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Kinetic to Saturation Model for Simulation of Soil Organic Carbon Increase to Steady State

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The use of mathematical models predicting SOC dynamics can provide relevant information about the C storage potential of agricultural soils. We evaluated three mathematical models (first-order kinetic, C saturation, and a proposed kinetic to saturation) predicting SOC dynamics and steady-state SOC of a Hapludoll from central Kansas. The study was based on a long-term experiment (17 yr) assessing soil tillage systems (chisel tillage [CT] and no-till [NT]) and N fertilizer sources (168 kg N ha^{-1} as NH_4NO_3 [MF], cattle manure [OF], and a control treatment without N [CO]. The soil under NT (0–5 cm) had significant SOC accumulation (>0.23 Mg C ha^{-1} yr^{-1}) regardless of fertilization source, while the CT soil had negligible changes in SOC (<0.12 Mg C ha^{-1} yr^{-1}) without the addition of organic fertilizer as an external C source. Organic fertilization increased the original SOC by 56 and 192%, reaching steady state at 15.9 and 28.0 Mg ha^{-1} in CT and NT soils, respectively. The SOC predicted by all three models had significant correlations (r > 0.80, p < 0.05) with measured SOC. However, the C saturation model overestimated the measured SOC under C-depleted conditions, failing RMSE and lack-of-fit tests, while the first-order kinetic model overestimated NT OF steady-state SOC by up to 58% in relation to the maximum SOC storage capacity determined for NT soils. The SOC predicted by the kinetic to saturation model agreed with both measured SOC and the maximum SOC storage capacity of NT soils. The kinetic to saturation model can be used for long-term simulation of SOC dynamics in soils that are either C depleted or close to saturation.

Abbreviations: SOC, soil organic carbon; CT, chisel tillage; NT, no-till; CO, control without nitrogen; MF, mineral nitrogen fertilization; OF, organic nitrogen fertilization.

Conservation agriculture as defined as minimal soil disturbance, permanent soil cover, and crop rotation can increase SOC, with mutual benefits for soil quality, food security, and climate change (Smith et al., 2007; Jat et al., 2014). No-till (NT) provides the least amount of soil disturbance, stimulates biological activity, and enhances aggregate formation and thus is a significant component of conservation agriculture (Fabrizzi et al., 2009; Six et al., 2000, 2004). Maximum SOC accumulation rates are usually achieved within 5 to 20 yr after the adoption of a NT system in C-depleted soils (West and Post, 2002; Lal, 2004; West and Six, 2007). Nonetheless, NT soils are considered a finite SOC pool serving as a C sink for up to 20 to 50 yr until SOC stabilizes at new steady-state levels (West and Post, 2002; West and Six, 2007).

The surface soil layers are more sensitive to soil management practices (Six et al., 2002) and are expected to reach steady state faster than deeper soil layers. Soil organic C is considered to be at steady state when SOC remains stable under continuous soil management practices and constant levels of C inputs (Paustian et al., 1997). Thus, at steady state, C inputs and C humification rates (k_1) are balanced by SOC stocks and SOC mineralization rates (k_2) (West and Six, 2007).

Core Ideas:

- **We evaluated SOC dynamics in a long-term soil tillage and N fertilization experiment.**
- **We proposed a kinetic to saturation model for long-term simulation of SOC dynamics.**
- **The model was accurate in C-depleted soils and accounted for SOC saturation process.**

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Soils can achieve different steady-state levels in response to different levels of C inputs and soil management practices (Bayer et al., 2006; Stewart et al., 2007). Nonetheless, saturation is another process impairing SOC accumulation when SOC stabilization mechanisms (i.e., physical and chemical) lose efficiency to protect newly added C (Stewart et al., 2007). At this point, the soil is no longer able to accumulate SOC regardless of increasing C input levels (Stewart et al., 2007; West and Six, 2007). Saturation would ultimately limit SOC accumulation and its determination is crucial for realistic projections of the soil's capacity to act as a C sink by mathematical models.

The first-order kinetic model proposed by Hénin and Dupuis (1945) has been widely used to assess SOC dynamics in long-term experiments (Dalal and Mayer, 1986; Bayer et al., 2006; Vieira et al., 2009). Less complex than the Century (Parton et al., 1987) and RothC (Jenkinson et al., 1987) models, the first-order kinetic model can be used to estimate the SOC dynamic coefficients (k_1 and k_2) and SOC at steady state (Bayer et al., 2006). The model predictions are consistent with observations in long-term experiments evaluating C dynamics in soils with initially low SOC stocks (Bayer et al., 2006; Vieira et al., 2009) but show low agreement in soils with recovered SOC (Six et al., 2002; Stewart et al., 2007). This discrepancy is related to the basic assumption of first-order kinetic models that increasing C inputs promote a linear increase in steady-state SOC (Stewart et al., 2007), while many studies have reported an asymptotic relationship of C inputs and SOC when the soil approaches C saturation (Six et al., 2002; Stewart et al., 2007; Gulde et al., 2008). Studies where SOC levels are at steady state or saturation are scarce, limiting the validation of C models.

The overestimation of steady-state SOC by the first-order kinetic model is due to the basic assumption that both k_1 and k_2 coefficients remain stable with time (Bayer et al., 2006). Stewart et al. (2007) proposed two mathematical models accounting for C saturation as a limiting factor for SOC accumulation. The simplest model (the C saturation model) assumes that the C humification rate (k_1) decreases as SOC approaches saturation, while the more complex (mixed model) has a labile and not saturable SOC pool and a more stable and saturable SOC pool (silt + clay) with constant SOC mineralization rates (k_2) for each pool. Although simpler than the mixed model, the C saturation model had better agreement with data observed in 11 long-term experiments that had asymptotic increases of SOC in response to C inputs (Stewart et al., 2007).

Carbon humification rates (k_1) are mostly regulated by C input quality (Balesdent and Balabane, 1996; Bolinder et al., 1999) as well as soil management practices (Allmaras et al., 2004; Lovato et al., 2004). The k_1 coefficient is generally assumed to be constant with time for a given soil tillage system and fertilization practice (Bayer et al., 2006). This assumption is contrary to the proposition of the C saturation model (Stewart et al., 2007). In contrast, the k_2 coefficient is likely to increase as the soil approaches saturation because C stabilization mechanisms gradually lose efficiency to protect the newly added C (Gulde et al., 2008; Stewart et al., 2007). Based on these assumptions, we propose a modification of the original first-order kinetic model, including the SOC saturation levels as a limiting factor for SOC accumulation. The proposed kinetic to saturation model assumes that k_2 would increase asymptotically as the soil approaches SOC saturation and the C stabilization mechanisms lose efficiency. The objective of this study was to evaluate the accuracy of the three mathematical models to predict SOC dynamics and steady-state SOC in a long-term experiment (17 yr) from central Kansas in response to soil tillage and N fertilization sources.

MATERIAL AND METHODS

Experimental Site and Soil Sampling

This study was based on a long-term experiment established in 1990 at the North Farm of Kansas State University in Manhattan, KS (39°12′42″ N, 96°35′39″ W). The local average annual precipitation is 800 mm, and the annual mean temperature is 11.4°C. The soil was a moderately well-drained Kennebec silt loam (a fine-silty, mixed, superactive, mesic Cumulic Hapludoll) (Table 1). The experiment was arranged in split-plot randomized blocks with four replications in plots with corn (*Zea mays* L.). The tillage systems were the main plots, and N sources were the subplots. The tillage systems were chisel plow and offset disk preplant (chisel tillage [CT]) and no-till (NT) by planting directly through the crop residues with minimal soil disturbance. The chisel plow and disking operations were performed to a depth of 15 and 10 cm, respectively. The N treatments were different sources: 168 kg N ha^{-1} as NH_4NO_3 (MF), 168 kg N ha^{-1} as cattle manure (OF), and a control (CO) without N amendment. Until 2001, the cattle manure was applied without previous treatment (fresh cattle manure), while after 2002 the manure was composted. The application of both fresh and composted cattle manure was made assuming that 30% of the organic N and 100% of the mineral N was available during each cropping season (Mikha and Rice, 2004).

Soil core samples were taken in the 0- to 5-, 5- to 15-, and 15- to 30-cm soil layers using a 5-cm-diameter soil probe in the second, fifth, ninth, 12th, 13th, 14th, and 17th yr of the experiment.

Table 1. Soil texture, chemical characteristics, and soil mass of the 0- to 5-cm layer of a Hapludoll from central Kansas under chisel tillage (CT), no-till (NT), and native prairie (Fabrizzi et al., 2009).

Tillage	pH	Bray P	Ca^{2+}	K^+	Mg^{2+}	Na^+	CEC†	Sand	Silt	Clay
		mg kg^{-1}					cmol$_c$ kg^{-1}	%		
NT	5.8	55.0	2137	318	265	10.2	18.4	12	68	20
CT	6.2	54.9	2260	371	297	14.5	17.1	10	70	20
Native prairie	5.7	65.0	2472	659	412	19.6	24.7	9	59	32

† Cation exchange capacity.

A nearby native prairie with the same soil type was also sampled in the 17th yr (2007) for comparison (Fabrizzi et al., 2009).

Samples were air dried and sieved (<2 mm), roots removed, and subsamples were finely ground for SOC content analysis. Soil bulk density was determined in the second, ninth, 12th, 13th, and 17th yr of the experiment by drying (105°C) and weighing intact soil core samples collected using a 5-cm-diameter soil probe. We focused our assessment on the top layer of this Hapludoll, which presented evidence that SOC steady-state or saturation levels were achieved in the 0- to 5-cm soil layer of both CT and NT treatments. This approach was used to test the implication of these processes on the predictions of the three mathematical models.

Carbon Inputs

The aboveground C inputs by corn residues were calculated by annually sampling corn plants from each plot and weighing the corn grain yield and stover dry biomass, assuming an average C content of 40% (Bayer et al., 2006). We assumed that the corn roots in the 0- to 5-cm soil layer contributed 10% of the aboveground C inputs. This value is within the estimates of the ratio of corn stover and root (0–7.6 cm) biomass in a long-term experiment with continuous corn in a Haplustoll from Minnesota (Huggins and Fuchs, 1997). The C input from manure was estimated by its C/N ratio (Eghball and Power, 1999) considering the measured total N content of the applied organic fertilizers. The direct contribution of corn- and manure-derived C inputs to the SOC in the 0- to 5-cm soil layer was estimated considering the redistribution of these residues due to chisel plow and disking operations in the CT treatments (Franzluebbers, 2002) by assessing changes in SOC in the 0- to 5- and 5- to 15-cm soil layers (Nicoloso, 2009). The corn grain yield and C inputs for the 1992 to 2001 and 2002 to 2007 periods are presented in Table 2.

Soil Organic Carbon Analysis and Calculations

Soil samples were analyzed for SOC content by dry combustion with a C/N elemental analyzer (Flash EA 1112 Series, Thermo Scientific). The mass of SOC in the 0- to 5-cm soil layer was calculated considering the SOC content and soil bulk density in each subplot and sampling year. The soil bulk density was not determined in the fifth and 14th years of the experiment. Thus, the mass of SOC in both years was estimated considering the soil bulk density measured in the second and 13th years. The temporal comparison of SOC according to soil tillage and fertilization practices was performed considering equivalent soil masses following the procedure described by Ellert and Bettany (1995). Briefly, the soil mass determined for the 0- to 5-cm soil layer of CT and NT plots in 1992 (second year) was used as a reference (590 Mg ha^{-1}). We verified an increase in the soil mass at this layer in the following sampling years for both CT (averaging 696, 691, 697, and 675 Mg ha^{-1} in the ninth, 12th, 13th, and 17th years, respectively) and NT plots (averaging 731, 732, 730, and 720 Mg ha^{-1} for the same years, respectively). The exceeding soil mass (>590 Mg ha^{-1}) was then attributed to the underlying soil layer (5–15 cm; data not shown) for the comparison of equivalent soil masses in the topsoil layer (0–5 cm).

Mathematical Models

The k_1 and k_2 coefficients were estimated by two different procedures. The first procedure (measured SOC method) followed the method described by Bayer et al. (2006), considering the relationship between SOC measured in 1992 (C_0), 1995,

Table 2. Corn grain yield, total C inputs by corn (stover + roots) and cattle manure, and C inputs allocated to the 0- to 5-cm soil layer as affected by no-till (NT), chisel tillage (CT), control without N (CO), mineral fertilizer (MF), and organic fertilizer (OF) management practices.

	CO		MF		OF		Mean	
Tillage	1992–2001	2002–2007	1992–2001	2002–2007	1992–2001	2002–2007	1992–2001	2002–2007
				Corn grain yield, Mg ha^{-1} yr^{-1}				
CT	4.3 ± 2.3†	4.1 ± 1.6	5.9 ± 2.3	9.4 ± 4.5	5.5 ± 2.2	9.1 ± 4.7	5.2 ± 2.3	7.6 ± 4.4
NT	3.9 ± 2.6	3.5 ± 1.3	6.0 ± 2.4	7.5 ± 3.6	5.7 ± 2.4	7.8 ± 4.2	5.2 ± 2.6	6.3 ± 3.6
				Total C inputs by corn (stover + roots) and manure, Mg ha^{-1} yr^{-1}‡				
CT	1.8	1.7	2.6	2.7	5.1	7.9	3.2	4.1
NT	2.0	1.5	2.8	2.5	5.0	7.8	3.3	3.9
Mean	1.9 d§	1.6 e	2.7 c	2.6 c	5.0 b	7.9 a	3.2	4.0
				C inputs allocated to the 0–5-cm soil layer, Mg ha^{-1} yr^{-1}¶				
CT	0.7	0.7	1.1	1.1	2.1	3.2	1.3	1.7
NT	2.0	1.5	2.8	2.5	5.0	7.8	3.3	3.9
				ANOVA, $p > F$				
	Tillage (T)	N	T × N	Period (P)	T × P	N × P	T × N × P	
Total	0.65	<0.01	0.59	<0.01	0.045	<0.01	0.47	

† Mean ± SD.

‡ Average external C input by fresh cattle manure (1992–2001) was 2.56 Mg C ha^{-1} yr^{-1} (average of 38.5 Mg ha^{-1} yr^{-1} of fresh manure on wet-weight basis) and by composted cattle manure (2002–2007) was 5.20 Mg C ha^{-1} yr^{-1} (average of 133.9 Mg ha^{-1} yr^{-1} of composted manure on wet-weight basis).

§ Means followed by different letters are significantly different by the LS Means test for N × P interaction ($p < 0.05$).

¶ 41% of total C inputs were allocated to the 0–5-cm soil layer due to residue redistribution by chisel plow and disk operations in CT treatments.

1999, and 2002 and the annual C inputs during the corresponding period (1992–1995, 1992–1999, and 1992–2002, respectively). The alternative procedure considered the relationship between annual C inputs (1992–2002) and SOC in 1992 (C_0) and 2002, which were estimated by linear regression analysis (SOC by linear regression method) rather than the actually measured SOC (Fig. 1). This alternative procedure was used to decrease errors in the estimates of the k_1 and k_2 coefficients due to the variability of C inputs among years, soil spatial variability, and errors in the determination of SOC. The 1992 to 2002 period was chosen for the assessment of the k_1 and k_2 coefficients because that was the last year of fresh manure application and the increase in SOC in the CT OF and NT OF treatments was still linear (Fig. 1). After the initial procedure, k_1 and k_2 were calculated as (Bayer et al., 2006)

$$k_2 = \frac{\ln(C_0) - \ln(a)}{t} \qquad [1]$$

$$k_1 = \frac{k_2 b}{1 - \exp(-k_2 t)} \qquad [2]$$

where k_2 is the SOC annual mineralization rate (yr^{-1}), k_1 is the added C annual humification rate (yr^{-1}), a is the angular coefficient of the fitted linear equation between C input and SOC during the considered period, and b is the remaining initial SOC (C_0) at time t. Both k_1 and k_2 coefficients were used to adjust the first-order kinetic model according to the method described by Bayer et al. (2006), using the following first-order kinetic equation (Dalal and Mayer, 1986):

$$C_t = C_0 \exp(-k_2 t) + \frac{A k_1}{k_2}\left[1 - \exp(-k_2 t)\right] \qquad [3]$$

where C_t is the SOC (Mg ha^{-1}) at time t (yr), and A is the annual C input (Mg ha^{-1} yr^{-1}).

The SOC at steady state (C_s) was calculated according to the first-order kinetic model as

$$C_s = \frac{A k_1}{k_2} \qquad [4]$$

The C saturation model was adjusted by deriving the following equation (Stewart et al., 2007):

$$\frac{dC_t}{dt} = A\left(1 - \frac{C_t}{C_m}\right) - k_2 C_t \qquad [5]$$

where C_m is the maximum SOC storage capacity for each soil tillage system (Mg ha^{-1}). The k_1 coefficient of the C saturation model would decrease as SOC increases, according to the SOC at a given time (C_t) and the maximum SOC storage capacity (C_m) for CT and NT soils ($1 - C_t/C_m$, as proposed), while the k_2 coefficient would remain constant and estimated as previously determined by Eq. [1]. The SOC at steady state (C_s) for the C saturation model was calculated according model as

$$C_s = \frac{A}{k_2 + A/C_m} \qquad [6]$$

We propose a modification of the original first-order kinetic model, including the SOC saturation level as a limiting factor for SOC accumulation. The proposed kinetic to saturation model assumes that the k_1 coefficient, calculated using Eq. [2], is constant with time, while the k_2 coefficient (Eq. [1]) increases asymptotically [$(C_{t-1} - C_0)/C_m$, as proposed) as the soil approaches SOC saturation and the C stabilization mechanisms (i.e., aggregation) lose efficiency. The proposed concept is described by

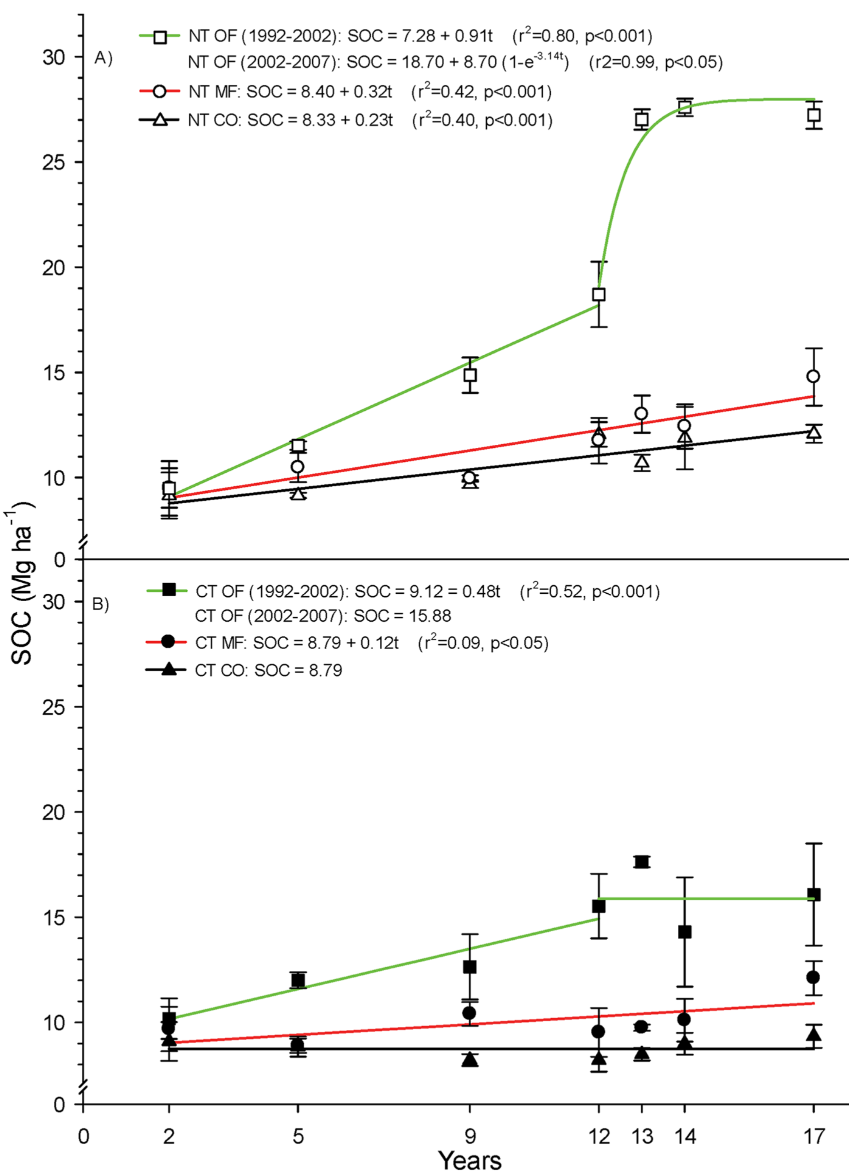

Fig. 1. Soil organic C (SOC) temporal dynamics in the surface 0- to 5-cm layer of a Hapludoll from central Kansas as affected by (A) no-till (NT) and (B) chisel tillage (CT) control without N (CO), mineral fertilizer (MF), and organic fertilizer (OF) management practices. The vertical bars are the mean's standard errors (*n* = 4).

$$C_t = C_0 \exp\left[-k_2 \exp\left(\frac{C_{t-1}-C_0}{C_\mathrm{m}}\right)t\right] + \frac{Ak_1}{k_2 \exp\left[\left(C_{t-1}-C_0\right)/C_\mathrm{m}\right]} \times\left\{1-\exp\left[-k_2 \exp\left(\frac{C_{t-1}-C_0}{C_m}\right)t\right]\right\} \quad [7]$$

where C_{t-1} is the SOC (Mg ha^{-1}) at time $t-1$ (yr). The SOC at steady state ($\mathrm{d}C/\mathrm{d}t = 0$) was calculated by deriving the following equation:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{Ak_1}{k_2 \exp\left[\left(C_t - C_0\right)/C_\mathrm{m}\right]} \quad [8]$$

Statistical Analysis

Analysis of variance was performed using SAS PROC MIXED (SAS Institute, 2002), and the means were compared by the differences in LS means. The mathematical models were evaluated by the correlation coefficient (r), lack-of-fit, and root mean square error (RMSE) tests using the software MODEVAL 1.1 for Excel in accordance with Smith et al. (1997). The results were considered significantly different at $p < 0.05$.

RESULTS AND DISCUSSION

Temporal Assessment of Soil Organic Carbon

During the 15-yr evaluation period (1992–2007), no significant change in SOC was observed in the surface soil layer (0–5 cm) of the CT CO treatment (Fig. 1b), while the initial SOC in the NT CO treatment increased by 39%, representing an SOC accumulation rate of 0.23 Mg C ha^{-1} yr^{-1} ($P < 0.05$) (Fig. 1a). When mineral fertilizer was applied, increasing corn yields and C inputs (Table 2), SOC increased by 20% in the CT MF (0.12 Mg C ha^{-1} yr^{-1}, $P < 0.001$) and 53% in the NT MF (0.32 Mg C ha^{-1} yr^{-1}, $P < 0.001$) treatments (Fig. 1). The CT OF and NT OF treatments had a distinct pattern of SOC dynamics according to the type of manure applied (Fig. 1). On average, the composted cattle manure input (5.2 Mg C ha^{-1} yr^{-1}) doubled the C input relative to the fresh cattle manure (2.5 Mg C ha^{-1} yr^{-1}) (Table 2). In the first 10 yr of fresh cattle manure amendment, both CT OF and NT OF had linear SOC increases of 0.74 ($P < 0.001$) and 0.91 ($P < 0.001$) Mg ha^{-1} yr^{-1}, respectively. After 2002, when the type of manure changed to composted cattle manure, the SOC in the CT OF treatment stabilized at 15.88 Mg ha^{-1}, while the NT OF treatment showed an asymptotic increase in SOC. After 5 yr of composted manure amendment, the SOC of the NT OF treatment stabilized at 28.03 Mg ha^{-1}. The SOC increased 56% and 177% over the initial SOC in the CT OF and NT OF treatments, respectively, by the end of the evaluated period (2007).

A complementary study evaluating soil aggregate distributions in the samples collected in 2007 from this same experiment revealed that the proportion of sand-free water-stable macroaggregates (>2000 μm) was threefold higher under NT than CT (data not shown, see Nicoloso, 2009) due to decreased soil disturbance with NT. Additionally, the C content within aggregates increased with aggregate size (data not shown), indicating a greater SOC stabilization capacity for NT (Mikha and Rice, 2004; Fabrizzi et al., 2009). The asymptotic relationship between C content within aggregates and increasing SOC levels (Stewart et al., 2007, 2008; Gulde et al., 2008), which was also verified in that assessment, confirmed soil C aggregate saturation as the mechanism limiting C accumulation in the 0- to 5-cm soil layer of the NT OF treatment (data not shown). Thus, the NT soil achieved saturation levels with SOC at 28.03 Mg ha^{-1} (Fig. 1a), limiting further SOC accumulation even under additional C inputs. Based on this evidence, we established the SOC of 28.03 Mg ha^{-1} as the maximum SOC storage capacity (C_m) for the NT soil. In contrast, the CT soil had no evidence of soil aggregate saturation, indicating that steady-state SOC at 15.88 Mg ha^{-1} was promoted by balanced C inputs and SOC losses in the 0- to 5-cm soil layer.

Estimating Mineralization and Humification Rate Coefficients

The k_1 and k_2 coefficients (Table 3) were estimated through the relationship of C inputs (Table 2) and SOC in the 0- to 5-cm soil layer (Fig. 1) (Bayer et al., 2006). To estimate the direct contribution of corn and manure residues in the 0- to 5-cm soil layer, we evaluated SOC dynamics in both the 0- to 5- and 5- to 15-cm soil layer. No changes in SOC in the 5- to 15-cm soil layer were noticed for NT treatments during the evaluation period (data not shown; see Nicoloso, 2009), indicating that the estimated corn- and manure-derived C inputs could be entirely allocated to the top layer (0–5 cm). Although no changes in SOC were noticed for the CT CO and CT MF treatments, the CT OF treatment had a significant SOC accumulation rate of 0.69 Mg ha^{-1} yr^{-1} in the 5- to 15-cm soil layer in the 1992 to 2002 period (data not shown; see Nicoloso, 2009). Thus, the SOC accumulation rate observed in the 0- to 5-cm soil layer represented 41% of the total SOC accumulation in the entire 0- to 15-cm soil layer (1.17 Mg ha^{-1} yr^{-1}) during the same period. Soil organic C accumulation in deeper soil layers is often observed in CT soils due to residue mixing by soil tillage operations (Franzluebbers, 2002; Campos et al., 2011). Based on these results, we considered that 41% of the total C inputs (Table 2) would be allocated to the 0- to 5-cm soil layer for the estimation of the k_1 and k_2 coefficients (Table 3) for the CT treatments.

The SOC dynamics coefficients (k_1 and k_2) were determined by the relationship between C inputs allocated to the 0- to 5-cm soil layer and SOC in the NT and CT treatments (Bayer et al., 2006) by both the measured SOC (for the 1992–1995, 1992–1999, and 1992–2002 periods) and SOC by linear regression (for the 1992–2002 period) methods (Table 3). There was high variability of the adjusted k_1 and k_2 coefficients when they were estimated using the SOC measured in 1995, 1999, and 2002. The estimates were probably affected by the variabil-

Table 3. Carbon humification (k_1) and soil organic C (SOC) mineralization (k_2) coefficients as affected by no-till (NT), chisel tillage (CT), control without N (CO), mineral fertilizer (MF), and organic fertilizer (OF) management practices as estimated by two different methods (measured SOC and SOC by linear regression).

Method	CT			NT		
	CO	MF	OF	CO	MF	OF
	k_1, yr^{-1}					
Measured SOC						
1995	0.727	0.750	0.767	0.157	0.160	0.160
1999	0.373	0.384	0.393	0.244	0.249	0.249
2002	0.828	0.851	0.868	0.273	0.278	0.278
Mean	0.643	0.661	0.676	0.225	0.229	0.229
SOC by linear regression	0.567	0.577	0.608	0.255	0.258	0.259
Mean CO	0.411 b†					
Mean MF	0.418 b					
Mean OF	0.434 a					
Mean CT	0.584 a					
Mean NT	0.257 b					
	k_2					
Measured SOC						
1995	0.086	0.108	0.124	0.023	0.036	0.035
1999	0.035	0.044	0.051	0.047	0.053	0.053
2002	0.086	0.092	0.097	0.033	0.037	0.036
Mean	0.069	0.081	0.091	0.034	0.042	0.041
SOC by linear regression	0.047	0.051	0.062	0.026	0.029	0.029
Mean CO	0.036 b					
Mean MF	0.039 ab					
Mean OF	0.046 a					
Mean CT	0.053 a					
Mean NT	0.028 b					
	ANOVA, $p > F$					
	Tillage		N		Tillage × N	
k_1	<0.01		0.015		0.28	
k_2	<0.01		0.025		0.13	

† Means followed by different letters are significantly different by the LS Means test on the comparison of the single effects of tillage and fertilization treatments ($p < 0.05$).

ity of C inputs among years, spatial soil variability, and errors in the determination of SOC. The high variability of the adjusted coefficients by this approach can also be seen in the literature, where Bayer et al. (2006) and Vieira et al. (2009) estimated a k_1 of 0.146 and 0.096 yr^{-1} and a k_2 of 0.019 and 0.012 yr^{-1} for the soil under NT in the 13th and 19th yr, respectively, in the same long-term experiment.

The k_1 determined with the measured SOC stocks at 1995, 1999, and 2002 ranged from 0.157 to 0.278 yr^{-1} for the NT treatments and from 0.373 to 0.868 yr^{-1} for the CT treatments. In a review of the humification coefficient of C added by corn residue to the soil, Bolinder et al. (1999) reported k_1 coefficients ranging from 0.077 (shoots) to 0.30 (roots) yr^{-1}. When corn shoots and roots were evaluated together, k_1 ranged from 0.163 to 0.23 yr^{-1}. Allmaras et al. (2004) reported a humification coefficient of corn residues of 0.26 and 0.11 yr^{-1} for NT and CT, respectively. The k_1 determined with the SOC stocks estimated by linear regression averaged 0.257 and 0.584 yr^{-1} for NT and CT, respectively. The higher k_1 coefficients verified in our study could be related to the shallow sampling depth and better soil–residue contact, resulting in higher recovery of C inputs as SOC in the 0- to 5-cm soil layer.

In the same way, the k_2 coefficient showed high variability when determined by the measured SOC method. The k_2 values ranged from 0.035 to 0.124 yr^{-1} for CT and from 0.023 to 0.053 yr^{-1} for NT treatments when estimated with SOC measured in 1995, 1999, and 2002. This large variation is unlikely to happen among years in C-depleted soils (C_t < 75% of C_m) like the Hapludoll evaluated in our study, where average initial SOC stocks in 1992 (C_0) represented only 33% of C_m determined for the NT soil and 23% considering the SOC in the native prairie. The average k_2 coefficients determined with the SOC by linear regression method for NT and CT treatments (0.028 and 0.053 yr^{-1}, respectively) was similar and higher than the coefficients estimated by Huggins et al. (2007) for NT and CT (0.022 and 0.030 yr^{-1}, respectively) using isotopic techniques. In our study, the SOC mineralization rates (k_2) for CT increased about twofold in relation to NT. The higher k_2 for CT was promoted by soil disruption and lower aggregate stability (Mikha and Rice, 2004; Fabrizzi et al., 2009), limiting SOC accumulation compared with NT (Bayer et al., 2006; Campos et al., 2011).

Evaluation of Mathematical Models

We used the k_1 and k_2 coefficients estimated by the linear regression method to predict SOC according to the first-order kinetic, C saturation, and kinetic to saturation models from Eq. [3], [5], and [7], respectively (Fig. 2). The predicted SOC values were compared with the measured SOC by correlation analysis and lack-of-fit and RMSE tests (Table 4). Equations [3], [6], and [8] were used to estimate steady-state SOC according to the same models using the measured maximum SOC storage capacity (C_m) for Eq. [6] and [8]. The estimated steady-state SOC values were then compared with the measured maximum SOC storage capacity for the 0- to 5-cm soil layer (C_m = 28.0 Mg C ha^{-1}) determined in the NT OF treatment (Table 5). Considering as a basic assumption that both k_1 and k_2 coefficients are valid for continuous C input levels from the same source under the same soil management practice, we simulated SOC dynamics by the three models using the annual C inputs allocated to the 0- to 5-cm soil layer observed in the CO, MF and OF treatments between 1992 and 2002 for both CT and NT treatments.

All three models had significant correlations (r > 0.80) between measured and predicted SOC (Table 4). However, the RMSE of the C saturation model (32.5) was higher than the confidence interval (RMSE 95% = 13.5) and also higher than the RMSE verified with the first-order kinetic (6.6) and kinetic to saturation models (7.1). These results indicate that both models, first-order kinetic and kinetic to saturation , can predict SOC within the error of the SOC measurements. The C saturation model also failed the lack-of-fit test, indicating that the predicted SOC does not represent the measured SOC.

The errors in SOC predicted by the C saturation model are probably related to the basic assumptions of the model that the C humification rate would decrease as SOC increases (Stewart et al., 2007) but the SOC mineralization rate (k_2) would not change. The C saturation model assumes that the C humification rate ($1 - C_t/C_m$, as proposed) is dependent on both SOC at a given time (C_t) and the maximum SOC storage capacity (C_m). Considering the initial SOC (1992) measured in the long-term experiment used in this study and the C_m determined for the NT soil (28.0 Mg ha^{-1}), the initial k_1 coefficients estimated by the C saturation model averaged 0.674 yr^{-1} for CT and NT soils. Thus, the C saturation model overestimated the initial k_1 coefficients by 15 and 162% in relation to the k_1 coefficients estimated by Eq. [2] for the CT and NT soils, respectively. The C saturation model predicts that the k_1 coefficients will then decrease until the SOC achieves a new steady state, where k_1 ranges from 0.635 to 0.453 yr^{-1} for the CT soils and 0.267 to 0.140 yr^{-1} for the NT soils according to the fertilization treatments. The initial SOC observed in this long-term experiment averaged 32% of the C_m of the0- to 5-cm soil layer. These results would explain why the C saturation model overestimated the SOC of C-depleted soils (C_t < 75% of C_m) when SOC accumulation followed a linear pattern.

In contrast, the kinetic to saturation model proposes that k_2 coefficients would increase asymptotically as SOC approaches the maximum storage capacity of the soil according to soil disturbance (Fig. 3). Our assumption is corroborated by studies suggesting that as SOC approaches saturation levels, C stabilization mechanisms (i.e., aggregation) lose efficiency to protect the newly added C (Gulde et al., 2008; Stewart et al., 2007). Although overestimating the predicted SOC in relation to the measured SOC when the soil was at linear SOC accumulation rates (Fig. 2b), the predictions of the C saturation model for steady-state SOC were within the maximum SOC storage capacity observed for the 0- to 5-cm

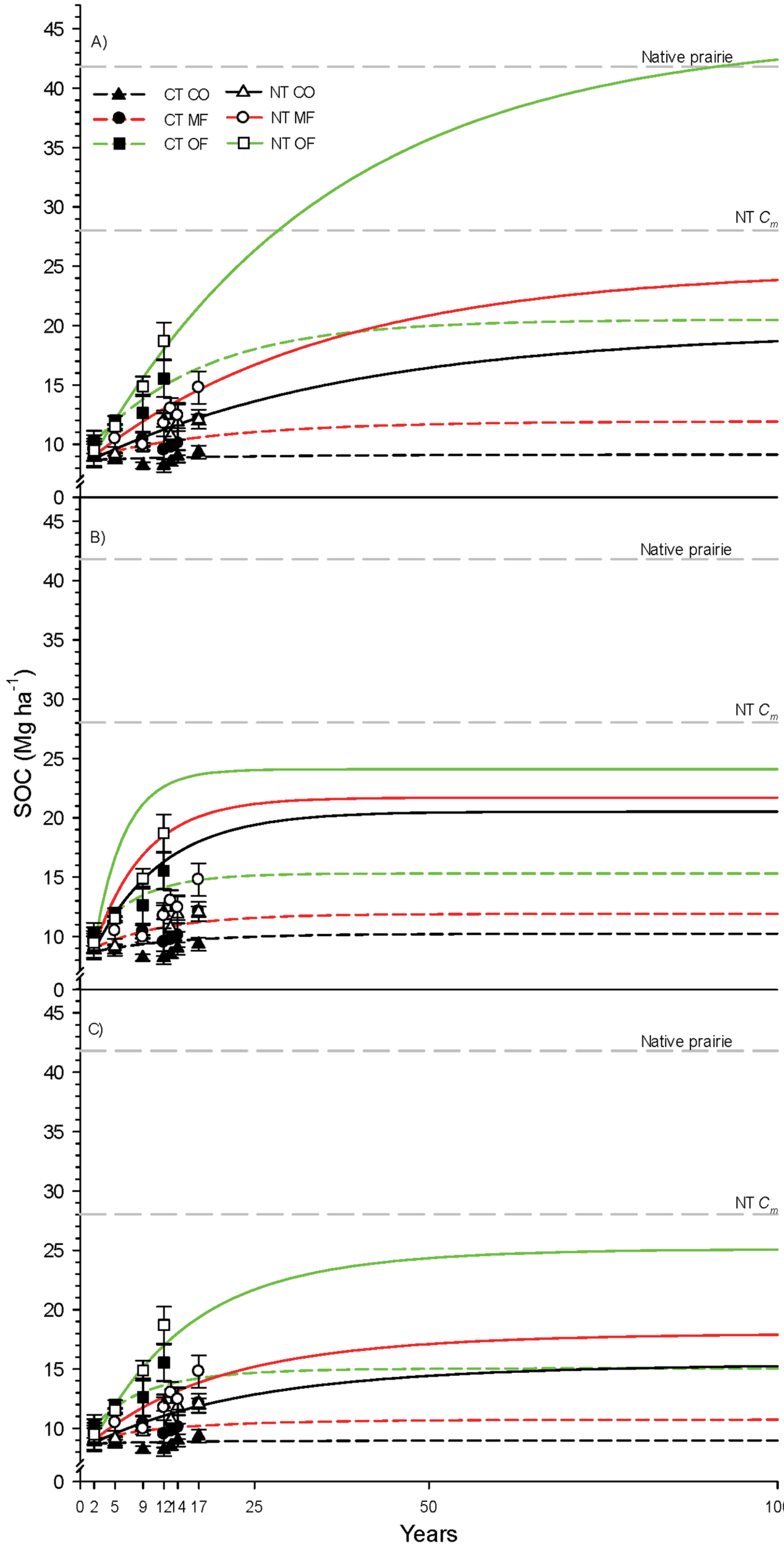

Fig. 2. Long-term simulation of soil organic C (SOC) in a Hapludoll from central Kansas as predicted by the (A) first-order kinetic, (B) C saturation, and (C) kinetic to saturation models according to soil tillage (chisel tillage [CT] or no-till [NT]) and fertilization practices (control with no N [CO], mineral fertilizer [MF], or organic fertilizer [OF]). The vertical bars are the mean's standard errors (*n* = 4) of the measured SOC. Reference SOC contents include SOC measured in a nearby native prairie and the maximum SOC storage capacity for CT and NT soils (C_m).

Table 4. Statistical analysis of the soil organic C measured and predicted by mathematical models.

Model	n†	r‡	LOFIT ($p > F$)§	RMSE¶	RMSE 95%
First-order kinetic	36	0.952	0.789	6.59	13.48
C saturation	36	0.800	<0.001	32.5	13.48
Kinetic to saturation	36	0.942	0.595	7.12	13.48

† Number of modeled values in all treatments (four observations for each modeled value).

‡ Correlation coefficient ($p < 0.05$).

§ p value (F test) of the lack-of-fit test; $p < 0.05$ indicates that the predicted SOC does not represent the measured SOC.

¶ Values of RMSE < RMSE 95% indicates that the predicted SOC errors are within the measured SOC errors.

Table 5. Steady-state soil organic C in a Hapludoll from central Kansas as predicted by three mathematical models according to soil tillage and fertilization practices.

Model	Tillage†	N source‡ CO	MF	OF
		Mg C ha^{-1} (%)		
First-order kinetic	CT	9.1 (32)§	11.9 (42)	20.5 (73)
	NT	19.5 (70)	24.7 (88)	44.5 (158)
C saturation	CT	10.2 (36)	11.9 (42)	15.3 (55)
	NT	20.5 (73)	21.7 (77)	24.1 (86)
Kinetic to saturation	CT	9.1 (32)	11.0 (39)	15.0 (54)
	NT	15.4 (55)	18.2 (65)	25.3 (93)

† NT, no-till; CT, chisel tillage.

‡ CO, control without N; MF, mineral fertilizer; OF, organic fertilizer.

§ Values in parenthesis are the percentage of the predicted steady-state SOC relative to the maximum SOC storage capacity (C_m = 28.0 Mg C ha^{-1}) determined for the NT OF treatment.

soil layer in the NT soil. Maximum steady-state SOC predicted for the CT OF and NT OF treatments were 15.3 and 24.1 Mg ha^{-1}, respectively (Table 5). These values correspond to 55 and 86% of C_m, respectively. Although the C saturation model was able to predict steady-state SOC according to the SOC storage capacity of the NT soils, we do not recommend this model for simulation of SOC, at least in C-depleted soils, based on the results of our study.

Long-term (100-yr) simulation of SOC according to the first-order kinetic model is presented in Fig. 2a. The SOC in the CT OF and NT OF treatments are expected to accumulate SOC at higher rates than the treatments where the only source of C is corn residues (CO and MF). However, long-term projections of SOC by the first-order kinetic model conflict with experimental evidence from the long-term experiment. The simulation indicates that after 30 yr, SOC in the NT OF treatment would overcome the C_m determined experimentally for the NT soil. Moreover, the model predicts that further SOC accumulation for the NT OF treatment will achieve the same SOC levels observed in the native prairie after 90 yr of continuous no-till and manure amendment. Steady-state SOC for the CT OF and NT OF treatments are predicted by the first-order kinetic model at 20.5 and 45.5 Mg ha^{-1} (Table 5). Thus, the steady-state SOC predicted for the NT OF treatment overestimated by 58% the C_m observed for the NT soil and by 9% the SOC levels of the native prairie. The overestimation of steady-state SOC by the first-order kinetic model was due to the basic assumption that both k_1 and k_2 coefficients should remain constant with time. Thus, the predicted steady state of SOC should respond linearly to increasing C inputs (Stewart et al., 2007), although several studies have reported asymptotic increases in SOC according to C input in C-rich soils (Gulde et al., 2008; Six et al., 2002; Stewart et al., 2007). Thus, the evidence found in our study supports the notion that although accurately predicting SOC dynamics in C-depleted soils, long-term projections of SOC by this first-order kinetic model should be avoided.

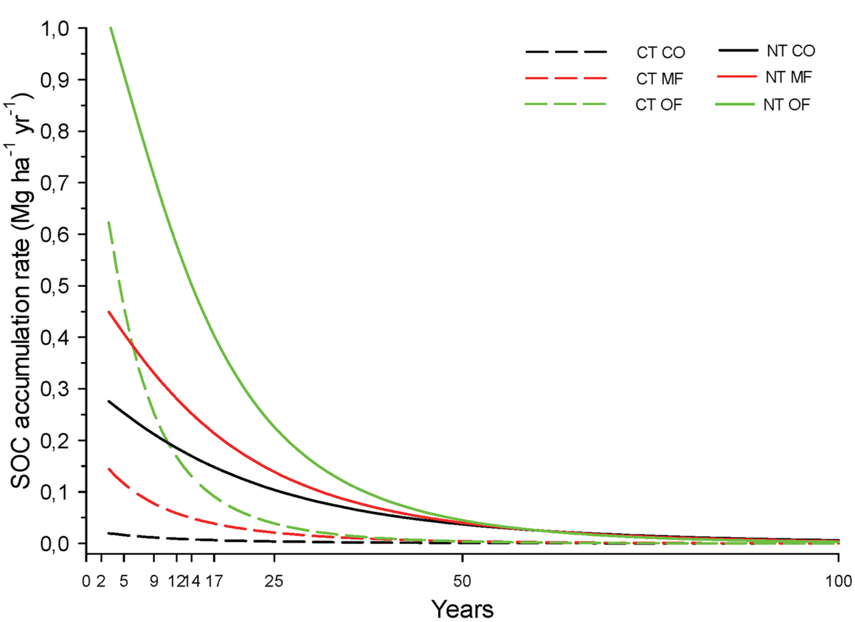

Fig. 3. Long-term simulation of soil organic C (SOC) accumulation rates in a Hapludoll from central Kansas as predicted by the kinetic to saturation model according to soil tillage (chisel tillage [CT] or no-till [NT]) and fertilization practices (control with no N [CO], mineral fertilizer [MF], or organic fertilizer [OF]).

Steady-state SOC as predicted by the kinetic to saturation model was within the maximum SOC storage capacity of the CT and NT soils, ranging from 9.1 to 15.0 Mg ha^{-1} (32–54% of C_m) for CT treatments and from 15.4 to 25.3 Mg ha^{-1} (55–93% of C_m) for NT treatments (Table 5). Thus, the modification proposed for the first-order kinetic model through the kinetic to saturation model was able to restrain the predicted SOC accumulation in corroboration with the experimental evidence from the long-term experiment. Soil organic C accumulation was limited by the increasing SOC mineralization coefficient as SOC approached the maximum SOC storage capacity (Fig. 3). The estimated k_2 coefficient would remain stable at 0.047 to 0.048 yr^{-1} in the CT CO treatment according to the 100-yr simulation but increase asymptotically from 0.050 to 0.057 yr^{-1}

(14%) for the CT MF treatment and from 0.062 to 0.084 yr^{-1} (35%) for the CT OF treatment during that period. For the NT treatments, the k_2 coefficient increased asymptotically from 0.026 to 0.033 yr^{-1} (27%) for the CO treatment, from 0.029 to 0.040 yr^{-1} (38%) for the MF treatment, and from 0.029 to 0.051 yr^{-1} (76%) for the OF treatment. The increasing k_2 would increase SOC turnover and ultimately limit SOC accumulation, as verified experimentally.

Soil organic C as predicted by the kinetic to saturation model for the CT CO treatment would remain stable during the simulation period at 9.1 Mg ha^{-1} (Fig. 2c). Long-term projections of SOC indicate that the MF and OF treatments would achieve 75% (West and Post, 2002) of the predicted SOC accumulation (difference between C_0 and predicted SOC at steady state) after 30 and 12 yr, respectively, of continuous C inputs under CT. After that, any further increase in SOC would be negligible as SOC accumulation rates decrease. Under NT, long-term simulation of SOC suggests that CO, MF, and OF treatments would achieve 75% of the predicted SOC accumulation after 37, 31, and 23 yr at 13.8, 15.9, and 21.2 Mg ha^{-1}, respectively. These results are within the estimates of 20 to 50 yr for the time span of NT soils to serve as a C sink (Lal, 2004; West and Post, 2002). However, we can predict that after 75 yr, the SOC of the NT CO treatment would be comparable to the SOC of the CT OF treatment. The SOC accumulation in the topsoil layer of the NT CO treatment would be sustained by the redistribution of N within the soil profile (Knops and Tilman, 2000) through organic N mineralization at deeper soil layers, N uptake and accumulation in surface roots and stover biomass, and deposition at the soil surface as crop residues.

The SOC accumulation rates decrease with the time of soil tillage and fertilizer management adoption in all treatments, following the pattern of the proposed kinetic to saturation model (Fig. 4). The SOC accumulation rates of the CT MF and CT OF treatments are predicted to range from 0.14 to 0.01 and 0.62 to 0.16 Mg C ha^{-1} yr^{-1}, respectively, when the soil would achieve 75% of the predicted SOC accumulation for these treatments. For the NT treatments, SOC accumulation rates predicted for the CO, MF, and OF treatments would range from 0.27 to 0.06 , 0.45 to 0.10 , and 1.00 to 0.26 Mg C ha^{-1} yr^{-1}, respectively, until the soil achieved 75% of predicted SOC accumulation for the same treatments. Thus, the NT soil under mineral fertilization was predicted to show significant SOC accumulation rates (>0.10 Mg C ha^{-1} yr^{-1}) for up to 31 yr. These predictions are within the SOC accumulation rates observed in the long-term experiment evaluated in this study.

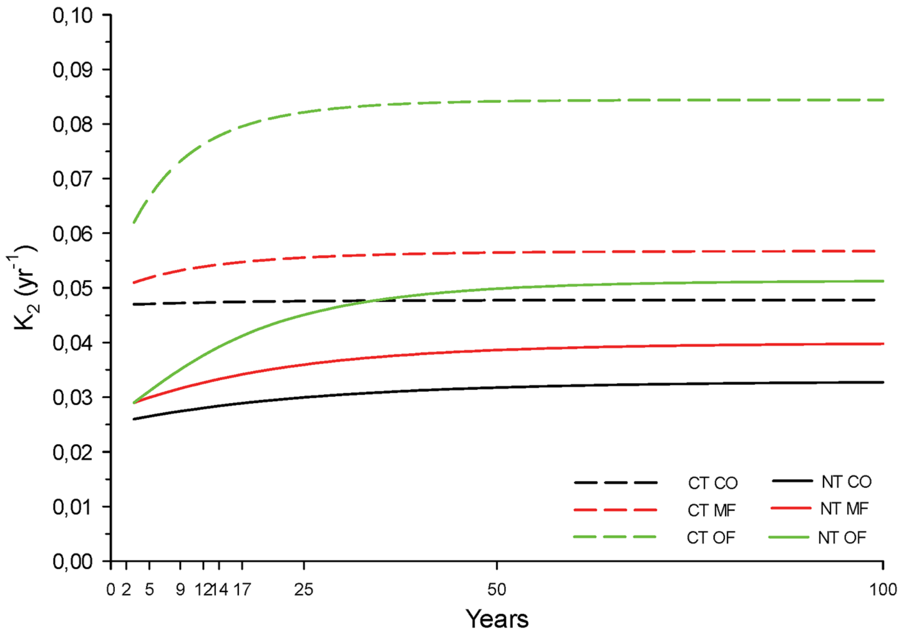

Fig. 4. Long-term simulation of the soil organic C mineralization coefficient (k_2) in a Hapludoll from central Kansas as predicted by the kinetic to saturation model according to soil tillage (chisel tillage [CT] or no-till [NT]) and fertilization practices (control with no N [CO], mineral fertilizer [MF], or organic fertilizer [OF]).

CONCLUSIONS

We evaluated three mathematical models simulating SOC dynamics and steady-state SOC by using a long-term experiment with frequent soil samplings for which the maximum SOC storage capacity was determined for NT and CT soils. The first-order kinetic model had good agreement with observations in C-depleted soils but failed to predict the steady-state SOC. The C saturation model accurately accounted for the SOC storage capacity of the CT and NT soils but overestimated SOC in C-depleted soils. The kinetic to saturation model showed better agreement with experimental data by proposing that the SOC mineralization rate would increase asymptotically, limiting the SOC storage capacity. This model should be used for long-term simulation of SOC dynamics in either C-depleted soils or those close to saturation .

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