

## DISSOLVED ORGANIC CARBON IN OLD FIELD SOILS: TOTAL AMOUNTS AS A MEASURE OF AVAILABLE RESOURCES FOR SOIL MINERALIZATION

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**Summary**—Dissolved organic carbon (DOC) and C and N mineralization were measured during a 210-day regulated *in vitro* incubation of soils from an old field successional sequence at Cedar Creek Natural History Area. The objective of the study was to evaluate the hypothesis that soil DOC constitutes a readily-available microbial resource, and that DOC concentrations are related to rates of biological decomposition and associated nutrient release from soil organic matter. Soils from five previously cultivated old fields undergoing secondary succession and an oak savanna were selected because they had demonstrated different patterns of C and N cycling. Although amounts of total C differed dramatically ( $496\text{--}1371\ \mu\text{mol g}^{-1}$ ), DOC concentrations of all soils at the time of collection were between 0.70 and  $1.30\ \mu\text{mol g}^{-1}$ . During the incubation, total and relative DOC concentrations generally remained constant or increased while mineralization rates decreased. When all soils and incubation intervals were considered, there was no obvious relationship between DOC and instantaneous rates of mineralization. Asymptotic exponential response curves did describe positive associations between DOC and  $\text{CO}_2\text{-C}$  mineralization rates at early incubation times ( $R^2 = 0.98$  for 14 and 35 days), but not later. Similar models did not show a strong relationship between DOC and net-N mineralization rates. By the end of the incubation, the DOC pool could potentially supply 1.5–3.4 days of total C mineralization, but the instantaneous C mineralization rate at any given DOC concentration was 3–10 times lower than at 14 days. These results reflect decreased DOC utilization relative to supply, and could be caused by the accumulation of recalcitrant DOC.

### INTRODUCTION

Considerable research has been conducted on the role of dissolved organic carbon (DOC) as the primary resource for biological decomposition in aquatic systems (Bott *et al.*, 1984; Meyer *et al.*, 1987), and as the immediately-available resource from degrading litter (Reinertsen *et al.*, 1984; Williams and Gray, 1974; Brown and Frederick, 1968). However, few studies have examined the specific role and function of DOC as a portion of labile organic matter in mineral soil, particularly with regards to C and N transformations.

Soluble C enters the soil profile as leachate from live and decaying above-ground phytomass (Qualls R. G., unpublished Ph.D. thesis, University of Georgia, 1989), and when plant roots and soil microorganisms release metabolic products or are degraded (Cronan, 1985; Martin, 1975). The concentration of DOC retained in a soil-water system depends on the adsorption characteristics of the soil and the supply (Nodvin *et al.*, 1986). Recent studies indicate that adsorption equilibria and solution parameters in soils may be the regulating mechanism for energy and nutrient translocation and export from surface horizons by leaching (Schoenau and Bettany, 1987; Qualls R. G., unpublished Ph.D. thesis, Univer-

sity of Georgia, 1989; Sollins and McCorison, 1981; Voroney *et al.*, 1981; Evans *et al.*, 1988). Loss or retention of soluble organics by soil horizons may be important in controlling nutrient turnover, particularly if the constituents provide a readily-available source of energy for soil microbes (Schoenau and Bettany, 1987; Dinwoodie and Juma, 1988).

Several researchers, particularly in studies of denitrification, have inferred that the amount of DOC in soil is a measure of the readily-available resource for microbial growth and biological decomposition. Burford and Bremner (1975) found a strong relationship between DOC concentrations and  $\text{CO}_2\text{-C}$  mineralization or denitrification capacities in a variety of soil types, and concluded that DOC is particularly susceptible to decomposition. Davidson *et al.* (1987) found no correlation between DOC and denitrification potentials using forested soils, but they did find a strong correlation between DOC and mineralizable  $\text{CO}_2\text{-C}$ . Powlson and Jenkinson (1976) observed a positive linear relationship between  $\text{CO}_2\text{-C}$  mineralized from soils during a 10 day incubation and organic C solubilized in a 0.5 M  $\text{K}_2\text{SO}_4$  extractant. In a study of old fields undergoing secondary succession and a late-successional forest, Zak *et al.* (1990) found microbial biomass C was highly correlated with DOC. For determining C mineralization kinetics in an anaerobic system, Gale and Gilmour (1988) used DOC as a measure of

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Table 1. Texture and taxonomic groupings for Cedar Creek soils

Field	Particle size distribution (mm)			Subgroup*	Series*
	Sand	Silt	Clay		
	2-0.05	0.05-0.002	<0.002		
	%				
12 yr	90	7	3	Typic udipsamment	Nymore sand
32 yr	89	7	4	Alfic udipsamment	Zimmerman fine sand
37 yr	90	6	4	Alfic udipsamment	Zimmerman fine sand
55 yr	90	6	4	Aquic udipsamment	Lino fine sand
62 yr	92	5	3	Typic udipsamment	Sartell fine sand
Oak savanna	94	4	2	Typic udipsamment	Sartell fine sand

\*Grigal *et al.* (1974).

simple sugars and organic acids, which they chose to represent as an intermediate pool in the decomposition of cellulose to CH<sub>4</sub> and CO<sub>2</sub>. DOC has also been included as a measure of readily-available organic matter in the PHOENIX model (McGill *et al.*, 1981), which predicts C and N dynamics in grassland soils.

To evaluate the hypothesis that DOC is a major resource used in the decomposition of soil organic matter and nutrient release, we monitored DOC concentrations and soil C and N mineralization rates during a regulated (temperature, moisture and aeration maintained at optimal mineralization conditions) *in vitro* incubation (Harmsen and van Schreven, 1955). Since decomposition rates during an incubation decrease linearly with the resource (van Veel and Paul, 1981), a comparison of DOC concentrations with instantaneous decomposition rates should demonstrate whether DOC concentrations influence decomposition (CO<sub>2</sub>-C mineralization) and nutrient (net-N mineralization) release.

The soils selected for this study were from five, previously cultivated old fields undergoing secondary succession, and an oak savanna site located in the Cedar Creek Natural History Area. Previous studies of these fields indicated that differences in DOC concentrations and patterns of C and N cycling are related to increases in soil organic matter with time since agricultural disturbance (Zak *et al.*, 1990).

## MATERIALS AND METHODS

### Site description

The old field successional sequence and the oak savanna are located at the Cedar Creek Natural History Area, 50 km north of Minneapolis, Minn. The study site is situated on a 200-km<sup>2</sup> glacial outwash plain, which is composed of well-sorted sediments of fine and medium sands. Prior to European settlement, this area was characterized by oak savanna and prairie, upland deciduous forest, and lowland marshes and swamps (Pierce R. L., unpublished M.S. thesis, University of Minnesota, 1954). Much of this original vegetation still remains, but the distribution has changed due to logging activities and clearing of land for cultivation.

Agricultural activities began in the late 1800s, but at various times over the last 60 yr, many of the fields

have been abandoned. Cropping histories for the old fields are scarce, but there is a reasonable amount of circumstantial evidence to show that inter-field differences are primarily due to disturbance history. These old-field soils are characterized by low resource availability (Zak *et al.*, 1990), a factor that appears to influence the course of secondary plant succession (Inouye *et al.*, 1987; Tilman, 1984, 1986).

Succession in the old fields has been allowed to proceed unabated, but the oak savanna is maintained with biannual fires, and was last burned in the spring of 1988, 1 yr prior to sampling. The uncultivated oak savanna represents one of the mature plant communities, but it is uncertain whether it will be the endpoint of old field succession, or whether the amounts of C and N being stored in the old fields will reach their original quantities prior to clearing and cultivation (Schlesinger, 1986). Plant community species composition and their effect on C and N distribution are reported by Cook and Allan (1992).

For this study, five previously cultivated old-fields, abandoned 12, 32, 37, 55 and 62 yr before sampling in 1989, and an uncultivated oak savanna, were chosen to encompass a range of successional stages. As much as possible, sampling was limited to similar landforms and soil groups (Table 1).

### Field sampling

Samples for each field and the oak savanna site were collected from five, circular sampling areas (1.13 m dia), spaced equidistant along a 20-m north-south transect. To determine porosity and calculate moisture content for the laboratory incubations, disturbed bulk density was estimated by measuring the volume of a known weight of soil after it had been sieved, loosely packed and remoistened. The procedure involved stacking two metal cores (76 mm i.d. × 38 mm) above a filter, loosely pouring the sieved (<2 mm) soil to just above the top of the lower metal core, slowly saturating the soil by spraying the top of the soil with water from a spray bottle, letting the soil drain freely overnight, removing the top core, trimming the soil to the top of the bottom core, and then determining the soil weight after drying at 105°C for 48 h. Two cores per field were prepared in this manner, with each core being prepared from a pooled sample of five 10 cm cores (4.7 mm i.d.), one from each sampling area. An

Table 2. Chemical and physical characteristics of Cedar Creek soils

Field	Total C ( $\mu\text{mol g}^{-1}$ )	Total Kjeldahl N ( $\mu\text{mol g}^{-1}$ )	C:N	Initial moisture content ( $\text{g g}^{-1}$ )	Soil pH	Disturbed bulk bulk density ( $\text{Mg m}^{-3}$ )	Porosity	Moisture content at 60% WFP ( $\text{g g}^{-1}$ )
12 yr	496	33.6	14.8	0.064	4.3	1.50	0.433	0.174
32 yr	560	37.8	14.8	0.076	4.6	1.48	0.442	0.179
37 yr	770	47.8	16.1	0.070	4.8	1.40	0.472	0.202
55 yr	902	60.7	14.9	0.070	4.9	1.29	0.513	0.239
62 yr	1371	87.8	15.6	0.052	4.7	1.26	0.524	0.250
Oak savanna	1100	67.8	16.2	0.040	4.8	1.26	0.524	0.250

average of the two bulk density measurements was used to calculate the total porosity and gravimetric water content at 60% water-filled pore space (WFP) (Table 2). Moisture contents at 60% WFP were used to support maximum aerobic microbial activity, and allow comparisons between different soil types (Linn and Doran, 1984).

On 25 April 1989, thirty 33 mm (i.d.)  $\times$  10 cm soil cores were collected from each sampling area and pooled for each field and the oak savanna. Initial moisture contents are reported in Table 2. Samples were stored at 4°C for no more than 3 days until they could be processed. Roots, rhizomes and particulate matter >2 mm were separated from the soil by sieving.

#### Laboratory incubation

Sieved soil was mixed thoroughly by hand, and field-moist aliquots were weighed for initial measurements of inorganic N and DOC. Soil for the incubation was split into "large" subsamples (700 g field-moist), required for analysis of DOC, and "small" subsamples (25 g field-moist), used to obtain soil respiration and inorganic-N measurements in a closed system. For each field, 12 large subsamples (3 replicates  $\times$  4 incubation periods) were placed in 2 litre Erlenmeyer flasks, and 21 small subsamples (3 replicates  $\times$  7 incubation periods) in 30-ml beakers. Container size and amount of soil were selected so that soil depths (about 2.5 cm) were nearly identical. Incubation began immediately after samples were weighed and brought to 60% WFP the following day.

Cotton stoppers allowed air exchange between the large samples and the atmosphere (preventing anaerobic conditions), but required incubation in ConViron model E15 growth chamber at ca 90% humidity to prevent rapid drying. The small samples were individually contained within closed systems (1 litre jars with rubber gasket lids), with about 2 mm of deionized water in the bottom of the container to maintain high humidity. The small samples were kept in a Precision model 818 incubator. The headspace was always replenished with fresh air before 2% of the O<sub>2</sub> in the ambient atmosphere was depleted. All samples were kept in a dark environment at 35°C ( $\pm$  2°). Samples were remoistened as necessary, and never allowed to dry below 50% WFP.

Three 700 g samples from each field and the oak savanna site were destructively sampled at 14, 35, 105 and 210 days, and analyzed for pH, inorganic-N and

total DOC. Three 25 g samples from each field and the oak savanna site were destructively sampled at 7, 21, 42, 70, 112, 161 and 207 days, and analyzed for pH and inorganic-N. Respired CO<sub>2</sub> from the small samples was trapped in 0.4–2.0 M NaOH during the incubation interval. Absorbed CO<sub>2</sub> was determined by precipitating BaCO<sub>3</sub> with BaCl<sub>2</sub>, and back-titrating the residual NaOH to a phenolphthalein endpoint (transition pH 8.0–9.6) with HCl using a Metrohm 665 Dosimat titrator.

#### Laboratory analysis

Air-dried soil was used to determine total C and total Kjeldahl-N; all other analyses were performed using field-moist or 60% WFP soil. All specific concentrations are reported in terms of oven-dry soil weight. Total Kjeldahl-N in soil was determined using a micro-Kjeldahl distillation apparatus to measure the amount of free NH<sub>4</sub><sup>+</sup> in soil digests (100:10:1 K<sub>2</sub>SO<sub>4</sub>:CuSO<sub>4</sub>·5H<sub>2</sub>O:Se in conc. H<sub>2</sub>SO<sub>4</sub>). Total C in soil was determined by dry combustion in a LECO automatic C analyzer (LECO, St Joseph, Mich.). Inorganic-N was extracted from 15 g soil samples with 10:1 (v/w) 2 M KCl, shaken for 1 h, and vacuum filtered through a previously rinsed, glass fiber prefilter without binders (PreSep G40) and a 0.2- $\mu\text{m}$  membrane (Gelman Metrical GA-8). KCl extracts were analyzed for total inorganic-N with a Wescan Ammonia Analyzer (Wescan Instruments, Santa Clara, Calif.) equipped with a Zn column to reduce NO<sub>3</sub><sup>-</sup> to NH<sub>4</sub><sup>+</sup>.

Water extracts (2:1 (v/w); Burford and Bremner, 1975) of 700 g samples were made with NANOpure deionized water (Sybron-Barnstead 4-module system with an ORGANICfree cartridge; DOC <5 mg l<sup>-1</sup>) and shaken on a reciprocating shaker for 15 min, then centrifuged at 9500 rev. min<sup>-1</sup> in a Sorvall SS-3 table top centrifuge. The supernatant was vacuum filtered as described above, and stored in polyethylene bottles at -15°C (long-term) or 4°C (short-term) prior to analysis. DOC was determined using a standard low temperature Dohrman DC-80 total organic C analyzer (Xertex/Dohrman, Santa Clara, Calif.).

Particle size analysis was performed according to Grigal (1973). Soil pH was measured in 2:1 (v/w) 10 mM CaCl<sub>2</sub> using an ORION 81-02 combination electrode.

#### Statistical analysis

C and N mineralization data were fitted to mathematical models using the non-linear regression

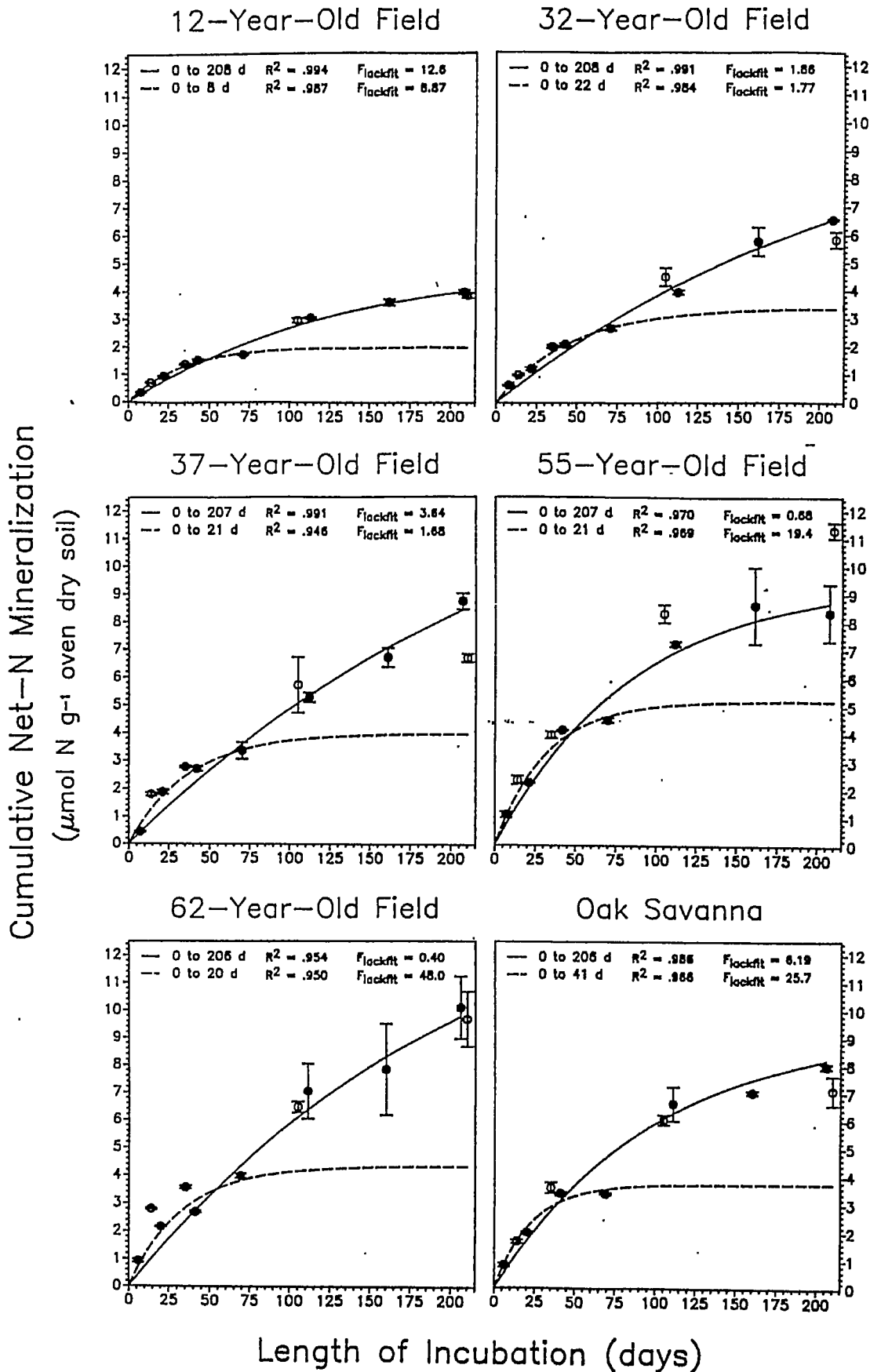


Fig. 1. Amounts of net-N released from 25 g (●) and 700 g (○) soil samples, and cumulative net-N predicted by an asymptotic first order exponential model fitted to 25 g data from the entire incubation period (—) and from the first few weeks of the incubation (---).

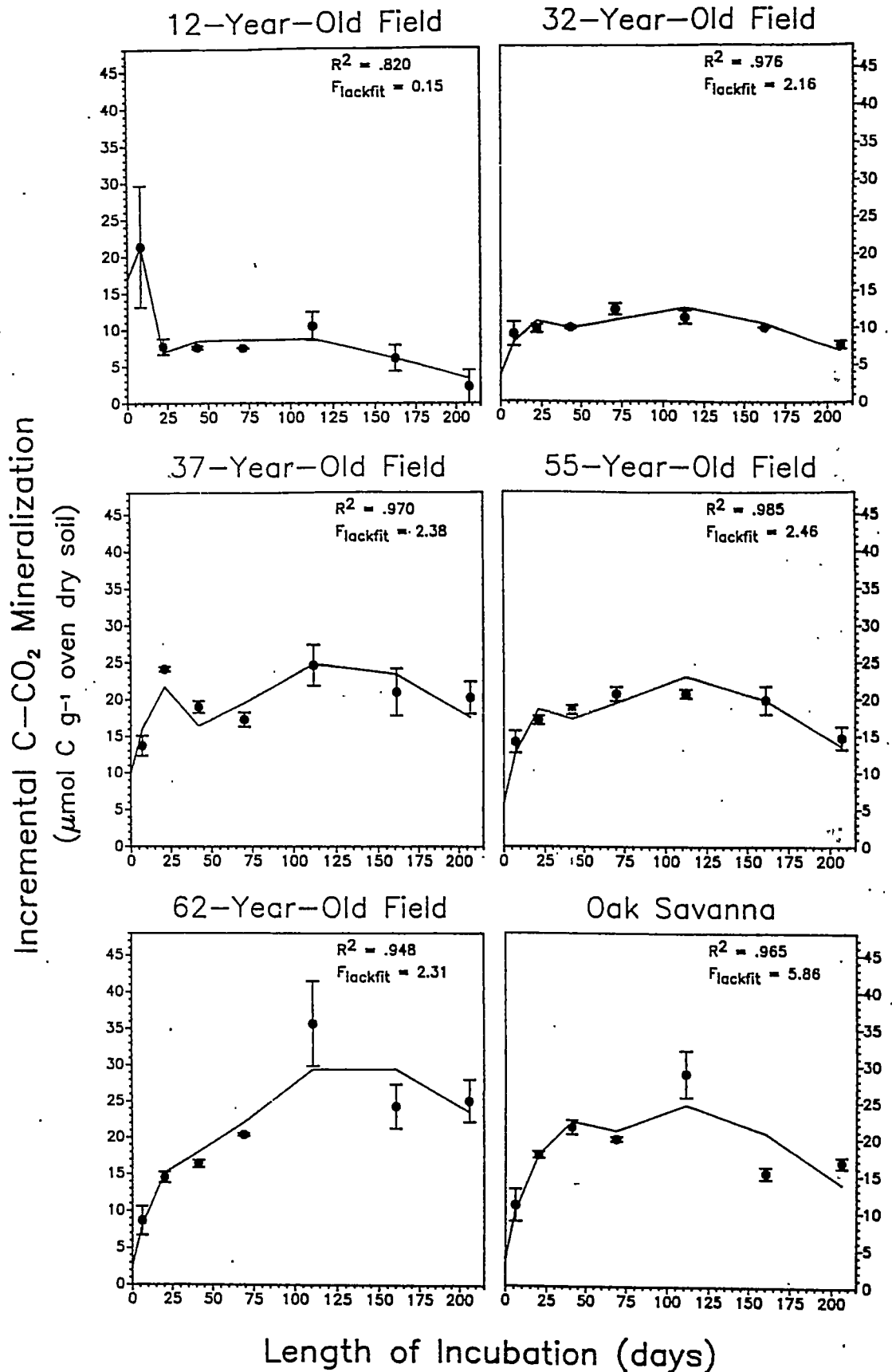


Fig. 2. Incremental amounts of CO<sub>2</sub>-C evolved from 25 g soil samples, and incremental CO<sub>2</sub>-C predicted by an incremental form of a first order asymptotic exponential model with a positive y-intercept for the interval between  $t = 0$  and  $t = 8-41$  days.

Table 3. Parameter estimates (standard errors in parentheses) for soil mineralization models

Field	CO <sub>2</sub> -C mineralization*				Net-N mineralization†		
	C <sub>0</sub> (μmol g <sup>-1</sup> )	C <sub>e</sub> (μmol g <sup>-1</sup> )	k × 10 <sup>-3</sup> (day <sup>-1</sup> )	C <sub>m</sub> : total C (%)	N <sub>0</sub> (μmol g <sup>-1</sup> )	k × 10 <sup>-3</sup> (day <sup>-1</sup> )	N <sub>m</sub> : total Kjeldahl N (%)
12 yr	51.6 (10.0)	16.9 (3.4)	11.33 (4.0)	13.8	5.11 (0.38)	7.37 (0.96)	15.2
32 yr	80.1 (5.6)	3.36 (0.88)	7.48 (1.03)	14.9	11.3 (2.0)	4.17 (1.04)	29.9
37 yr	193 (23)	9.85 (1.82)	4.69 (0.99)	26.3	15.8 (3.3)	3.69 (1.04)	33.0
55 yr	150 (8)	5.72 (1.20)	6.76 (0.71)	17.3	9.56 (0.97)	11.6 (2.6)	15.7
62 yr	280 (64)	2.40 (2.56)	3.39 (1.17)	20.6	16.0 (6.0)	4.58 (2.46)	18.2
Oak savanna	155 (12)	3.55 (2.84)	7.16 (1.31)	14.4	9.42 (0.86)	9.96 (1.59)	13.9

\*C<sub>m</sub> = C<sub>0</sub> exp<sup>-kt</sup> (exp<sup>kt</sup> - 1) + C<sub>e</sub> and C<sub>m</sub> = C<sub>0</sub> exp<sup>-kt</sup> (exp<sup>kt</sup> - 1) (segmented at 8–41 days), where

C<sub>m</sub> = potentially mineralizable organic C (amount present at t = 0).

C<sub>e</sub> = intercept ~ easily mineralizable fraction.

C<sub>0</sub> = C<sub>m</sub> - C<sub>e</sub>.

k = proportionality constant.

t = length of time from start of incubation (days).

i = length of interval preceding time t (days).

†N<sub>m</sub> = N<sub>0</sub> (1 - exp<sup>-kt</sup>), where

N<sub>m</sub>, N<sub>0</sub> = potentially mineralizable organic N (amount present at t = 0).

k = proportionality constant.

t = length of time from start of incubation (days).

program (NLIN) in SAS (SAS Institute, 1985). Cumulative amounts of net-N mineralized during the initial flush and over the course of the entire incubation were fitted to a first order asymptotic exponential model (Fig. 1). The first-order kinetics model was selected on the basis of goodness-of-fit statistics and model simplicity (only two variables are estimated).

Since the C mineralization data were incremental rather than cumulative, amounts of CO<sub>2</sub>-C mineralized were fitted to an incremental form of the first-order rate equation (Fig. 2) (Ellert and Bettany, 1988). To account for an initial flush of mineralization, the model was given a positive y-intercept for the interval between t = 0 and t = 8–41 days. Visual observations and F<sub>lackfit</sub> values (ratio of the lack-of-fit mean square to the pure error mean square) were used to determine the length of the CO<sub>2</sub>-C model segments.

First order derivatives of the cumulative CO<sub>2</sub>-C and net-N mineralization models were used to estimate instantaneous rates of mineralization during the incubation.

## RESULTS

Initial physical and chemical soil conditions are shown in Table 2. The Cedar Creek soils had accumulated organic C and N since agricultural disturbance, and similar C:N ratios illustrate the close correspondence of accrued C and N resources in these soils (Zak *et al.*, 1990). While the pH of these soils was low prior to incubation (4.3–4.9), biodegradation products and nitrification during the incubation did not cause values to fall below pH 4.1.

Figure 1 shows cumulative first-order equations fitted to cumulative amounts of net-N mineralized from the 25 g samples. The amount of net-N mineral-

ized from the 700 g samples has been overlaid to illustrate the reasonable propinquity of the two incubation methods. Neither the cumulative first order model selected, nor any other models which demonstrate continuously decreasing rates, could explain all the perturbations in the data, particularly during the first 69–70 days of the incubation. The leveling-off of mineralization during this initial period differed from the overall kinetic model, which oversimplified the biological processes (France and Thornley, 1984). Modeling this initial period separately, the cumulative amount of net-N mineralized from the six soils, about 2.0–5.2 μmol N g<sup>-1</sup>, was not very different from the amount of microbial N (0.95–5.7 μmol N g<sup>-1</sup>) determined by Zak *et al.* (1990) for these same soils in the spring of 1987. This may indicate the turnover of a large fraction of the original biomass, which may have been detrimentally influenced by the pretreatment (i.e. sieving and physical disruption), or the removal of the rhizosphere microhabitat (Ross *et al.*, 1985; Clarholm, 1985; Robertson *et al.*, 1988).

Actual incremental amounts of CO<sub>2</sub>-C mineralized from the Cedar Creek soils, and the incremental CO<sub>2</sub>-C predicted by the segmented first-order kinetics models are presented in Fig. 2. Parameter estimates for CO<sub>2</sub>-C and net-N mineralization are summarized in Table 3. The coefficient of determination (R<sup>2</sup>) is included on Figs 1 and 2 only as a summary statistic for measuring model adequacy (Kvalseth, 1985). A better measure to describe the fit of the model to the actual data is F<sub>lackfit</sub> (Ellert and Bettany, 1988).

The older fields and oak savanna demonstrated significantly higher CO<sub>2</sub>-C and net-N mineralization potentials (C<sub>m</sub> and N<sub>m</sub>) than the younger fields. However, measures of soil mineralization did not indicate any trends with age of field greater than 12 yr

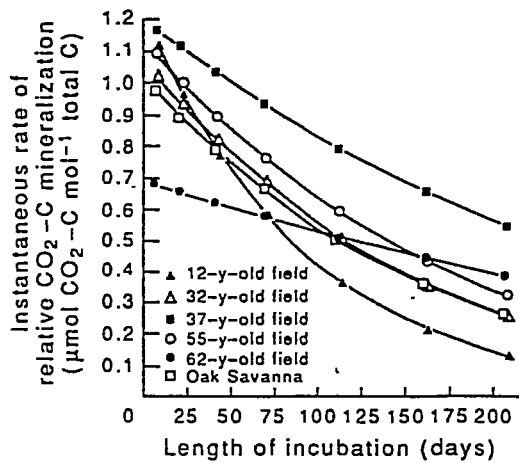


Fig. 3. Relative decomposability of soil organic matter during the incubation of Cedar Creek soils.

(net-N) and 32 yr ( $\text{CO}_2\text{-C}$ ) (Table 3). Higher  $C_0$  values for 37 and 62 yr old fields corresponded with higher proportions of prairie graminoid cover (>60%; Cook and Allan, 1992).

Potential mineralization estimates were normalized as percentages of the total resource ( $C_m$ : total C and  $N_m$ : total Kjeldahl-N; Table 3) to facilitate comparison of soils with different amounts of total C and N. Relative potential mineralization values differed among the fields, but failed to show a trend with time since agricultural disturbance.

To illustrate changes in mineralization during the incubation, instantaneous rates of relative  $\text{CO}_2\text{-C}$  mineralization ( $\text{CO}_2\text{-C}$  mineralization: total C) were plotted against the duration of the incubation at each sampling (Fig. 3). This approach is useful to compare decomposition rates among different soils, but it demands cautious interpretation. By equating relative rates with biodegradability, we assume that the process is limited primarily by resource quality, not the soil population or physico-chemical environment (Swift *et al.*, 1979). While all the old fields and the oak savanna demonstrated decreases in overall resource quality with the duration of incubation, there appeared to be inter-field differences in the proportion of labile and recalcitrant substances.

Initial amounts of soil DOC showed slight increases with time since disturbance, from 0.70 to  $1.30 \mu\text{mol C g}^{-1}$  (Fig. 4). During the incubation, specific ( $\mu\text{mol C g}^{-1}$  oven dry soil) and relative (DOC: total C) DOC concentrations increased significantly from initial amounts in fields older than 32 yr and the oak savanna. The two youngest fields did not show this trend; their DOC concentrations decreased after the first few weeks of the incubation, and subsequently remained low (12 yr old field) or increased only slightly (32 yr old field).

The potential capacity of soil DOC to support mineralization increased during the incubation. At 14 days, the soil DOC pool represented up to 2.2 times the amount of  $\text{CO}_2\text{-C}$  mineralized  $\text{day}^{-1}$ , but the capacity to support total C mineralization

(estimated using a conservative value of 65% microbial efficiency; van Veen and Paul, 1981) was limited to less than 1 day for all fields. However, by 210 days, amounts of DOC represented 4.3 to 9.7 times the amount of  $\text{CO}_2\text{-C}$  mineralized  $\text{day}^{-1}$ , and could support 1.5–3.4 days of total C mineralization.

To test the hypothesis that mineralization rates are a function of DOC, instantaneous rates were plotted against the specific concentration of soil DOC at each DOC sampling time [Fig. 5(a,b)]. No obvious relationships were found using the combined data from the five old fields and the oak savanna. However, a relationship between DOC and instantaneous  $\text{CO}_2\text{-C}$  mineralization was apparent when the soils were analyzed for each individual incubation period. The relationship was described by an asymptotic exponential growth rate curve ( $R^2 = 0.985$  to  $0.652$ ), but the distribution of the data call this model into question. Because the data are unevenly spread across the range of DOC,  $R^2$  values are artificially inflated. Without further information, we feel it is reasonable to question the strength and significance of these relationships. This curve fitting was even poorer with instantaneous net-N mineralization rates [Fig. 5(b)]. However, even if this regression model is incorrect, it appears that there was a decrease in the mineralization rate response to the size of the DOC pool as the incubation proceeded. The instantaneous rate of  $\text{CO}_2\text{-C}$  mineralization was 3–10 times higher at 14 days than at 210 days for any given DOC concentration.

## DISCUSSION

Inter-field comparisons indicated that  $\text{CO}_2\text{-C}$  and net-N mineralization kinetics in old field soils at Cedar Creek were not monotonically related to time since disturbance. While initial amounts of organic C and N may have been responsible for early successional (12–37 yr) increases in potential mineralization (Zak *et al.*, 1990), data from this study suggest that this was not the case for mid to late old field succession, where total C and N are not closely related to mineralization rates.

The proportion of soil organic matter potentially mineralized in this study approximated values reported by Houot *et al.* (1989). However, relative mineralization rates reported by Zak *et al.* (1990) are similar among Cedar Creek soils ( $4.4 \pm 0.7\%$ ), and considerably lower than those measured by us. Furthermore, Zak *et al.* measured higher soil DOC concentrations, and found that DOC increased with field age in close correspondence with increased total C. The differences between our results may be due to seasonal changes (Sarathchandra *et al.*, 1988) or different DOC and mineralization assessment techniques. Zak *et al.* used dry soil for DOC extractions, which can result in greater aggregate disruption and increase measured concentrations by as much as 10-fold higher than moist soil extractions (Davidson

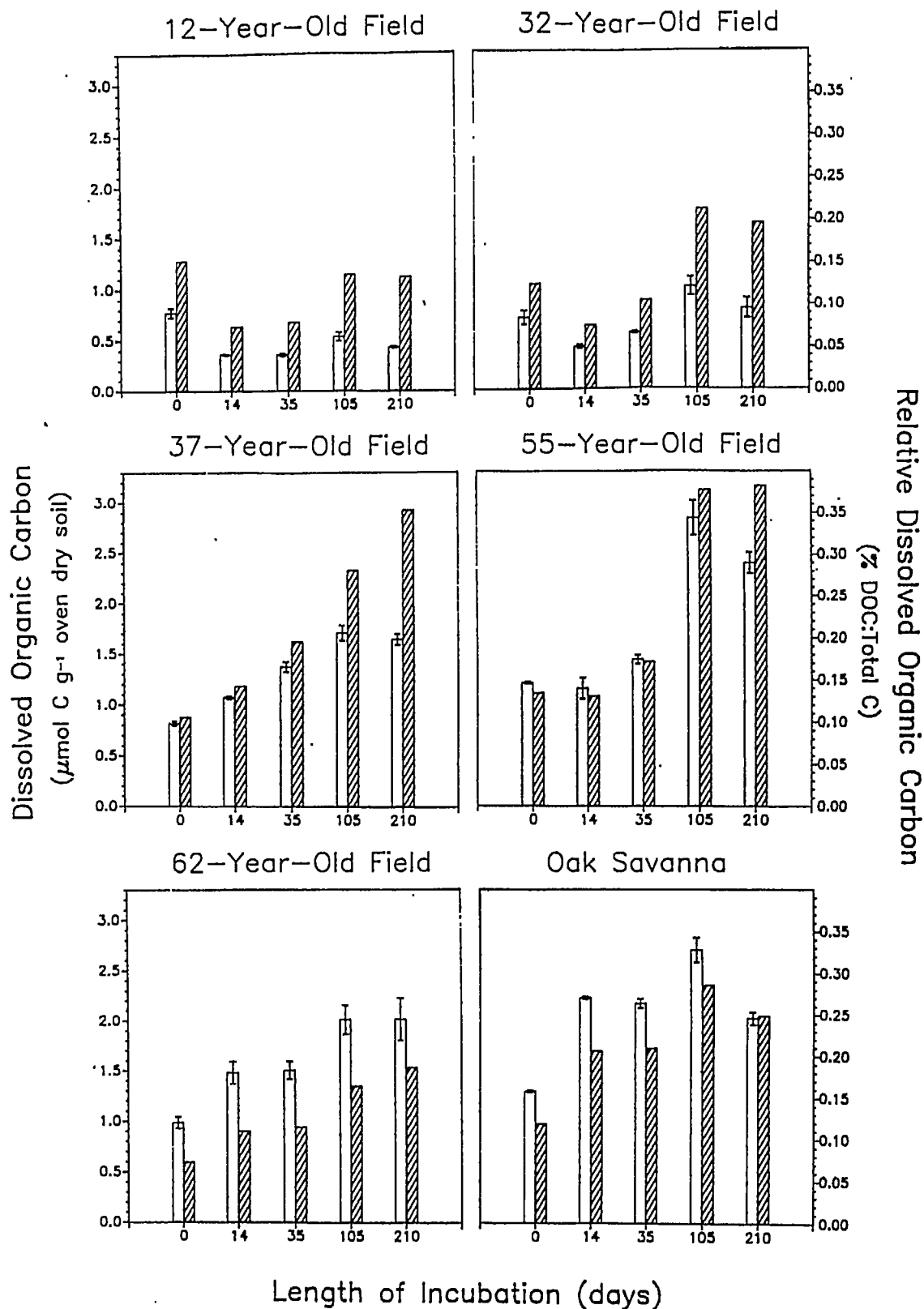


Fig. 4. Specific (open bar) and relative percent (hatched bar) DOC concentrations of Cedar Creek soils during incubation.

*et al.*, 1987). The dry soil extraction may be an index of soil biomass, resulting in better correlations with C mineralization rates (Davidson *et al.*, 1987).

Few studies have satisfactorily demonstrated that DOC is the organic resource of decomposers, and many have not considered the dynamic nature of the DOC pool. In some cases, initial, point-time



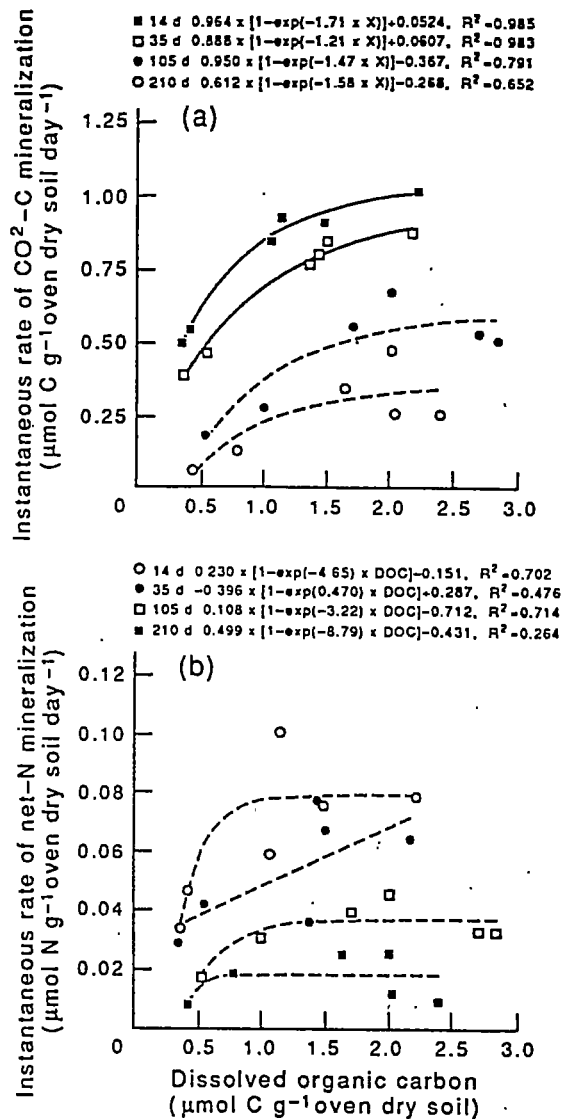


Fig. 5. Relationships between DOC and instantaneous rates of (a)  $\text{CO}_2\text{-C}$  and (b) net-N mineralization during the incubation of Cedar Creek soils.

measurements of DOC were correlated with the cumulative amount of organic matter or nutrient released during an incubation (Burford and Bremner, 1975; Davidson *et al.*, 1987; Reinertsen *et al.*, 1984). Since the initial concentration of DOC in soil typically does not exceed 1% of the total C (Zak *et al.*, 1990; Burford and Bremner, 1975; Dinwoodie and Juma, 1988; Martin, 1975; Smith *et al.* 1986; this study, Fig 4), it has been concluded that measured  $C_{\text{min}}$  is equal to the DOC plus some fraction of water-insoluble C (Burford and Bremner, 1975; Davidson *et al.*, 1987). These interpretations predict that DOC is completely utilized (readily-available) and in finite supply. These assumptions need to be tested by measuring DOC over time and turnover rates.

Where DOC has been measured over time in a laboratory incubation (Smith *et al.*, 1986; Jenkinson and Powlson, 1976), the size of the DOC pool decreases during the first few weeks. We observed this

change in soils of 12 and 32 yr old fields, but not in soils of fields older than 32 yr or the oak savanna. Moreover, prolonged incubation of the 32 yr old field demonstrated that the reduction may be temporary, rather than a steady-state condition. We attempted a different approach to evaluate the relationship between the DOC pool and mineralization rates. Changes in the size of soil DOC pools during the incubation were compared to instantaneous mineralization rates. Since the size of the DOC pool generally remained constant or increased while mineralization rates decreased, we found an increased potential for the DOC to support total mineralization (up to several days), but a decreased mineralization rate response to soil DOC concentrations. These results reflect decreased DOC utilization relative to supply, and suggest either decreased biodegradability (i.e. quality) of DOC, decreased microbial activity (for some reason other than the absence of an available energy source), or a transition to a separate, insoluble energy source. While C and N cycling through soil organic matter are closely related, poor correlations between the DOC pool and the liberation of inorganic N during decomposition demonstrated that the relationship is not necessarily direct.

Information on the biodegradability of soil DOC is clearly lacking. In relatively few studies has the heterogeneity of DOC been considered. It is assumed that all the dissolved substances are labile and utilized rapidly (e.g. Burford and Bremner, 1975; Gale and Gilmour, 1988). However, recalcitrant molecules may represent a significant portion of the DOC (Qualls R. G., unpublished Ph.D. thesis, University of Georgia, 1989; Aoyama, 1985; Meyer *et al.*, 1987). This may explain why the DOC pool present at the end of the incubation had the potential to supply 1.5–3.4 days of total C mineralization, and yet mineralization rates were much lower than at the onset of the incubation. In the following paper (Cook and Allan, 1992), we report our attempt to characterize DOC quality during these incubations by fractionation techniques.

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#### REFERENCES

- Aoyama M. (1985) Properties of fine and water soluble fractions of several composts: I. Micromorphology, elemental composition and nitrogen mineralization of fractions. *Soil Science and Plant Nutrition* 31, 189–198.
- Bott T. L., Kaplan L. A. and Kuserk F. T. (1984) Benthic biomass supported by streamwater dissolved organic matter. *Microbial Ecology* 10, 335–344.

- Brown J. R. and Frederick L. R. (1968) Decomposition of the water-soluble fraction of sudangrass residue in soil. *Plant and Soil* 28, 467-470.
- Burford J. R. and Bremner J. M. (1975) Relationships between the denitrification capacities of soils and total, water-soluble and readily decomposable soil organic matter. *Soil Biology & Biochemistry* 7, 389-394.
- Clarholm M. (1985) Possible roles for roots, bacteria, protozoa and fungi in supplying nitrogen to plants. In *Ecological Interactions in Soil: Plants, Microbes and Animals* (A. H. Fitter, Ed.), pp. 355-365. Blackwell, Oxford.
- Cook B. D. and Allan D. L. (1992) Dissolved organic carbon in old field soils: compositional changes during the biodegradation of soil organic matter. *Soil Biology & Biochemistry* 24, 595-600.
- Cronan C. S. (1985) Comparative effects of precipitation acidity on three forest soils: carbon cycling responses. *Plant and Soil* 88, 101-112.
- Davidson E. A., Galloway L. F. and Strand M. K. (1987) Assessing available carbon: comparison of techniques across selected forest soils. *Communications in Soil Science and Plant Analysis* 18, 45-64.
- Dinwoodie G. D. and Juma N. G. (1988) Allocation and microbial utilization of C in two soils cropped to barley. *Canadian Journal of Soil Science* 68, 495-505.
- Ellert B. H. and Bettany J. R. (1988) Comparison of kinetic models for describing net sulfur and nitrogen mineralization. *Soil Science Society of America Journal* 52, 1692-1702.
- Evans A. Jr, Zelazny L. W. and Zipper C. E. (1988) Solution parameters influencing dissolved organic carbon amounts in three forest soils. *Soil Science Society of America Journal* 52, 1789-1792.
- France J. and Thornley J. H. M. (1984) *Mathematic Models in Agriculture: A Quantitative Approach to Problems in Agriculture and Related Sciences*. Butterworths, London.
- Gale P. M. and Gilmour J. T. (1988) Net mineralization of carbon and nitrogen under aerobic and anaerobic conditions. *Soil Science Society of America Journal* 52, 1006-1011.
- Grigal D. F. (1973) Note on the hydrometer method of particle-size analysis. Scientific Journal Series, Paper No. 8438, University of Minnesota Agricultural Experiment Station.
- Grigal D. F., Chamberlain L. M., Finney H. R., Wroblewski D. V. and Gross E. R. (1974) Soils of the Cedar Creek Natural History Area. Miscellaneous Report 123-1974, University of Minnesota Agricultural Experiment Station.
- Harmsen G. W. and van Schreven D. A. (1955) Mineralization of organic nitrogen in soil. *Advances in Agronomy* 3, 299-398.
- Houot S., Molina J. A. E., Chaussod R. and Clapp C. E. (1989) Simulation by NCSOIL of net mineralization in soils from the Deherain and 36 Parcelles fields at Grignon. *Soil Science Society of America Journal* 53, 451-455.
- Inouye R. S., Huntly N. J., Tilman D., Tester J. R., Stillwell M. and Zinnel K. C. (1987) Old-field succession on a Minnesota sand plain. *Ecology* 68, 12-26.
- Jenkinson D. S. and Powlson D. S. (1976) The effects of biocidal treatments on metabolism in soil: I. Fumigation with chloroform. *Soil Biology & Biochemistry* 8, 167-177.
- Kvalseth T. O. (1985) Cautionary note about  $R^2$ . *The American Statistician* 39, 279-285.
- Linn D. M. and Doran J. W. (1984) Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Science Society of America Journal* 48, 1267-1272.
- Martin J. K. (1975)  $^{14}\text{C}$ -Labelled material leached from the rhizosphere of plants supplied continuously with  $^{14}\text{CO}_2$ . *Soil Biology & Biochemistry* 7, 395-399.
- Meyer J. L., Edwards R. T. and Risley R. (1987) Bacterial growth on dissolved organic carbon from a blackwater river. *Microbial Ecology* 13, 13-29.
- McGill W. B., Hunt H. W., Woodmansee R. G. and Reuss J. O. (1981) PHOENIX, a model of the dynamics of carbon and nitrogen in grassland soils. *Ecological Bulletin* 33, 49-115.
- Nodvin S. C., Driscoll C. T. and Likens G. E. (1986) Simple partitioning of anions and dissolved organic carbon in a forest soil. *Soil Science* 142, 27-35.
- Powlson D. S. and Jenkinson D. S. (1976) The effects of biocidal treatments on metabolism in soil: II. Gamma irradiation, autoclaving, air-drying and fumigation. *Soil Biology & Biochemistry* 8, 179-188.
- Reinertsen S. A., Elliott L. F., Cochran V. L. and Campbell G. S. (1984) Role of available carbon and nitrogen in determining the rate of wheat straw decomposition. *Soil Biology & Biochemistry* 16, 459-464.
- Robertson K., Schnurer J., Clarholm M., Bonde T. A. and Rosswall T. (1988) Microbial biomass in relation to C and N mineralization during laboratory incubations. *Soil Biology & Biochemistry* 20, 281-286.
- Ross D. J., Speir T. W., Tate K. R. and Orchard V. A. (1985) Effects of sieving on estimations of microbial biomass, and carbon and nitrogen mineralization, in soil under pasture. *Australian Journal of Soil Research* 23, 319-324.
- Sarathchandra S. U., Perrot, K. W., Boase M. R. and Waller J. E. (1988) Seasonal changes and the effects of fertiliser on some chemical, biochemical and microbiological characteristics of high-producing pastoral soil. *Biology and Fertility of Soils* 6, 328-335.
- SAS Institute (1985) *SAS User's Guide: Statistics, Version 5*. SAS Institute, Cary, N.C.
- Schlesinger W. H. (1986) Changes in soil carbon storage and the associated properties with disturbance and recovery. In *The Changing Carbon Cycle* (J. R. Trabalka and D. E. Reichle, Eds), pp. 194-220. Springer, New York.
- Schoenau J. J. and Bettany J. R. (1987) Organic matter leaching as a component of carbon, nitrogen, phosphorus, and sulfur cycles in a forest, grassland, and gleyed soils. *Soil Science Society of America Journal* 51, 646-651.
- Smith J. L., McNeal B. L., Cheny H. H. and Campbell G. S. (1986) Calculation of microbial maintenance rates and net nitrogen mineralization in soil at steady-state. *Soil Science Society of America Journal* 50, 332-338.
- Sollins P. and McCorison F. M. (1981) Nitrogen and carbon solution chemistry of an old growth coniferous forest watershed before and after cutting. *Water Resources Research* 17, 1409-1418.
- Swift M. J., Heal O. W. and Anderson J. M. (1979) *Decomposition in Terrestrial Ecosystems*. University of California Press, Berkeley, Calif.
- Tilman D. (1986) Nitrogen-limited growth in plants from different successional stages. *Ecology* 67, 555-563.
- Tilman G. D. (1984) Plant dominance along an experimental nutrient gradient. *Ecology* 65, 1445-1453.
- van Veen J. A. and Paul E. A. (1981) Organic carbon dynamics in grassland soils. I. Background information and computer simulation. *Canadian Journal of Soil Science* 61, 185-201.
- Voroney R. P., van Veen J. A. and Paul E. A. (1981) Organic C dynamics in grassland soils. II. Model validation and simulation of the long-term effects of cultivation and rainfall erosion. *Canadian Journal of Soil Science* 61, 211-224.
- Williams S. T. and Gray T. R. G. (1974) Decomposition of litter on the soil surface. In *Biology of Litter Decomposition* (C. H. Dickinson and G. J. F. Pugh, Eds), Vol. II, pp. 611-631. Academic Press, London.
- Zak D. E., Grigal D. F., Gleeson S. and Tilman D. (1990) Carbon and nitrogen cycling during old-field succession: constraints on plant and microbial productivity. *Biogeochemistry* 11, 111-129.