

The Role of Soil Characteristics on Temperature Sensitivity of Soil Organic Matter

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The uncertainty associated with how projected climate change will affect global C cycling could have a large impact on predictions of soil C stocks. The purpose of our study was to determine how various soil decomposition and chemistry characteristics relate to soil organic matter (SOM) temperature sensitivity. We accomplished this objective using long-term soil incubations at three temperatures (15, 25, and 35°C) and pyrolysis molecular beam mass spectrometry (py-MBMS) on 12 soils from 6 sites along a mean annual temperature (MAT) gradient (2–25.6°C). The Q_{10} values calculated from the CO_2 respired during a long-term incubation using the Q_{10-q} method showed decomposition of the more resistant fraction to be more temperature sensitive with a Q_{10-q} of 1.95 ± 0.08 for the labile fraction and a Q_{10-q} of 3.33 ± 0.04 for the more resistant fraction. We compared the fit of soil respiration data using a two-pool model (active and slow) with first-order kinetics with a three-pool model and found that the two and three-pool models statistically fit the data equally well. The three-pool model changed the size and rate constant for the more resistant pool. The size of the active pool in these soils, calculated using the two-pool model, increased with incubation temperature and ranged from 0.1 to 14.0% of initial soil organic C. Sites with an intermediate MAT and lowest C/N ratio had the largest active pool. Pyrolysis molecular beam mass spectrometry showed declines in carbohydrates with conversion from grassland to wheat cultivation and a greater amount of protected carbohydrates in allophanic soils which may have led to differences found between the total amount of CO_2 respired, the size of the active pool, and the Q_{10-q} values of the soils.

Abbreviations: MAT, mean annual temperature; PCA, principle component analysis; PLS, partial least square; py-MBMS, pyrolysis molecular beam mass spectrometry; SOC, soil organic C; SOM, soil organic matter.

Temperature is an important factor controlling SOM turnover and understanding how temperature affects SOM decomposition will allow us to better predict how global climate change will affect SOM stocks. Understanding the temperature sensitivity of SOM decomposition is challenging because SOM is composed of many different organic C compounds, with differing inherent kinetic properties (Davidson and Janssens, 2006). To simplify the process of modeling SOM decomposition, this range of compounds is usually classified into a small number of discrete, kinetically defined pools with some portion of SOM being easily decomposable and the rest comprising one or more other pools decomposing more slowly.

In most decomposition models, temperature effects are modeled as a decomposition rate multiplier for fixed SOM pools (Lloyd and Taylor, 1994; Del Grosso et al., 2005), but some recent studies have hypothesized that temperature may actually alter the amount of substrate that would be considered easily decomposable (Zogg et al., 1997; Zak et al., 1999; Dalias et al., 2003; Rasmussen et al., 2006). The most broadly used terrestrial C models typically have a fixed Q_{10} of 1.5 to 2.0 or an Arrhenius-type function with the same respiration-temperature relationship to each of the different SOM pools (Melillo et al., 1995; Burke et al., 2003; Friedlingstein et al., 2006). Many recent studies have found that different SOM pools have different temperature responses, although consensus on their apparent

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Table 1. Characteristics of the six locations, sampled in the spring of 2005, used in our long-term incubation.

Site	GPS location	MAT/MAP†	Soil taxonomy	Treatment	% Clay	Vegetation	Year converted to present land use	Citation
Indian Head, SK ARGCN	50.533 N -103.517 W	2°C/421 mm	Udic Boroll	Native grassland	50	Grassland containing predominantly cool season grasses Spring-wheat-based rotations	1957	Campbell et al. 1997
Mandan, ND NGPRL	46.767 N -100.917 W	5°C/402 mm	Typic Argiboroll	Cultivated	61	Warm mixed grass prairie	1984	Black & Tanaka 1997
Akron, CO CGPRS	40.150 N -103.150 W	9.2°C/420 mm	Aridic Paleustoll	Cultivated	33	Continuous spring wheat	1957	Halvorson et al. 1997
Vernon, TX Waggoner Ranch	33.939 N -99.413 W	17°C/665 mm	Typic Paleustoll	Native grassland	31	Grassland with a mix of C ₄ and C ₃ grasses	~1980	Martin et al. 2003
Alajuela, Costa Rica Alajuela Research Station	N/A	20°C/ N/A	Hydric Melanudand	Native forest	9	Tropical forest with predominantly C ₃ species C ₄ warm season grasses	1979	N/A‡
Rodônia, Brazil Nova Vida Ranch	10.168 S -62.824 W	25.6°C/2200 mm	Paleudult & Kanduidult	Native forest	30	Open humid tropical forest with predominantly C ₃ species C ₄ warm season grasses	1972	Cerri et al. 2004

†MAT, mean annual temperature; MAP, mean annual precipitation.

‡N/A, not available.

temperature sensitivities has not yet been reached (Davidson and Janssens, 2006). Some have found that the more labile SOM is more temperature sensitive (Liski et al., 1999; Giardina and Ryan, 2000), while others have found that the less labile SOM is more temperature sensitive (Bosatta and Ågren, 1999; Bol et al., 2003; Knorr et al., 2005; Fierer et al., 2005). Still other studies have found results indicating different SOM fractions have the same temperature sensitivity (Fang et al., 2005; Conen et al., 2006).

Not only can temperature have variable effects on the organic matter within a soil, but also between soils with different MAT. Fang et al. (2005) predicted the greatest loss of SOM will be in soils where the present MAT < 4°C and that SOM loss will decrease with increasing MAT. Trumbore et al. (1996) predicted that a 0.5°C rise in temperature could cause a release of approximately 1.4 Pg of C from forest soils, with much of this response occurring in the tropics. Temperature may also have varying effects on the soil depending on the type of organic matter in the soil. Soils under long-term cultivation would likely have less labile C compared with native soils with minimal disturbance.

Apparent temperature responses can vary substantially when different methods are used to assess temperature sensitivity and similar methods have found varying results between different soils (e.g., Conen et al., 2006 and Vanhala et al., 2007). Even after accounting for other factors ameliorating temperature controls on decomposition, such as substrate availability, soil moisture, and soil texture, there is significant variation in decomposition responses to differences in temperature (e.g., Fissore et al., 2009; Gillabel et al., 2010). These inconsistencies make it difficult to make any broad generalizations about the temperature sensitivity of SOM with varying quality.

The objective of this study was to explain differences in the temperature sensitivities of SOM decomposition between different soils. We hypothesize that the more resistant SOM is more temperature sensitive than labile SOM because it is comprised of more complex molecules that have slower decomposition rates and presumed higher activation energies. Higher activation energy has been demonstrated to be related to greater temperature sensitivity (Bosatta and Ågren 1999; Mikan et al., 2002). We expanded on previous incubation studies, both in terms of incubation duration and number of soils examined- and employed curve fitting and molecular beam mass spectrometry to characterize the SOM in the soils. Soils from paired sites with different long-term land uses along a MAT gradient were used to compare similar soils with differing amounts and types of SOM. By utilizing this multi-approach method we sought a better understanding of the apparent temperature sensitivity of SOM.

MATERIALS AND METHODS

Sample Sites

Surface soil samples were collected from six sites along a MAT gradient (2–25.6°C). Each of the temperate sites had a native grassland and cultivated land use (Indian Head, SK; Mandan, ND; Akron, CO; and Waggoner Ranch, TX) and the tropical sites had a native forest and pasture land use (Alajuela, Costa Rica, and Nova Vida

Ranch, Brazil; Table 1). Samples were collected from three locations separated by several meters each (field replicate $n = 3$) within each land use. Surface litter and aboveground vegetation were cleared away before sampling. Small pits were dug to a depth of 20 cm, and samples were collected from 0 to 20 cm. Soils were packaged and transported to the laboratory, where rocks, surface litter, and root materials were removed. Our soil incubation is an analytical technique, not used to understand rates of respiration in the field. To maximize the likelihood of observed meaningful respiration, the soil was homogenized by gently breaking large soil clods by hand and passing the soil through a 2-mm sieve. Soil samples were air-dried and stored at room temperature until incubations began. Soil organic C (SOC) and total N concentrations were determined with a LECO CHN-1000 autoanalyzer (LECO Corp., St. Joseph, MI).

Laboratory Incubation

Four laboratory replicates from composite field samples from each site and treatment combination were incubated at 15, 25, and 35°C for 588 d. For each sample, 80 g of soil were wetted up to 60% water filled pore space to optimize microbial activity (Linn and Doran, 1984). Gravimetric soil moisture was periodically checked throughout the incubation and water was added when water loss was >5% of initial water added. Samples were placed in sealed canning jars fitted with septa, along with scintillation vials containing 20 mL of water to maintain humidity. Incubation starting days were staggered by replicate and each replicate of a soil was measured on a different day to take into account daily measurement variability. Soils were pre-incubated for 3 d at 25°C and then 4 d at the respective incubation temperature before measurements to allow the soil to equilibrate after wetting up (Paul et al., 2001). Headspace gas samples were analyzed for CO₂ concentration using a Li-Cor LI-6252 infra red gas analyzer (IRGA) (LI-COR Biosciences, Lincoln, NE). Jars were flushed with compressed tank air before CO₂ concentrations reached 5% (v/v) to prevent CO₂ concentration from inhibiting microbial activity. Through the majority of the incubation periods CO₂ concentrations were well below the 5% level and O₂ concentrations were well above 10%(v/v), which is thought to be the point where microbial activity may be limited (Kandeler, 2007). The CO₂ measurements were taken daily during the first 2 wk of the incubation, weekly for the next 2 wk, and then every 4 wk thereafter, generating a total of 36 sampling times over the course of 588 d. Statistical comparisons of cumulative respiration were done by treating the six different sites as random variable replicates (PROC MIXED, SAS Institute, Cary NC).

Temperature Sensitivity

We wanted to compare the temperature sensitivity of labile and more resistant SOM from our soil incubation to test our hypothesis that the more resistant SOM is more temperature sensitive than labile SOM because it is comprised of more complex molecules that have slower decomposition rates and higher activation energies. Temperature sensitivity of SOM decomposition was determined using the Q_{10-q} method described by Conant et al. (2008a) utilizing the CO₂ respired from our long-term incubations. The method involves determining the amount of time needed for a given amount of C to be respired at

a given temperature. The time required to respire a fixed amount of C at two temperatures is then used to calculate a Q₁₀ value. There are two assumptions associated with this method (Conant et al., 2008a). The first is that changes in decomposition rates during the incubation are due to changes in available and easily decomposable substrate. The second is that the effect temperature has on the sequence in which SOM compounds are decomposed is small relative to the effect of temperature on decomposition rates. While soil microbial biomass has been found to decline over time in long-term incubations (Follett et al., 2007), this decline in biomass has not been found to limit the microorganism's capacity to decompose organic matter in long-term incubations (Follett et al., 2007; Steinweg et al., 2008). Because of this we believe that our first assumption that changes in decomposition rates are due to changes in easily decomposable substrate is reasonable.

The Q_{10-q} values for the more labile portion of the SOM were determined by dividing the time taken to respire the initial 0.5% (w/w) of soil C at 25°C by the time taken at 35°C. For the more resistant portion, the time taken to respire the last 0.5% of soil C respired at 25°C temperature (e.g., Colorado Native 12.5–13.0% soil C respired) was divided by the time taken to respire the same portion of soil C at 35°C. We were interested in examining the responses of rates of decomposition of a fixed amount of soil C. The first 0.5% and last 0.5% of SOM respired are operational definitions of labile SOM and more resistant SOM and are subsequently referred to as the labile and more resistant fraction. Since incubation starting days were staggered by replicate and each replicate of a soil was measured on a different day, the time it took to respire a given amount of soil C for the two temperatures was paired by replicate. The 15°C respiration data were not used due to the limited amount of C respired by the Costa Rica pasture soil. Statistical comparisons of Q_{10-q} values were done by treating the six different sites as random variable replicates (PROC MIXED, SAS Institute, Cary NC). Comparisons between Q_{10-q} values and the other soil characteristics were performed with the average from each soil.

Curve Fitting

We used CO₂ respiration results from the 15, 25, and 35°C incubations for curve fitting. Curve fitting was utilized as a method to describe the size and kinetics of the SOM as one means of characterizing the SOM at our sites. The respiration results from the four laboratory replicates of each site–treatment–temperature combination were averaged, and mean respiration rates were used to determine pool size and decomposition rate constants by curve fitting. Pool size and decomposition rate constants were determined using a two-pool model where the two pools, active (C_a) and slow pools (C_s), sum to the total soil C (C_{soil}):

$$C_{soil} = C_a + C_s \quad [1]$$

We used a two-pool first-order equation (Andren and Paustian, 1987):

$$C_{cum}(t) = C_a(1 - e^{-k_a t}) + C_s(1 - e^{-k_s t}) \quad [2]$$

where C_{cum}(*t*) is the cumulative soil respiration at time *t* (μg C g⁻¹ soil), C_a is the size of the active fraction (μg C g⁻¹ soil), and C_s is the

size of the slow fraction ($\mu\text{g C g}^{-1}$ soil). The parameters k_a and k_s are the decomposition rate constants (d^{-1}) for the active and slow pools, respectively. We used data from rate curves rather than cumulative respiration because this minimized error accumulation through time (Hess and Schmidt, 1995). We used the following rate form of Eq. [2] from Paul et al. (2001) to determine parameter estimates:

$$\frac{\Delta C_{cum}}{\Delta t} = C_a * k_a (e^{-k_a t}) + C_s * k_s (e^{-k_s t}) \quad [3]$$

where $\Delta C_{cum}/\Delta t$ is in units of $\mu\text{g C g}^{-1}$ soil d^{-1} . The size of the active and slow pools adds up to the total amount of C in the soil (C_{soil}) (Eq. [1]); causing C_s to be determined by the difference of the total soil C and the active pool C. This method of curve fitting also implies that changes in respiration rate over the course of an incubation are due to changes in SOM lability.

A three-pool model with first-order kinetics has been found to effectively describe SOC dynamics (Paustian et al., 1992); because of this result we also fit our respiration rate curves to a three-pool first-order equation. We used the same rate equation as the two-pool model (Eq. [3]) and included a resistant pool that was estimated to be 50% of the total soil C. The decomposition rate for the resistant pool was estimated using a field mean residence time of 500 yr and a Q_{10} adjustment of 2 for the different incubation temperatures. This calculation was only done for comparative purposes. Parameter estimates and subsequent temperature sensitivity calculations were derived from the two-pool equation.

Best fit parameters (C_a , k_a , and k_s) for the two-pool model were estimated using nonlinear regression of the CO_2 evolved with time in SAS v9.2 PROC NLIN with the Gauss method (SAS Institute, Cary NC). The only restriction imposed on parameters is that the values had to be greater than zero. There were three instances (North Dakota native grassland 15°C, Colorado native grassland 15°C, and Colorado cultivated 15°C) where slow pool decomposition rates were not positive and these three soils were not used in subsequent analyses. The errors associated with model parameters are standard error of the model determined in SAS NLIN. Statistical comparisons of active pool size were done by treating the six different sites as random variable replicates (PROC MIXED, SAS Institute, Cary NC).

Pyrolysis-Molecular Beam Mass Spectrometry

Chemical composition of SOM was characterized using py-MBMS (Magrini et al., 2002; Hoover et al., 2002). Two subsamples (~0.1 g) from each field replicate sample were weighed in quartz boats and pyrolyzed in a reactor consisting of a quartz tube (2.5-cm i.d.) with He flowing through at 5 L min^{-1} heated and maintained at 500°C. The molecular beam system consisted of an ExtrelTM Model TQMS C50 mass spectrometer for both pyrolysis and combustion vapor analysis. Mass spectral data from m/z 20 to 500 were acquired on a Teknivent Vector 2TM data acquisition system using 22 eV electron impact ionization and programmed storage in a personal computer. Repetitive scans (typically one 480 amu scan s^{-1}) were recorded during the evolution of a pyrolysis wave from each soil sample.

Overall, 36 samples were collected from the field (6 sites \times 3 field replicates \times 2 land uses). Two aliquots from each of these 36 were analyzed by py-MBMS, resulting in 72 total spectra. Two spectra from

the analyses of samples from Saskatchewan and one from North Dakota were excluded from further analysis due to data quality issues (reduced signal), leaving a total of 69 spectra.

Signal intensities from individual spectra (m/z 20–500) were standardized to 100% total ion intensity (TII, the sum of the intensity for each m/z), and reduced data sets (m/z 57–500) were used in the multivariate analyses to omit the small mass units typical of water, CO_2 , and other volatiles. We used principal component analysis (PCA) to group samples by similarity with samples having similar chemical compositions being tightly grouped in a PCA score plot, while samples with dissimilar and heterogeneous compositions were more scattered (Schulten et al., 1988). Eight principal components and full cross validation were used to build the PCA model to determine whether SOM composition could be grouped by site or land use. Partial least squares (PLS) regression analysis was used to predict the dependent variables (i.e., the model estimates for respiration rates during incubation at 15, 25, and 35°C) from our set of independent variables (i.e., the signal intensities from the py-MBMS spectra). Two PLS regressions were performed: one for the respiration rates early in the incubation when the respiration is mostly from the active pool (Day 5 of the incubation), and one for respiration rates later in the incubation when the respiration is mostly from the slow pool (Day 225 of the incubation). Full cross-validation and Martens' uncertainty test were used to determine statistically significant correlations between py-MBMS spectral data and the biological properties of the samples. Partial least squares analyses were performed iteratively to determine which independent variables were significant based on Martens' uncertainty test, and then subsequent PLS analyses were performed using only the significant variables. This process was repeated until all independent variables were found to be significant. All multivariate analyses were performed using the Unscrambler v.8.0 software package (CAMO Process AS, Oslo, Norway).

RESULTS

Site Comparisons

Soil organic C (SOC) concentrations (0–20 cm) ranged from 6.9 to 200 g kg^{-1} among the six sites (Table 2). The Costa Rican soil is allophanic and consequently had much higher SOC concentrations than the other five sites. Soil organic C and total N concentrations differed between land use within each site (except for Texas), with SOC and total N concentrations decreasing after land-use conversion at Saskatchewan, North Dakota, Colorado, and Costa Rica.

Due to the large differences in SOC content among soils, the total amount of C respired was standardized for the initial amount of SOC. When sites were treated as replicates and the amount of cumulative CO_2 was pooled, after 588 d of incubation, the cumulative amount of SOC respired was statistically greater under warmer incubation temperatures ($p < 0.001$). There was not a significant land use difference in the cumulative amount of CO_2 respired across all 12 soils.

Table 2. Soil characteristics, cumulative respiration after 588 d of incubation, and Q_{10-q} for the six sites and land-use types examined in the cross site comparison. (mean \pm 1 standard deviation†, $n = 4$)

Site‡	Land use§	SOC g kg ⁻¹	Total N g kg ⁻¹	C/N	Cumulative respiration (% total soil C)			Q_{10-q} ¶	
					15°C	25°C	35°C	Labile#	More resistant††
SK	NG	37.1	3.58	10.4	6.52 \pm 0.37	10.40 \pm 0.60	14.37 \pm 0.23	1.6 \pm 0.0	2.5 \pm 0.2
SK	C	22.9	2.04	11.2	4.33 \pm 0.14	7.73 \pm 0.53	13.05 \pm 0.50	2.0 \pm 0.1	3.3 \pm 1.3
ND	NG	32.4	2.93	11.0	3.93 \pm 0.30	8.14 \pm 0.68	15.03 \pm 2.90	1.7 \pm 0.1	2.7 \pm 0.2
ND	C	28.0	2.40	11.7	5.17 \pm 0.16	9.17 \pm 0.44	11.32 \pm 1.06	1.5 \pm 0.1	1.3 \pm 0.2
CO	NG	11.6	1.35	8.6	9.64 \pm 0.65	17.93 \pm 0.53	30.20 \pm 2.39	1.5 \pm 0.1	2.8 \pm 0.3
CO	C	6.9	1.00	6.9	7.45 \pm 0.25	13.09 \pm 1.58	24.04 \pm 2.58	2.2 \pm 0.2	4.6 \pm 1.4
TX	NG	11.2	1.29	8.7	9.60 \pm 0.46	14.96 \pm 1.10	24.36 \pm 0.43	2.0 \pm 0.2	3.4 \pm 0.5
TX	C	10.2	1.25	8.1	8.62 \pm 0.20	15.61 \pm 0.68	23.22 \pm 1.60	1.6 \pm 0.1	3.1 \pm 0.2
CR	NF	200.2	16.60	12.1	2.04 \pm 0.10	4.21 \pm 0.27	9.70 \pm 0.53	1.9 \pm 0.2	4.1 \pm 0.4
CR	P	141.6	10.45	13.5	1.29 \pm 0.05	2.68 \pm 0.07	5.65 \pm 0.17	2.9 \pm 0.3	6.5 \pm 0.4
BR	NF	10.6	1.09	9.7	5.72 \pm 0.54	11.81 \pm 0.74	19.50 \pm 2.28	2.2 \pm 0.3	1.4 \pm 0.3
BR	P	14.1	1.33	10.6	6.76 \pm 0.36	10.65 \pm 0.45	21.60 \pm 0.97	2.4 \pm 0.4	4.2 \pm 0.6

† Standard deviation reported in table is from laboratory replicate.

‡ SK, Saskatchewan; ND, North Dakota; CO, Colorado; TX, Texas; CR, Costa Rica; BR, Brazil.

§ NG, native grassland; NF, native forest; C, cultivated; P, pasture.

¶ Q_{10-q} was calculated using respiration from the 35/25°C cumulative respiration.

Labile was considered the first 0.5% SOC respired in the incubation.

††More resistant was considered the last 0.5% SOC respired in the incubation.

Temperature Sensitivity

Q_{10-q} values for the labile fraction varied from 1.5 to 2.9 and Q_{10-q} values for the more resistant fraction varied from 1.3 to 6.5. In all but two instances the labile fraction had a smaller Q_{10-q} value than the more resistant fraction (Table 2) with North Dakota cultivated and Brazil native forest being the two exceptions. For the North Dakota cultivated and the Brazil native forest the Q_{10-q} values for the more resistant fraction were much lower than the values for the more resistant fraction of the other soils. The Costa Rica pasture site had the highest Q_{10-q} values overall (Table 2). When sites were treated as replicates and Q_{10-q} values were pooled there was a significant difference in Q_{10-q} values for the labile and more resistant fractions ($p = 0.0026$) with the Q_{10-q} for the labile fraction being 1.95 ± 0.08 and the more resistant fraction being 3.33 ± 0.04 . There was no significant land-use treatment effect ($p = 0.127$) or land use by SOM fraction effect ($p = 0.338$). There was a slight positive trend with MAT and Q_{10-q} values for the labile fraction ($r^2 = 0.336$, $p = 0.048$), but no correlation between MAT and Q_{10-q} values for the more resistant fraction ($r^2 = 0.092$, $p = 0.337$) for the sites. There was no trend with the soil C/N ratio and the Q_{10-q} values for the labile ($r^2 = 0.112$, $p = 0.288$) or more resistant fraction ($r^2 = 0.056$, $p = 0.457$).

Curve Fitting

Respiration rates declined over time for all soils at all three incubation temperatures with the two tropical sites (Costa Rica and Brazil) having a much more rapid decline in respiration rates early in the incubation compared with the other four sites (Fig. 1). Respiration rates leveled off for all soils by the end of the incubation, but differences in the respiration rates among the

three incubation temperatures were still apparent at the end of the incubation (Fig. 1).

The two-pool equation fit the respiration data fairly well; an exception to this was the Costa Rica native forest soil at 35°C where the two-pool equation overestimated the respiration rate later in the incubation (Fig. 1). We also fit the data to a three-pool first-order equation. In the three-pool model, the resistant pool was fixed at half of the total SOM, causing the slow pool to be approximately half the size of the slow pool in the two-pool model. Although estimates of the active pool size and decomposition rate were not statistically different between the two-pool and three-pool equation, the three-pool equation consistently had a smaller active pool compared with the two-pool equation by an average of 5%. The three-pool equation consistently had a higher decomposition rate of the active pool compared with the two-pool equation by an average of 6% (Table 3). We used the simpler two-pool model in all subsequent analysis, realizing that the resistant pool contributes only slightly to the measured respiration because of its high mean residence time.

The native grassland Colorado soil had the largest active pool, comprising between 9.4 and 14.0% of total SOC at the different temperatures. The Costa Rica native forest soil had the smallest active pool, comprising between 0.1 and 1.0% of total SOC (Table 4). When sites were treated as replicates and active pool sizes were pooled, in the native grassland/cultivated sites (Saskatchewan, North Dakota, Colorado, and Texas) the native treatment had a significantly larger active pool than the cultivated treatment ($p = 0.003$). The size of the active pool at 25°C was negatively correlated with the C/N ratio of the soil ($r^2 = 0.34$, $p = 0.045$ for all soils; Fig. 2). The relationship between the active pool and C/N was improved when the Colorado cultivated and

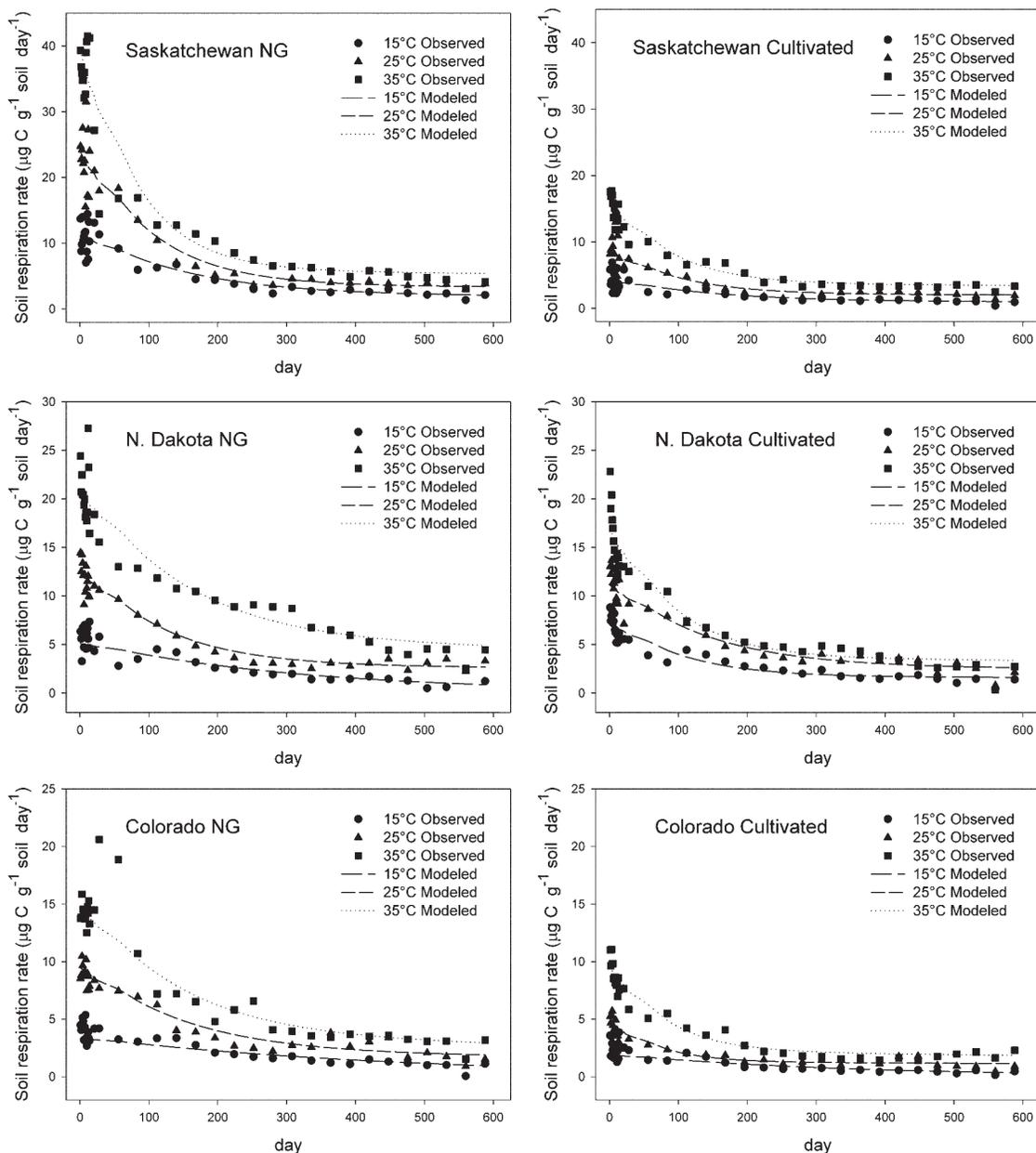


Fig. 1. Decomposition rates over time at 15, 25, and 35°C for the twelve soils. NG is native grassland and NF is native forest. Values represent means ($n = 4$). Figure 1 is continued on next page.

Brazil native forest soils were removed ($r^2 = 0.84, p = 0.0002$), which appeared to behave differently than the other soils. There was also a slight correlation with the size of the active pool at 25°C and the Q_{10-q} value calculated for the labile fraction ($r^2 = 0.35, p = 0.044$) with soils having smaller active pools also having higher Q_{10-q} values for the labile fraction, but this correlation seemed to be strongly driven by the Costa Rica pasture soil (data not shown).

Some studies have hypothesized that temperature may alter the amount of substrate that would be considered easily decomposable (Zogg et al., 1997; Zak et al., 1999; Dalias et al., 2003; Rasmussen et al., 2006). Because of this, no restrictions were placed on the size of the pools and pool sizes varied with temperature if it provided the best fit of the data. In all but four instances (North Dakota cultivated 35°C, Texas cultivated 25°C,

Brazil native forest 25°C, Costa Rica pasture 25°C) there was an increase in active pool size with temperature. For the four soils where the active pool size declined with increasing temperature, it was likely due to high initial respiration rates that quickly declined over time. The decomposition rates of the slow pool increased with increasing incubation temperature for all of the soils and the decomposition rate for the active pool increased with increasing temperature in only half the instances (Table 4).

Soil Organic Matter Composition

A large proportion of the mass spectra of each sample could be classified using previously identified marker signals associated with several classes of compounds in the literature (Sorge et al., 1993; Schulten, 1996), leaving only $6.7 \pm 2.5\%$ of TII unidentified (Table 5). The volatile fraction (m/z 20–56)

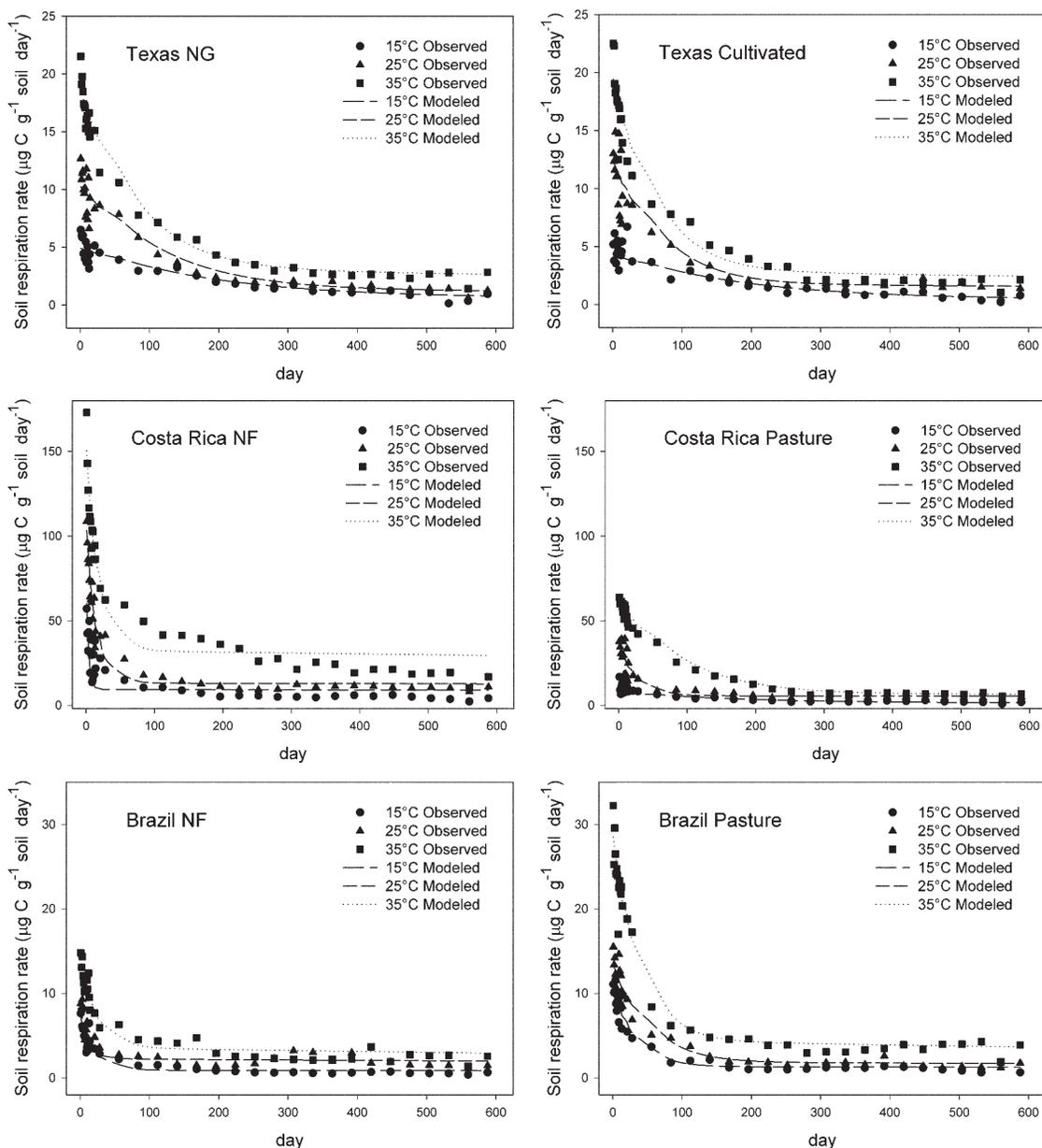


Fig. 1. cont. Decomposition rates over time at 15, 25, and 35°C for the twelve soils. NG is native grassland and NF is native forest. Values represent means ($n = 4$).

represented $50.9 \pm 4.5\%$ of the total signal intensity, dominated by m/z 44 (CO_2). The largest classes of identified compounds were various N-containing compounds ($11.9 \pm 1.8\%$ of TII) and carbohydrates ($10.6 \pm 2.6\%$ of TII). The various N-containing compounds are identified by Schulten (1996) as heterocyclic N-containing compounds, though it is possible that the heterocyclic N is formed by the pyrolysis process (Sharma et al.,

2003). Peptides, phenols and lignin monomers, lipids, and alkyl aromatics were also significant contributors (in decreasing order), while sterols and lignin dimers each contributed $< 1\%$ of TII (Table 5). The conversion of native grasslands to agriculture caused a decline in carbohydrates in the temperate soils. There was essentially no change in the proportion of carbohydrates in Costa Rica with conversion from native forest to pasture. There

Table 3. Parameter estimates averaged across all soils and temperatures and fit estimates for the two-pool and three-pool models for the six sites and land use types examined in the cross site comparison.

Model	Active pool	Active pool decomp. Rate	Slow pool	Slow pool decomp. rate	Resistant pool	Resistant pool decomp. rate	RMSE†	$R_a^{2\ddagger}$
	mg C g ⁻¹ soil	d ⁻¹	mg C g ⁻¹ soil	d ⁻¹	mg C g ⁻¹ soil	d ⁻¹		
2 pool	1.06	2.85E-02	42.84	1.36E-04	.	.	2.07	0.83
3 pool	1.00	3.03E-02	20.95	3.10E-04	21.95	1.76E-05	2.05	0.83

† RMSE, Root Mean Square Error.

‡ R_a^2 , adjusted r-square.

Table 4. Size of the active pool and active and slow pool decomposition rates at 15, 25, and 35°C for the two-pool model for the six sites and land-use types examined in the cross site comparison. Error is model standard error.

Site †	Land use‡	Inc. temp	Active pool	Active pool decomp. rate	Slow pool decomp. rate
		°C	% total soil C	d ⁻¹	d ⁻¹
SK	NG	15	3.7 ± 1.3	6.7E-03 ± 1.97E-03	5.6E-05 ± 2.24E-05
		25	5.3 ± 1.4	10.3E-03 ± 2.56E-03	10.1E-05 ± 3.22E-05
		35	6.7 ± 2.1	13.5E-03 ± 4.15E-03	17.2E-05 ± 5.83E-05
SK	C	15	2.1 ± 1.5	6.8E-03 ± 4.03E-03	4.3E-05 ± 2.52E-05
		25	2.6 ± 1.2	10.8E-03 ± 4.73E-03	9.6E-05 ± 2.70E-05
		35	4.2 ± 0.7	12.6E-03 ± 2.12E-03	17.3E-05 ± 1.89E-05
ND	NG	15	ND§	ND	ND
		25	3.5 ± 0.7	8.7E-03 ± 1.48E-03	8.8E-05 ± 1.33E-05
		35	7.2 ± 2.5	6.7E-03 ± 1.89E-03	16.7E-05 ± 4.48E-05
ND	C	15	2.0 ± 0.5	10.3E-03 ± 2.35E-03	6.0E-05 ± 1.03E-05
		25	4.0 ± 1.4	7.6E-03 ± 2.26E-03	9.9E-05 ± 2.57E-05
		35	4.0 ± 1.1	11.7E-03 ± 2.94E-03	13.5E-05 ± 2.76E-05
CO	NG	15	ND	ND	ND
		25	9.4 ± 2.4	6.9E-03 ± 1.42E-03	18.5E-05 ± 4.46E-05
		35	14.0 ± 2.7	7.1E-03 ± 1.08E-03	33.1E-05 ± 5.38E-05
CO	C	15	ND	ND	ND
		25	3.1 ± 1.0	16.0E-03 ± 5.11E-03	19.1E-05 ± 2.94E-05
		35	7.3 ± 1.3	14.4E-03 ± 2.48E-03	35.2E-05 ± 4.00E-05
TX	NG	15	7.0 ± 2.7	5.4E-03 ± 1.66E-03	5.9E-05 ± 4.35E-05
		25	8.9 ± 2.0	9.0E-03 ± 1.80E-03	12.5E-05 ± 4.59E-05
		35	10.0 ± 1.2	13.8E-03 ± 1.60E-03	31.4E-05 ± 3.85E-05
TX	C	15	6.8 ± 3.9	5.5E-03 ± 2.51E-03	4.7E-05 ± 6.21E-05
		25	6.7 ± 2.8	15.7E-03 ± 6.53E-03	18.6E-05 ± 8.59E-05
		35	8.8 ± 1.4	18.7E-03 ± 2.99E-03	31.7E-05 ± 5.19E-05
CR	NF	15	0.1 ± 0.0	289E-03 ± 68.7E-03	4.6E-05 ± 0.72E-05
		25	0.6 ± 0.1	76.4E-03 ± 8.34E-03	6.6E-05 ± 0.81E-05
		35	1.0 ± 0.1	62.2E-03 ± 8.81E-03	16.3E-05 ± 1.41E-05
CR	P	15	0.7 ± 0.4	6.2E-03 ± 2.56E-03	1.0E-05 ± 0.61E-05
		25	0.5 ± 0.1	49.4E-03 ± 11.2E-03	4.0E-05 ± 0.78E-05
		35	3.2 ± 0.3	11.7E-03 ± 0.91E-03	4.8E-05 ± 0.62E-05
BR	NF	15	1.1 ± 0.2	56.1E-03 ± 11.4E-03	8.6E-05 ± 1.90E-05
		25	0.6 ± 0.1	111E-03 ± 21.5E-03	21.4E-05 ± 2.11E-05
		35	2.1 ± 0.3	49.2E-03 ± 9.52E-03	34.5E-05 ± 3.46E-05
BR	P	15	1.9 ± 0.3	35.9E-03 ± 6.00E-03	9.6E-05 ± 1.75E-05
		25	3.7 ± 0.7	22.3E-03 ± 4.23E-03	13.7E-05 ± 2.55E-05
		35	6.0 ± 0.7	29.1E-03 ± 3.76E-03	33.5E-05 ± 3.94E-05

† SK, Saskatchewan; ND, North Dakota; CO, Colorado; TX, Texas; CR, Costa Rica; BR, Brazil.

‡ NG, native grassland; NF, native forest; C, cultivated; P, pasture.

§ND values were not determined because the model calculated negative decomposition rates for the slow pool for these samples

was an increase in carbohydrates with conversion from native forest to pasture in Brazil, consistent with the increase in SOM in the pasture (Table 5). There did not appear to be any correlation with the Q_{10-q} value of the labile or resistant fraction and the percentage of various compounds in each soil (data not shown).

In many of the sites, there were differences in the abundance of chemical compounds identified with py-MBMS between the native and cultivated/pasture treatments. Figure 3 illustrates the differences in chemical composition between the native and cultivated soils for the Saskatchewan site, as an example. The Saskatchewan native grassland had a greater abundance of the lower m/z compounds especially m/z 57 and 96 which are

associated with carbohydrates and m/z 67 and 81, which are associated with various N compounds. The cultivated soil had a greater abundance of higher molecular weight compounds, many of which are associated with lipids, lignin, and alkyl aromatics.

Principal components analysis was unable to significantly distinguish SOM composition when all samples were analyzed together (Fig. 4). The first four principal components combined explained 43% of the variance. Taken together, PCA scores of samples were not tightly grouped on the basis of site or land use, with the exception that native forest and grassland samples appear to be more tightly grouped than cultivated samples. There was minor separation of samples by site along the PC 1

axis, but SOM composition from those sites was comparatively heterogeneous. Significant clustering was observed on the basis of land-use treatment when sites were analyzed individually (data not shown), although there were no consistent trends across sites. The PCA score results suggest that SOM composition in the allophanic Costa Rica samples was highly homogeneous. Principle component analysis loadings were dominated by low molecular weight and odd-numbered m/z fragments, which are likely derived from carbohydrate, amino acid, and peptide side-chains (data not shown).

Sequential application of the Martens' uncertainty test found a small number of m/z values that were significantly correlated to respiration rates at Day 5 of the incubation (Table 6). Partial least square regression using this reduced set of independent variables was able to explain 65% of the variance using the first four components. Respiration rates at Day 5 of the incubation were highly correlated with low molecular components associated primarily with carbohydrates, peptides and various N compounds. Regression against respiration rates at Day 225 of the incubation resulted in more m/z values that were significantly correlated (Table 6), but each correlation coefficient was smaller than those for Day 5. Partial least square regression of the reduced set of independent variables was able to explain 59% of the variance using the first four components. The additional m/z values were generally higher molecular weights. Some were associated with phenols and lignin monomers, lignin dimers, and lipids, but many were not identified by Schulten (1996), Hempfling and Schulten (1990), or Gillespie et al. (2009) as marker signals for specific compounds classes.

DISCUSSION

During the incubation, the total amount of SOC respired increased with warmer incubation temperatures for all twelve soils. Similar responses across the MAT range of 2 to 25.6°C (Table 2) could suggest that increasing global temperatures

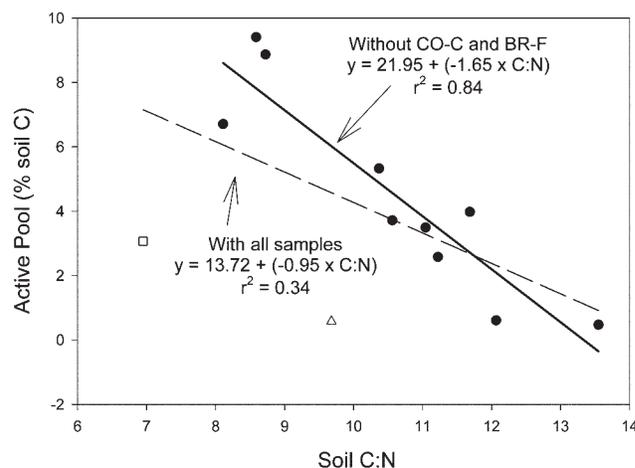


Fig. 2. Correlation between the C/N ratio of the soil and the size of the active pool in percentage of total SOC for the 12 soils sampled. All sites are represented by closed circles except Colorado cultivated (CO-C), an unfilled square, and Brazil native forest (BR-NF), an unfilled triangle.

may affect soils equally. The low respiration rates per unit SOC for the allophanic, Costa Rica soils were likely due to the unique mineral composition. Protective effects of amorphous aluminum, iron, and allophanic material have been shown to contribute to the much higher SOM concentrations found in these types of soils (Munevar and Wollum, 1977; Boudot et al., 1986; Martin and Haider, 1986; McKeague et al., 1986). The characteristics that cause SOM accumulation are also likely responsible for the minimal loss of SOC on incubation (Boudot et al., 1988). Respiration rates declined over time in all the soils with the differences in respiration rates between temperatures still apparent at the end of the incubation. Correlations from PLS regression analysis of the py-MBMS products versus the respiration rates could be an indication that higher molecular weight compounds, which tend to be more resistant SOM, were being utilized in the later stages of the incubation. These

Table 5. Proportions (%) of ion intensity attributable to carbohydrates, peptides, phenols, lignin dimers, lipids, alkyl-aromatics, various N-containing compounds (VCN), sterols and the remaining unknown m/z for each of the soils sampled. (mean ± 1 standard deviation, n = 6)

Site†	Land use‡	m/z 20–56	Carbs	Peptides	Phenols & lignin monomers	Lignin dimers	Lipids	Alkyl aromatics	VNC	Sterols	Unknown
SK	NG	52.8	11.0	9.7	4.0	0.3	1.8	2.5	12.9	0.3	4.7
	C	59.0	8.0	8.2	3.0	0.6	2.5	1.9	9.6	0.6	6.6
ND	NG	52.8	11.0	9.1	3.9	0.3	2.0	2.2	13.1	0.3	5.1
	C	54.4	10.1	9.4	4.0	0.3	1.8	2.1	13.1	0.3	4.5
CO	NG	51.8	9.7	8.5	3.9	0.6	3.3	2.5	11.5	0.7	7.5
	C	48.5	8.1	8.4	4.0	1.0	5.7	2.4	9.2	1.1	11.5
TX	NG	53.4	9.1	8.8	3.3	0.6	3.3	2.4	11.0	0.8	7.3
	C	52.1	8.0	7.5	3.5	0.9	4.8	2.2	9.3	1.1	10.7
CR	NF	41.0	15.6	12.3	6.0	0.5	2.9	2.3	14.2	0.4	4.8
	P	47.5	15.4	11.2	4.6	0.3	1.8	2.1	13.3	0.3	3.5
BR	NF	50.0	9.6	9.4	4.2	0.6	3.3	2.1	12.8	0.6	7.5
	P	47.6	11.8	10.3	4.4	0.5	2.8	2.5	13.4	0.6	6.2
Mean		50.9 ± 4.5	10.6 ± 2.6	9.4 ± 1.4	4.1 ± 0.7	0.5 ± 0.2	3.0 ± 1.2	2.3 ± 0.2	11.9 ± 1.8	0.6 ± 0.3	6.7 ± 2.5

† SK, Saskatchewan; ND, North Dakota; CO, Colorado; TX, Texas; CR, Costa Rica; BR, Brazil.

‡ NG, native grassland; NF, native forest; C, cultivated; P, pasture.

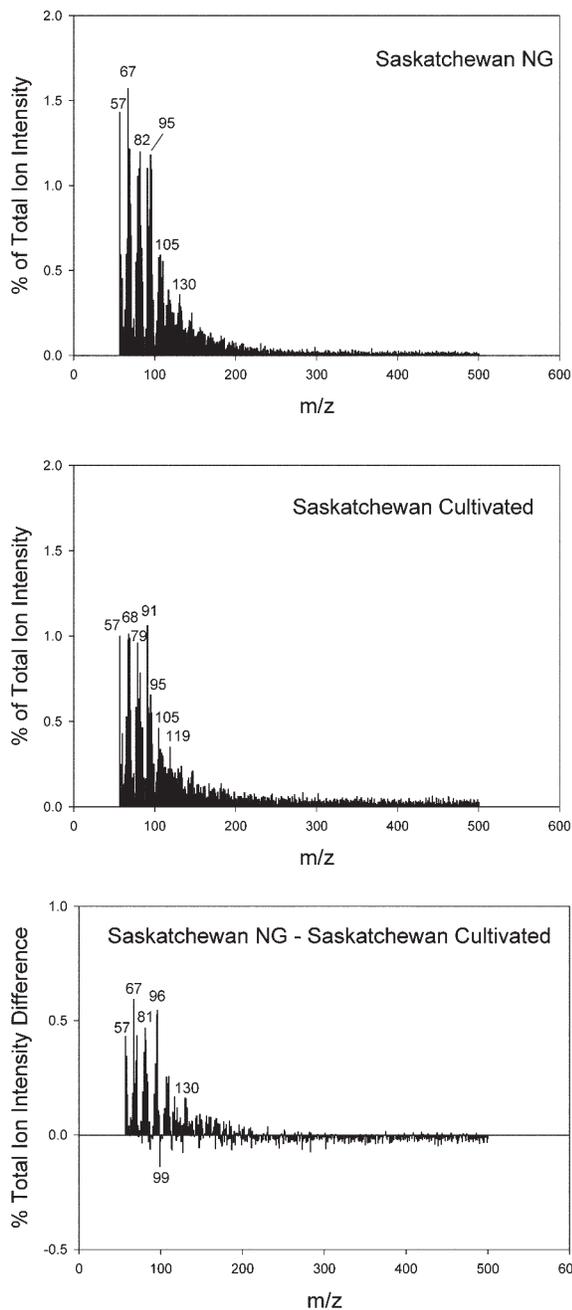


Fig. 3. Normalized mass spectrum for spectral range $m/z = 57-500$ from the pyrolysis molecular beam mass spectrometry analysis of Saskatchewan native grassland (NG), Saskatchewan cultivated, and the difference between the two spectra. In the difference graph m/z that are more abundant in the native grassland are positive and m/z that are more abundant in the cultivated are negative. Spectra are means of six samples.

correlations support the first assumption of the Q_{10-q} method, that changes in decomposition rates are driven by changes in easily decomposable substrate.

In most instances the more resistant SOM was more temperature sensitive than the labile SOM. We utilized the same method of determining temperature sensitivity of SOM decomposition as described by Conant et al. (2008a) along with two of the same sites (Colorado and Texas) and observed similar results with an expanded set of sites. Our results and

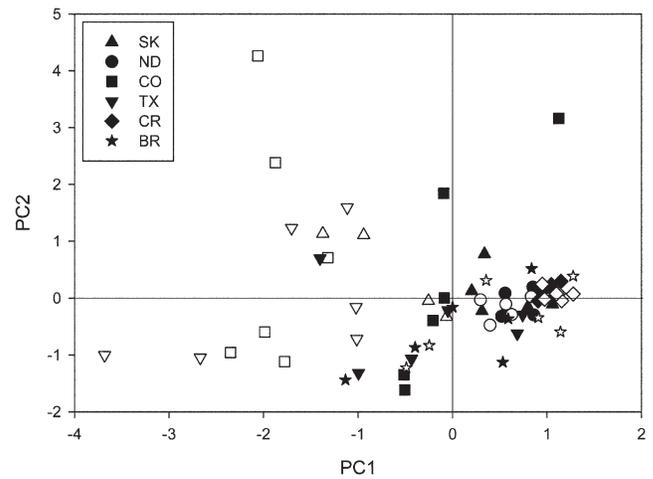


Fig. 4. Principle component analysis scores of whole-soil samples analyzed by py-MBMS for the twelve soils sampled. Closed symbols are native treatments, open symbols are cultivated or pasture treatments.

those of Conant et al. (2008a) are consistent with multiple other studies (Bosatta and Ågren, 1999; Bol et al., 2003; Fierer et al., 2005; Knorr et al., 2005; Conant et al., 2008b). However, it is important to point out that there were two soils in our study that did not follow this overall trend and in those two soils the more resistant fraction had a lower Q_{10-q} value than the labile fraction and the Q_{10-q} value of the more resistant fraction was also much lower than those determined for the other soils. For the North Dakota cultivated soil, the Q_{10-q} value calculated throughout the course of the incubation varied very little and the Brazil forest soil increased to a value of 4.5 and then declined down to 1.4 (data not shown). Our results illustrate how a study that utilizes a single soil for determining temperature sensitivity of SOM decomposition could possibly come to a different conclusion with regards to SOM temperature sensitivity.

We compared the temperature sensitivity of the first 0.5% (w/w) soil C respired to the last 0.5% (w/w) soil C respired. Since this is an operationally defined fraction it is possible that a longer incubation could affect the results. Respiration rates had leveled off by the end of the incubation and we don't believe extending our incubation further would alter our results significantly because we would not be accessing a different pool of SOM at this point. Incubations are limited by the fact that the truly resistant C with mean residence times of millennia is not accessed by the microbes and we are more likely just accessing the rather large intermediate pool of SOM. There is a possibility that our cut off limit of flushing jars before CO_2 reached 5%(v/v) may have caused an inhibition of microbial activity, although there was no indication in the respiration data that this occurred. If there was any inhibition of microbial activity it would have likely occurred early in the incubation at the warmer incubation temperatures, when respiration rates were high. If this did occur it may have caused us to underestimate the Q_{10-q} for the labile fraction and the size of the active pool at the warmer incubation temperatures. Although we believe that any underestimation would have been slight and not change the overall trends.

The estimated size of the active pool for all the sites ranged from 0.1 to 14.0% of initial SOC (Table 4). This range for the active pool is slightly wider than results found by Rey and Jarvis (2006), which ranged from 0.27 to 11.4%. Many other studies have estimates that fall within these ranges (Collins et al., 2000; Haile-Mariam et al., 2000; Cochran et al., 2007). Our wider range of estimates for the active pool is likely due to the wide range of soils and incubation temperatures utilized. The soils from the two central sites, Texas and Colorado, respired the most total SOC by the end of the incubation and had the largest active pools, contrary to the comparison of forested tropical soils and dry forested temperate soils by Trumbore (1993) in which the tropical soils were comprised of more labile C in the upper 22 cm than temperate soils. The larger active pools in our temperate soils and higher cumulative respiration could be due to the greater amount of N in the soils, which indicates a higher proportion of proteinaceous constituents. Our results are consistent with Thomsen et al. (2008), who found the C/N ratio to be an indicator of the decomposability of the SOM in a soil, with soils having lower C/N ratios having greater CO₂ evolution up to a certain threshold.

Temperature-induced changes in pool sizes could be an indication that warmer temperatures may enable microbes to quickly decompose a larger portion of SOM. Increased active pool size with increased temperature evidenced in this study indicates that at warmer temperatures SOM otherwise unavailable to microbes at lower temperatures becomes available for decomposition. This could be attributed to shifts in microbial community composition at different temperatures (Zogg et al., 1997; Zak et al., 1999), changes in substrate use (Andrews et al., 2000; Schimel and Mikan, 2005), or the overcoming of biochemical resistance of SOM by microbes (Conant et al., 2008a).

We utilized different land use treatments at these sites to compare soils with the same MAT but varying amounts and types of SOM, since soils under long-term cultivation would likely have less easily decomposable SOM than the native counterparts. For the four native grassland/cultivated sites, the native grassland treatments respired a greater amount of total soil C and had larger active pools than their cultivated counterparts. The native grassland soils had greater percentages of carbohydrates as found by py-MBMS, which could be the reason for the greater respiration and larger active pool. Plante et al. (2009), also utilizing py-MBMS, found that cultivation resulted in significant decreases in carbohydrates, peptides, and phenols. Surprisingly, the decline in carbohydrates with cultivation did not result in significant trends in Q_{10-q} values with land use. Our MAT gradient also did not produce consistent trends with regards to temperature sensitivity. It may have been that differences in soil characteristics among sites were too great to elucidate trends with MAT.

Different stabilization mechanisms may alter the reaction rate of SOM decomposition as much as the temperature sensitivity of the SOM. The Costa Rica site with its very low decomposition because of the interactions with sesquioxides had

40 to 42% of its pyrolysis products identified as carbohydrates, peptides, and various N containing materials that are normally considered to be more easily decomposable and contribute to the size of the active pool as measured in this study. The Colorado soils had much less of their pyrolysis products identified as carbohydrates and N containing materials yet the size of the active pool was 2 to 14 times the size of that of Costa Rica at 35°C. The otherwise decomposable materials are protected in the Costa Rica soils with the Costa Rica pasture soil having noticeably higher Q_{10-q} values for the labile and more resistant fraction. This suggests that the adsorbed materials have even greater temperature sensitivity than soils that have less SOM stabilization. This could mean that the mineral associated SOC constituents could be more affected by global climate change.

We were unable to link differences between apparent temperature sensitivity of SOM, measured as Q_{10-q}, to MAT at the site, land use, the size of the active pool, or the chemical composition of SOM determined by py-MBMS. This lack of a strong correlation between methods that characterize the organic matter and the Q_{10-q} values could indicate that chemical stabilization with silt and clay is a greater determinant of temperature sensitivity than biochemical stabilization through the inherent makeup of the organic matter.

The size of our estimated active pool did increase with warmer incubation temperatures for most soils indicating that there may be changes in microbial community or function with temperature that should be considered in model incorporation. Our results indicate that although individual soils may have varying apparent temperature sensitivities for labile versus more resistant SOM depending on the inherent characteristics of the soil, overall the more resistant SOM tends to be more temperature sensitive. Although not directly studied in our experiment, our results indicate that physicochemical stabilization may be a more important determinant of temperature sensitivity of SOM than biochemical stabilization. Understanding the differences between inherent and apparent temperature sensitivity is an area that still requires more investigation to better model temperature effects on SOM decomposition.

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