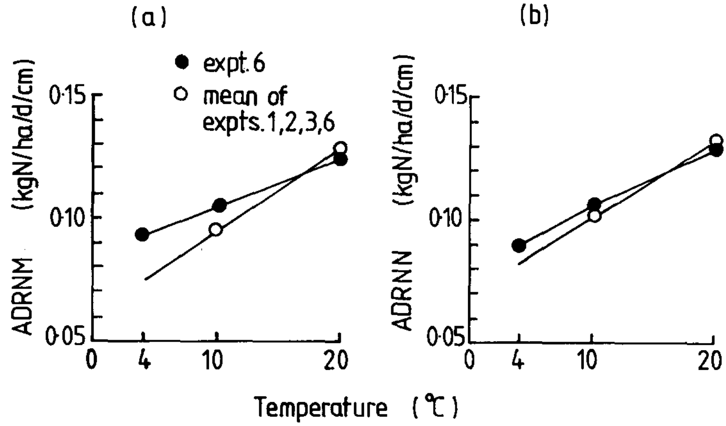

Fig. 7. The relationship between soil temperature and average daily rates of (a) net mineralization (ADRNM) and (b) net nitrification (ADRNN), at optimal θ.

given the simplifying assumptions made in this model. The detailed modelling procedure were as follows.

Soil temperature. Expressions relating ADRNM and ADRNN to temperature T were derived from the results of experiments 1, 2, 3 and 6 (Table 4) in which values of θ were similar and assumed to be optimal for both mineralization and nitrification. Arithmetic means of ADRNM and ADRNN from these 4 experiments were calculated for 10 and 20°C and the equation for the straight-line passing through the means when plotted against T (°C) was found. The assumption of a linear relationship over the range $2°C < T < 20°C$ was supported by data from experiment 6, for 4, 10 and 20°C (Fig. 7). For net mineralization:

$$ADRNM_{max} = 0.0034T + 0.061 \quad (4)$$

where $ADRNM_{max}$ is the average daily rate of net mineralization at optimal soil moisture content (kg N ha^{-1} day^{-1} cm^{-1}) in the 2–10 cm depth interval of grassland soil and T is the weekly mean soil temperature (°C). Likewise for net nitrification:

$$ADRNN_{max} = 0.0031T + 0.070 \quad (5)$$

Soil moisture. It is clear from the literature that the exact form of the relationship between soil moisture and either mineralization or nitrification varies with soil type, depending on moisture-holding characteristics, porosity, organic matter levels and pH. Data from experiments 1–6 were insufficient to quantify the relationship between moisture content and ADRNM or ADRNN. However, the optimal value of matric suctions for mineralization has been given in the range 0.15–0.5 bars[34] or 0.1–0.33 bars[47], approximating to soil water contents at field capacity. Little mineralization has been observed at soil water contents below permanent wilting point[40]. A near linear relationship between N mineralized and soil water content in the range wilting point and field capacity has been reported[39,47].

It was assumed that both ADRNM, and ADRNN decreased linearly with decreasing volumetric moisture fraction, from maxima at field capacity (θ_{fc}) to zero at 15 bars tension, permanent wilting point (θ_{pwp}). Estimates of θ_{fc} and θ_{pwp} for the 0–15 cm depth were 0.64 and 0.37 respectively, and for the 15–35 cm depth were 0.55 and 0.28[25]. A moisture coefficient, M, where $0 \leqslant M \leqslant 1$, expressed the depressive effect of sub-optimal moisture contents on both $ADRNM_{max}$ and $ADRNN_{max}$. In the 0–15 cm depth interval:

$$M = 3.70\theta - 1.37 \tag{6}$$

where $0.37 \leqslant \theta \leqslant 0.64$; $M = 0$ for $\theta < 0.37$ and $M = 1$ for $\theta > 0.64$.
In the 15–35 cm depth interval:

$$M = 3.70\theta - 1.04 \tag{7}$$

where $0.28 \leqslant \theta \leqslant 0.55$; $M = 0$ for $\theta < 0.28$ and $M = 1$ for $\theta > 0.55$.
It was assumed that M was independent of temperature for a given θ. Therefore at a given temperature:

$$ADRNM(\theta) = M \times ADRNM_{max} \tag{8}$$

and:

$$ADRNN(\theta) = M \times ADRNN_{max} \tag{9}$$

where ADRNM (θ) and ADRNN (θ) are the average daily rates of net mineralization and net nitrification respectively (kg N ha^{-1} ha^{-1} day^{-1} cm^{-1}) at a specified value of θ.

Profile depth. The relationship between profile depth and ADRNM and ADRNN was derived from the experimental results for the 2–10, 15–20 and 25–30 cm depths in experiment 5 (Fig. 5). As θ varied in these 3 intervals, the effect of depth was confounded with the effect of soil moisture. Appropriate values of ADRNM and ADRNN (Table 4) for each interval were therefore converted to theoretical values of optimal θ, termed $ADRNM'_{max}$ and $ADRNN'_{max}$, using

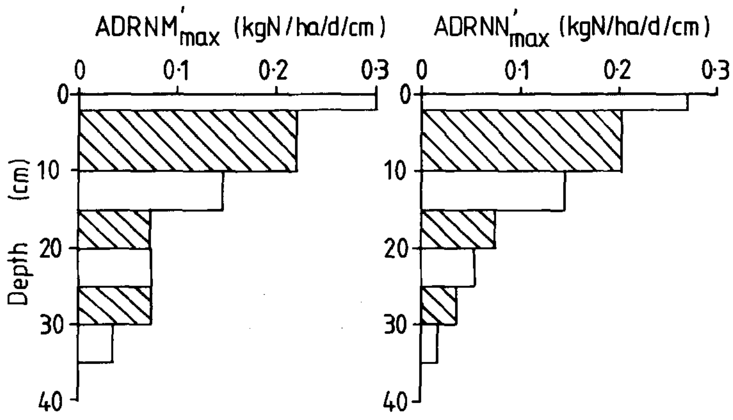

Fig. 8. The relationship between profile depth and the theoretical values of average daily rates of net mnineralization ($ADRNM'_{max}$) and net nitrification ($ADRNN'_{max}$), at 10°C and optimal θ. *Hatched* bars are derived from measured values, *unhatched* bars from estimated values.

equations (8) and (9) with appropriate values of M from equations (6) and (7). The profile was then divided into the 0–2, 2–10 cm and five layers each 5 cm width, to a depth of 35 cm. $ADRNM'_{max}$ and $ADRNN'_{max}$ in the 10–15 and 20–25 cm layers were esimated as the arithmetic means of rates in the layers immediately above and below; and in the 30–35 cm layer as half the rate at 25–30 cm. The rates in the 0–2 cm layer were estimated by linear extrapolation from measured rates in the 2–10 and 15–20 cm layers. The histograms of measured and interpolated values of $ADRNM'_{max}$ and $ADRNN'_{max}$ are shown in Fig. 8. $ADRNM'_{max}$ and $ADRNN'_{max}$ in each layer were then expressed as fractions of the values in the 2–10 cm layer, giving a series of depth coefficients termed d_m and d_n for net mineralization and net nitrification respectively (Table 6). It was assumed that T and M did not influence d_m or d_n.

Synthesis. $ADRNM_{max}$ and $ADRNN_{max}$ in the 2–10 layer were predicted from temperature data (Fig. 6) by equations (4) and (5). From weekly mean values of θ in the 0–15, 15–25 and 25–35 cm layers (Fig. 6) moisture coefficients were given by equations (6) and (7). Weekly net mineralization, WNM (kg N ha^{-1} wk^{-1}), in each of these 3 layers is then:

$$WNM_{0-15} = 7\, M_{0-15}\, ADRNM_{max} \sum_{x=1}^{3} d_{m,x} W_x \qquad (10)$$

$$WNM_{15-25} = 7\, M_{15-25}\, ADRNM_{max} \sum_{x=4}^{5} d_{m,x} W_x \qquad (11)$$

$$WNM_{25-35} = 7\, M_{25-35}\, ADRNM_{max} \sum_{x=6}^{7} d_{m,x} W_x \qquad (12)$$

Table 6. Depth coefficients for net mineralization (d_m) and net nitrification (d_n), expressing rate in layer x relative to rate in layer 2 at optimal volumetric moisture fraction

Depth (cm)	Profile layer	Depth coefficients d_m	d_n
0–2	1	1.36	1.29
2–10	2	1.00	1.00
10–15	3	0.66	0.67
15–20	4	0.31	0.32
20–25	5	0.32	0.26
25–30	6	0.32	0.17
30–35	7	0.16	0.09

where M_{0-15}, M_{15-25} and M_{25-35} are moisture coefficients for the 3 layers; $d_{m,x}$ is the depth coefficient for net mineralization in layer x (x = 1, 2, 3.....7; Table 6) and W_x is the width (cm) of layer x. Summing equations (10), (11) and (12) with input from equations (4), (6) and (7) and values of $d_{m,x}$ from Table 6 gives:

$$WNM_{0-35} = 7(0.0034T + 0.061)(51.874\theta_A + 11.655\theta_B + 8.88\theta_C - 24.979) \qquad (13)$$

where WNM_{0-35} is the weekly net mineralization (kg N ha^{-1} wk^{-1}) from 0 to 35 cm, T is the weekly mean soil temperature at 10 cm depth (°C), θ_A, θ_B and θ_C the weekly mean volumetric moisture fractions (cm^3 cm^{-3}) in the 0–15, 15–25 and 25–35 cm layers respectively.

Weekly net nitrification (kg N ha^{-1} wk^{-1}) from 0 to 35 cm, WNN_{0-35}, was derived similarly, using values of $d_{n,x}$ and $ADRNN_{max}$ in place of $d_{m,x}$ and $ADRNM_{max}$. The final equation was:

$$WNN_{0-35} = 7(0.0031T + 0.070)(51.54\theta_A + 11.1\theta_B + 4.81\theta_C - 23.556) \qquad (14)$$

where the terms are as for equation (13).

Model output. The model predicted an annual net mineralization and net nitrification of 350 and 346 kg N ha^{-1} respectively between 1 September 1980 and 31 August 1981. The predicted seasonal pattern (Fig. 9) was broadly as expected although the model appeared to exaggerate the effect of soil moisture relative to soil temperature. For example, during June and July a sharp decline in the weekly mineralization was predicted inspite of high soil temperatures. During the winter the predicted rate of mineralization was surprisingly high,

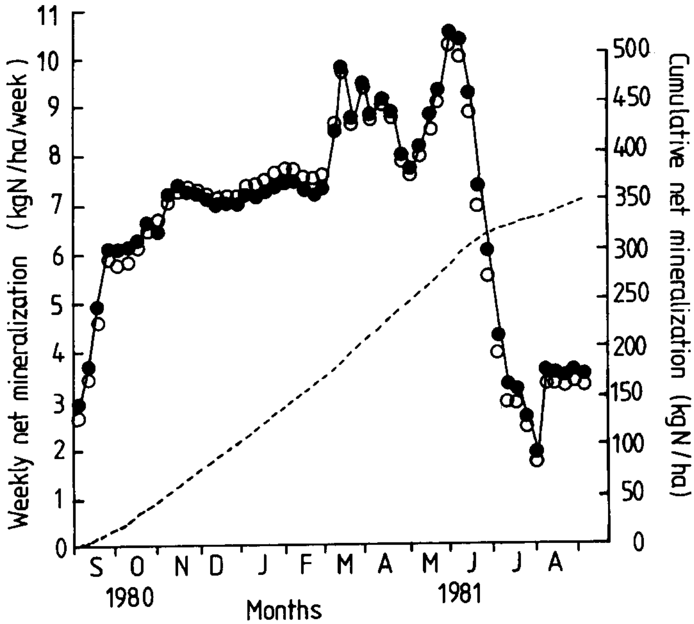

Fig. 9. Predicted weekly net mineralization (•) and net nitrification (○) in the Wytham grassland soil between 1 September 1980 and 31 August 1981. Cumulative net mineralization (-----) is also shown.

at 7–7.5 kg N ha^{-1} wk^{-1}. The occurrence of the peak rates during the spring is explained by the effect of rising soil temperature reinforcing the effect of high soil moisture. A sharp increase in mineralization during September was predicted in response to the rewetting of the dry soil[6].

General discussion

The design and empirical base of this model means that it is only suitable for prediction of net mineralization and net nitrification in soil at Wytham. Appropriate incubation experiments and consequent adjustment of temperature, moisture and depth components would be required if it was to be tested on other soils. However, the output of the model may be put into context by reference to literature reports of rates of mineralization of soil organic N. Ball and Ryden[5] quote total N values of 5–15 tonnnes N ha^{-1} in the root zone for grassland soils which, depending on soil type, climate and management, might be mineralizing at the rate of 3–7.5% in the top 15 cm each year. A 3% mineralization rate would produce 150–450 kg N ha^{-1} yr^{-1}. Other reports[8,19] suggest that the net rate of mineralization of soil organic N conforms to a first order reaction with rate constant of between

0.01 and 0.04 y^{-1}. The total N content of the Wytham grassland soil (C:N ratio 7–9) was calculated[31] as 9850 kg ha^{-1} 30 cm^{-1}. A net mineralization of 350 kg N ha^{-1} y^{-1}, as predicted by our model, would require a first-order mineralization rate constant of 0.036 y^{-1}. Furthermore, the predicted weekly rates of net mineralization (2–11 kg N ha^{-1}) are comparable to those reported in Canadian field experiments[26,28] with fallow Bainsville clay loam soil, where three years data gave a range of 1.12–12.6 kg N ha^{-1} for weekly rates of net mineralization over the growing season.

Our predicted net release of 350 kg N ha^{-1} y^{-1} for the Wytham grassland soil is much higher than the range 17–86 kg ha^{-1} y^{-1} quoted for UK grasslands in The Report of The Royal Society Study Group[41]. However, it is recognized that with permanent grass and swards sown on old grassland soils, in which the soil organic matter content has reached equilibrium, quantities of N released maybe appreciably higher than those quoted[58].

In our model we have regarded net mineralization and net nitrification as zero-order reactions. This approach is simplistic. In the turnover of soil organic matter it is probable that there is a continuum of materials with respect to ease of decomposability and hence a continuum of simultaneous decay rates[21]. Recent models have considered five[21] or more[22,56] discrete fractions. However, treatments of the net release of mineral N from soil organic matter as overall zero – or first-order reactions[8,46] have successfully described behaviour observed in incubation experiments[1,16,51]. It has been suggested that the rather indeterminate kinetics of mineralization are best described as 'conglomerate kinetics', in view of the large number of processes possibly involved[1]. Nitrification has also been modelled in terms of zero- and first-order kinetics[3,52].

With regard to other assumptions underlying the model, the emphasis temperature and soil moisture as determining environmental variables finds some support. Cambell *et al.*[9] obtained reasonable results using regression analysis to relate changes in soil NO_3 concentrations to soil temperature and moisture under laboratory and field conditions. Davy and Taylor[14] found that seasonal fluctuations in soil pH, total N, total P and organic matter tended to be small and to show no obvious correlation with changes in N mineralization rate. There is limited evidence for a linear dependence of nitrification upon temperature[38], although in general it has been considered that the decline in mineralization with decreasing temperature follows an asymptotic curve that approaches zero[20]. The kinetic forms of expressions describing the reponses of these N transformations to environmental variables may vary depending on whether net or gross processes are being considered.

We have assumed that the optimal soil moisture content is independent of soil temperature and *vice versa*. However, in common with other authors[11,27] we recognise the need to consider the interactive effect of moisture content and temperature on both ammonification and nitrification in any refinement of this model.

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References

1 Addiscott T M 1983 Kinetics and temperature relationships of mineralization and nitrification in Rothamsted soils with differing histories. J. Soil Sci. 34, 343–353.

2 Anderson O E and Purvis E R 1955 Effect of low temperature on nitrification of ammonia in soils. Soil Sci. 80, 313–318.

3 Ardakani M S, Schulz R K and McLaren A D 1974 A kinetic study of ammonium and nitrite oxidation in a soil field plot. Soil Sci. Soc. Am. Proc. 38, 273–277.

4 Avery B W and Bascomb C L (Eds.) 1974 Soil Survey Laboratory Methods. Soil Survey Tech. Mon. No. 6. Soil Survey, Harpenden Herts.

5 Ball P R and Ryden J C 1984 Nitrogen relationships in intensively managed temperate grasslands. Plant and Soil 76, 23–33.

6 Birch H F 1958 The effect of soil drying on humus decomposition and nitrogen availability. Plant and Soil 10, 9–13.

7 Bremner J M 1965 Nitrogen availability indexes. *In* Methods of Soil Analysis, Pt. 2. Agronomy 9, 1324–1345. Eds. C A Black *et al.* Am. Soc. Agron. Madison, Wisconsin.

8 Burns I G 1980 A simple model for predicting the effects of winter leaching of residual nitrate on the nitrogen fertilizer needs of spring crops. J. Soil Sci. 31, 187–202.

9 Cambell C A, Biederbeck V O and Hinman W C 1975 Relationships between nitrate in summer-fallowed surface soil and some environmental variables. Can. J. Soil Sci. 55, 213–223.

10 Cambell C A, Stewart D W, Nickolaichuck W and Biederbeck V O 1974 Effects of growing season, soil temperature, moisture, and NH_4-N on soil nitrogen. Can. J. Soil Sci. 54, 403–412.

11 Cameron D R and Kowalenko C G 1976 Modelling nitrogen processes in soil: mathematical development and relationships. Can. J. Soil Sci. 56, 71–78.

12 Cook G W and Cunningham R K 1958 Soil nitrogen. III. Mineralizable nitrogen determined by an incubation technique. J. Sci. Fd. Agric. 9, 324–330.

13 Crooke W M and Simpson W F 1971 Determination of ammonium in Kjeldahl digests of crops by an automated procedure. J. Sci. Fd. Agric. 22, 9–10.

14 Davy A J and Taylor K 1974 Seasonal patterns of nitrogen availability in contrasting soils in the Chiltern Hills. J. Ecol. 62, 793–807.

15 Dubey H D 1968 Effect of soil moisture levels on nitrification. Can. J. Microbiol. 14, 1348–1350.

16 Farooqi M A R, Hanif M and De Mooy C J 1983 Nitrogen mineralization potential and urea hydrolysis under aerobic and anaerobic conditions. Commun. Soil Sci. Plant Anal. 14, 29–47.

17 Frederick L R 1956 The formation of nitrate from ammonium nitrogen in soils. I. Effect of temperature. Soil Sci. Soc. Am. Proc. 20, 496–500.

18 Gasser J K R 1961 Effects of air drying and air dry storage on the mineralizable nitrogen in soils. J. Sci. Fd. Agric. 12, 778–784.

19 Greenland D J 1971 Changes in the nitrogen status and physical conditions of soils under pastures with special references to the maintenance of the fertility of Australian soil used for growing wheat. Soils Fertil. 34, 237–251.

20 Harmsen G W and Kolenbrander G J 1965 Soil inorganic nitrogen. *In* Soil Nitrogen. Eds. W V Bartholomew and F E Clark. pp 43–92. Am. Soc. Agron., Madison, Wisconsin.

21 Jenkinson D S and Rayner J H 1977. The turnover of organic matter in some Rothamsted classical experiments. Soil Sci. 123, 298–305.

22 Juma N G and Paul E A 1981 Simulation of mineralization and immobilization of soil nitrogen. *In* Simulation of Nitrogen Behaviour in Soil-Plant Systems. Eds. M J Frissel and J A Van Veen. pp 145–154. PUDOC, Wageningen.

23 Justice J K and Smith R I 1962 Nitrification of ammonium sulfate in a calcareous soil as influenced by combinations of moisture, temperature, and levels of added nitrogen. Soil Sci. Soc. Am. Proc. 26, 246–250.

24 Keeney D R 1982 Nitrogen availability indices. *In* Methods of Soil Analysis Pt. 2. Eds. A L Page *et al.* pp 711–733. Am. Soc. Agron., Madison, Wisconsin.

25 Kneale W R 1983 The movement of water and solutes in the structural clay soil of the Wytham catchment, Oxford. D. Phil. Thesis (unpublished). Dept. Agric. Sci., University of Oxford, 335 p.

26 Kowalenko C G 1978 Nitrogen transformation and transport over 17 months in field fallow microplots using 15-N. Can. J. Soil Sci. 58, 69–76.

27 Kowalenko C G and Cameron D R 1976 Nitrogen transformations in an incubated soil as affected by combinations of moisture content and temperature and adsorption-fixation of ammonium. Can. J. Soil Sci. 56, 63–70.

28 Kowalenko C G and Cameron D R 1978 Nitrogen transformations in soil-plant systems in three years of field experiments using tracer and non-tracer methods on an ammonium-fixing soil. Can. J. Soil Sci. 58, 195–208.

29 Litchfield M H 1967 The automated analysis of nitrite and nitrate in blood. Analyst. London 92, 132–136.

30 Low A J and Piper F J 1970 The ammonification and nitrification in soil of urea with and without buret. J. Agric. Sci., Camb. 75, 301–309.

31 Macduff J H 1983 The dynamics of mineral nitrogen in the soils of a small agricultural catchment. D. Phil. Thesis (unpublished). Dept. Agric. Sci., University of Oxford, 357 p.

32 MacDuff J H and White R E 1984 Components of the nitrogen cycle measured for cropped and grassland soil-plant systems. Plant and Soil 76, 35–47.

33 Macura J and Malek I 1958 Continuous flow methods for the study of microbiological processes in soil samples. Nature London 182, 1796–1797.

34 Millar R D and Johnson D D 1964 Effect of soil moisture tension on carbon dioxide evolution, nitrification, and nitrogen mineralization. Soil Sci. Soc. Am. Proc. 28, 644–647.

35 Ministry of Agriculture, Fisheries and Food 1976 The agricultural climate of England and Wales. Tech. Bull. 35, HMSO, London, 147 p.

36 Misra C, Nielsen D R and Bigger J W 1974 Nitrogen transformations in soil during leaching. II. Steady-state nitrification and nitrate reduction. Soil Sci. Soc. Am. Proc. 38, 294–299.

37 Page E R 1975 The location and persistence of ammonia (aqueous, anhydrous + 'N-serve') injected into a sandy loam soil, as shown by the changes in concentration of ammonium and nitrate ions. J. Agric. Sci., Camb. 85, 65–74.

38 Parker D T and Larson W E 1962 Nitrification as affected by temperature and moisture content of mulched soils. Soil Sci. Soc. Am. Proc. 28, 644–647.

39 Reichman G A, Grunes D L and Viets Jr. F G 1966 Effects of soil moisture on ammonification and nitrification in two northern plain soils. Soil Sci. Soc. Am. Proc. 30, 363–366.

40 Robinson J B D 1957 The critical relationship between soil moisture content in the region of the wilting point and mineralization of native soil nitrogen. J. Agric. Sci., Camb. 49, 100–105.

41 Royal Society, London 1983 The nitrogen cycle of The United Kingdom. Report of Royal Society Study Group. Royal Society, London, 264 p.
42 Sabey B R, Bartholomew W C, Shaw R and Pesek J 1956 Infleunce of temperature on nitrification in soil. Soil Sci. Soc. Am. Proc. 20, 357–360.
43 Sabey B R, Frederick L R and Bartholomew W C 1959 The formation of nitrate from ammonium nitrogen in soils. III. Influence of temperature and initial population of nitrifying organisms on the maximum rate and delay period. Soil Sci. Soc. Am. Proc. 23, 462–465.
44 Sabey B R, Frederick and Bartholomew W V 1969 The formation of nitrate from ammonium nitrogen in soils. IV Use of daily and maximum rate phases for making quantitative predictions. Soil Sci. Soc. Am. Proc. 33, 276–278.
45 Sabey B R and Johnson D D 1971 Effect of soil moisture tension on nitrate accumulation in Drummer silty clay loam. Soil Sci. Soc. Am. Proc. 35, 848–850.
46 Shearer G, Duffy J, Kohl D H and Commoner B 1974 A steady state model of isotopic fractionation accompanying nitrogen transformations in soil. Soil Sci. Soc. Am. Proc. 38, 315–322.
47 Stanford G and Epstein E 1974 Nitrogen mineralization water relations in soils. Soil Sci. Soc. Am. Proc. 38, 103–107.
48 Stanford G, Carter J N and Smith S J 1974 Estimates of potentially mineralizable soil nitrogen based on short-term incubation. Soil Sci. Soc. Am. Proc. 38, 99–102.
49 Stanford G, Carter J N, Westerman D J and Meisinger J J 1977 Residual nitrate and mineralizable soil nitrogen in relation to nitrogen uptake by irrigated sugar beets. Agron. J. 69, 303–308.
50 Stanford G, Frere M H and Schwaninger D H 1973 Temperature coefficient of soil nitrogen mineralization. Soil Sci. 115, 321–323.
51 Stanford G and Smith S J 1972 Nitrogen mineralization potential of soils. Soil Sci. Soc. Am. Proc. 36, 465–472.
52 Starr J L, Broadbent F E and Nielson D R 1974 Nitrogen transformations during continuous leaching. Soil Sci. Soc. Am. Proc. 38, 283–289.
53 Tabatabai M A and Al-Khafaji A A 1980 Comparison of nitrogen and sulphur mineralization in soils. Soil Sci. Soc. Am. Proc. 44, 1000–1006.
54 Tinsley J 1950 The determination of organic carbon in soils by dichromate mixtures. Trans. 4th Int. Congr. Soil Sci. 1, 161–164.
55 Tyler K B, Broadbent F E and Hill G N 1959 Low temperature effects on nitrification in four Californian soils. Soil Sci. 87, 123–129.
56 Van Veen J A and Paul E A 1981 Organic carbon dynamics in grassland soils. 1. Background information and computer simulation. Can. J. Soil Sci. 61, 185–201.
57 White R E, Wellings S R and Bell J P 1983 Seasonal variations in nitrate leaching in structured clay soils under mixed land use. Agric. Water Mgt. 7, 391–410.
58 Whitehead D C 1970 The role of nitrogen in grassland productivity. Commonw. Bur. Pastures and Field Crops Bull. 48, 202 p. Commonw. Agric. Bur., Farnham Royal.