The composition of soil, particularly its organic matter content, reflects its role as a major controller of ecosystem functioning and soil fertility (Paul and Collins 1998, Basso et al. 2011, Bhardwaj et al. 2011). Soil organic matter (SOM), the largest global reservoir of terrestrial organic carbon (C), contains three to four times as much stored C as either the atmosphere or plant biomass. The soil biota, consisting of microorganisms as well as fauna, account for 1–3% of total soil C and complete the terrestrial C cycle by mineralizing SOM to carbon dioxide (CO₂) (Paul and Collins 1998, Robertson and Paul 2000). Soil organic matter is a complex, multi-structured, multicomponent pool of organic materials including decomposing plant residues, associated microorganisms and their products, and a biochemically transformed fraction, sometimes called humic material, that is complex in structure and often associated with soil minerals. Microbially derived C, because of its unique chemical structure and intimate association with minerals, is selectively protected and represents a particularly important component of total SOM. This pool serves as a dynamic source of labile nutrients and contributes to soil aggregate formation and erosion resistance (Robertson and Paul 1998, Grandy and Neff 2008).

The investigation of SOM dynamics provides a wealth of information on how organisms, including vegetation and soil biota, interact with climate, parent material, landscape, and management over time to influence ecosystem functioning (Collins et al. 1997). One of the most promising approaches for understanding SOM dynamics uses long-term incubations, together with tracers and density fractionation, to interpret SOM pools and their turnover.

The multiple components that make up SOM can be divided into three pools based on their turnover times (Paul et al. 2001a, b). The most labile, active pool is
Soil Organic Matter Dynamics

small at ~5% of total SOM. It includes some of the interaggregate fraction (i.e., not contained within soil aggregates) of plant residues and a portion of the soil biotic biomass, and has mean residence times (MRTs) of months to years. The slow pool, with MRTs ranging from months to decades, accounts for ~40% of total SOM and is a major source of soil nutrients that change with long-term management. Slow pool dynamics are controlled by aggregation and the association of microbial products with the calcium (Ca) and sesquioxide minerals as well as some silt and clay components. The SOM within soil aggregates (intraaggregate fraction) has both young and old constituents, with MRTs of decades. The oldest SOM is associated with silt and clay and is defined as the resistant pool; it is measured as the SOM that remains after acid hydrolysis. This third pool has the longest MRTs (century to millennia) and is best measured by carbon dating (Leavitt et al. 1996, Paul et al. 1997a).

Because SOM is a heterogeneous material including components with a wide range of turnover in response to abiotic and biotic controls, we currently cannot directly isolate and analyze SOM fractions based on their turnover dynamics. For example, there appears to be some old C (possibly charcoal) associated with the actively decomposing, recently added plant particulate material. On the other hand, old fractions such as the clays (Haile-Mariam et al. 2008) have some recently absorbed young microbial products. Old, resistant, non-hydrolyzable C is also known to contain recent plant-derived lignin that is not soluble in acid, even though on average the pool is very old (Paul et al. 2006).

Soils of the Kellogg Biological Station Long-term Ecological Research Site (KBS LTER) are ideal for studying how organisms, climate, parent material, landscape, and management influence SOM composition, dynamics, and ecosystem functioning. KBS soils developed in a moderately humid, temperate climate on glacial outwash over a period of ~18,000 years. They are moderately fertile Typic Hapludalfs (NRCS 1999) developed in an environment with a mean annual temperature of 9.0°C and annual precipitation of ~1,000 mm, under a northern, mixed hardwood forest with grassland openings attributed to fires promoted by native inhabitants ~700 c.e. (Robertson and Hamilton 2015, Chapter 1 in this volume). In the late nineteenth and early twentieth centuries, these soils were further disturbed by widespread deforestation and cultivation.

The soils underlying the KBS LTER consist of two main series: (1) Oshtemo: coarse-loamy, mixed, mesic, Typic Hapludalfs and (2) Kalamazoo: fine-loamy, mixed, mesic Typic Hapludalfs (Austin 1979, Mokma and Doolittle 1993, Crum and Collins 1995). The 0- to 20-cm surface layer has a texture of 39% sand, 43% silt, and 18% clay. This grades to 87% sand at a depth of 50–100 cm with 5% silt and 8% clay. Surface horizons can contain a small amount of inorganic C arising from the application of agricultural lime (mainly calcium and magnesium carbonates); in deeper horizons the presence of inorganic C reflects the calcareous origin of parent materials (Hamilton et al. 2007). Soil organic matter in surface horizons ranges from <10 to more than 30 g C kg⁻¹ depending on landscape position, vegetation, and management history (Syswerda et al. 2011).

The organic matter content of soils reflects the balance between photosynthesis and decomposition, the two major driving factors in the global C cycle.
Decomposition transforms plant residues into microbial products that can become stabilized in the soil matrix, thereby maintaining 5–10% of the plant residue C as SOM (Follett et al. 1997). As the recipients of decomposition processes, soils represent a valuable storehouse of information on past vegetation, climate, and disturbance. They are also a major source of nutrients, especially nitrogen (N), and provide physical structure and moisture retention. Interactions of SOM within the soil matrix—particularly of silts and clays, but also aggregation with sand particles—determine the rooting environment for plants and both the storage and movement of soil moisture essential for plant growth.

The major factors controlling SOM dynamics are: (1) the quality of the incoming substrates, (2) the role of the soil biota and especially the microorganisms, (3) physical protection such as in aggregation, (4) interaction with the soil matrix such as the silts and clays as well as Ca and sesquioxides, and (5) the chemical nature of the SOM itself. These factors interact and are best studied together.

However, because soil takes so long to form and because SOM is such a small fraction of bulk soils, examination of these factors must involve long-term studies on well-characterized sites. Sites such as those in the LTER Network can supply the continuity and replication required to investigate SOM transformations and dynamics. In this chapter, we synthesize studies from the KBS LTER that focus on SOM dynamics in agricultural soils. We begin by examining soils of the Main Cropping System Experiment (MCSE, Table 5.1) and discuss the effect of landscape, vegetation, and agricultural management on SOM dynamics. We then discuss the biochemical controls on SOM dynamics, particularly as characterized by examining the size and turnover rates of important SOM constituents. And we end with an examination of the role of C inputs and microbial activities on the fate of C in agricultural soils.

Effect of Landscape, Vegetation, and Management on Soil Organic Matter Dynamics

Soils at the KBS LTER are prone to periodic drought, with some historical erosion, and thus have lower SOM content compared to some other nonglaciated cultivated soils in the Great Lakes region (Table 5.2). The Deciduous Forest system of the KBS LTER MCSE (Table 5.1) is representative of the native soil of the region (see Robertson and Hamilton 2015, Chapter 1 in this volume, for a description). The C in the SOM (hereafter referred to as soil organic carbon, SOC) of surface soils (0–20 cm; Table 5.2) has a MRT of 422 years, as determined by carbon dating (Paul et al. 2001a). This increases to 1712 years at 50- to 100-cm depth. Using acid hydrolysis to identify the old, resistant SOC (Paul et al. 2006, Plante et al. 2006), which is called non-hydrolyzable C (NHC), Paul et al. (2001a) found that 56% of the total SOC in the surface layer is NHC and is 977 years old (Table 5.2). Deeper in the forest soil profile (50- to 100-cm layer), the NHC accounts for only 23% of the SOC but is 4406 years old.

Such soil characterizations are most informative when examined in comparisons. Unifying concepts such as the content and structure of SOM and the role of the soil
Soil Organic Matter Dynamics

biota in ecosystem functioning are best studied by examining a range of soils under long-term management (Paul et al. 1997b). This is illustrated by comparing KBS native soil with two additional, related soils from the Great Lakes region of North America. The Hoytville, Ohio, soil also developed under Oak-Hickory vegetation in a similar manner to KBS, but on lower landscape elevations that had more moisture and higher clay contents. It has 17.8 g C kg\(^{-1}\) soil with an MRT of 920 years in

Table 5.1. Description of the KBS LTER Main Cropping System Experiment (MCSE).\(^a\)

<table>
<thead>
<tr>
<th>Cropping System/Community</th>
<th>Dominant Growth Form</th>
<th>Management</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Annual Cropping Systems</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional (T1)</td>
<td>Herbaceous annual</td>
<td>Prevailing norm for tilled corn–soybean–winter wheat (c–s–w) rotation; standard chemical inputs, chisel-plowed, no cover crops, no manure or compost</td>
</tr>
<tr>
<td>No-till (T2)</td>
<td>Herbaceous annual</td>
<td>Prevailing norm for no-till c–s–w rotation; standard chemical inputs, permanent no-till, no cover crops, no manure or compost</td>
</tr>
<tr>
<td>Reduced Input (T3)</td>
<td>Herbaceous annual</td>
<td>Biologically based c–s–w rotation managed to reduce synthetic chemical inputs; chisel-plowed, winter cover crop of red clover or annual rye, no manure or compost</td>
</tr>
<tr>
<td>Biologically Based (T4)</td>
<td>Herbaceous annual</td>
<td>Biologically based c–s–w rotation managed without synthetic chemical inputs; chisel-plowed, mechanical weed control, winter cover crop of red clover or annual rye, no manure or compost; certified organic</td>
</tr>
<tr>
<td><strong>Perennial Cropping Systems</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alfalfa (T6)</td>
<td>Herbaceous perennial</td>
<td>5- to 6-year rotation with winter wheat as a 1-year break crop</td>
</tr>
<tr>
<td>Poplar (T5)</td>
<td>Woody perennial</td>
<td>Hybrid poplar trees on a ca. 10-year harvest cycle, either replanted or coppiced after harvest</td>
</tr>
<tr>
<td>Coniferous Forest (CF)</td>
<td>Woody perennial</td>
<td>Planted conifers periodically thinned</td>
</tr>
<tr>
<td><strong>Successional and Reference Communities</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Early Successional (T7)</td>
<td>Herbaceous perennial</td>
<td>Historically tilled cropland abandoned in 1988; unmanaged but for annual spring burn to control woody species</td>
</tr>
<tr>
<td>Mown Grassland (never tilled) (T8)</td>
<td>Herbaceous perennial</td>
<td>Cleared woodlot (late 1950s) never tilled, unmanaged but for annual fall mowing to control woody species</td>
</tr>
<tr>
<td>Mid-successional (SF)</td>
<td>Herbaceous annual + woody perennial</td>
<td>Historically tilled cropland abandoned ca. 1955; unmanaged, with regrowth in transition to forest</td>
</tr>
<tr>
<td>Deciduous Forest (DF)</td>
<td>Woody perennial</td>
<td>Late successional native forest never cleared (two sites) or logged once ca. 1900 (one site); unmanaged</td>
</tr>
</tbody>
</table>

\(a\)Site codes that have been used throughout the project’s history are given in parentheses. Systems T1–T7 are replicated within the LTER main site; others are replicated in the surrounding landscape. For further details, see Robertson and Hamilton (2015, Chapter 1 in this volume).
the surface layer (Table 5.2). Soil at 50- to 100-cm depth contains 4.3 g C kg\(^{-1}\), with an MRT of 6607 years, and thus has higher SOC content and is older than KBS soil. The long time required for SOM development is reflected in the MRT of 9875 years for the oldest NHC fraction, which accounts for 44% of total SOC at 50–100 cm. The grassland-derived soil from Lamberton, Minnesota, shows similar SOC levels and proportions of NHC as the forest-derived Hoytville soil. The Lamberton SOC has somewhat longer MRTs than Hoytville and substantially longer MRTs than those of KBS. In all cases, a strong relationship exists between the MRT of the SOC and the amount of SOC present, indicating the time it takes for SOM to accumulate.

Long-term incubations of these soils (Collins et al. 2000) showed that although SOC from deeper depths in the profile had very long MRTs, when brought into the laboratory and disturbed, the samples released nearly as much CO\(_2\) per unit of SOC as did soil from the surface horizons. This implies that the long MRTs were the result of matrix interactions, such as those with silt and clay, and profile position and not necessarily intrinsic chemistry. Labile constituents are decomposed early in the incubation and thus largely control the size of the active SOC pool. This was confirmed by the observation that the stable C isotope ratios of CO\(_2\) produced in incubations of soils obtained from cultivated sites moved toward the ratio produced by native-site soils late in their long-term incubation. At that point in the incubation, microbes are decomposing the older, native-derived materials. The stable C isotope ratio of the respired CO\(_2\) of the cultivated sites’ SOC did not become equal to that of CO\(_2\) from the native sites’ SOC because the total CO\(_2\) evolved was less than 10% of the total SOC (Collins et al. 1999).

<table>
<thead>
<tr>
<th>Soil(^{a})</th>
<th>SOC (g kg(^{-1}))</th>
<th>MRT (years)</th>
<th>NHC (%)</th>
<th>MRT NHC (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBS LTER, MI (Forest)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–20 cm</td>
<td>10.7 (0.5)</td>
<td>422 (51)</td>
<td>56</td>
<td>977 (50)</td>
</tr>
<tr>
<td>25–50 cm</td>
<td>2.6 (0.4)</td>
<td>933 (67)</td>
<td>23</td>
<td>895 (54)</td>
</tr>
<tr>
<td>50–100 cm</td>
<td>1.3 (0.1)</td>
<td>1712 (50)</td>
<td>21</td>
<td>4406 (65)</td>
</tr>
<tr>
<td>Hoytville, OH (CT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–20 cm</td>
<td>17.8 (0.7)</td>
<td>920 (53)</td>
<td>46</td>
<td>1770 (45)</td>
</tr>
<tr>
<td>25–50 cm</td>
<td>8.6 (0.40)</td>
<td>2627 (55)</td>
<td>45</td>
<td>5660 (870)</td>
</tr>
<tr>
<td>50–100 cm</td>
<td>4.3 (0.1)</td>
<td>6607 (79)</td>
<td>44</td>
<td>9875 (75)</td>
</tr>
<tr>
<td>Lamberton, MN (CT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–20 cm</td>
<td>17.9 (1.0)</td>
<td>1100 (53)</td>
<td>49</td>
<td>1510 (45)</td>
</tr>
<tr>
<td>25–50 cm</td>
<td>8.7 (0.7)</td>
<td>3100 (55)</td>
<td>45</td>
<td>3965 (65)</td>
</tr>
<tr>
<td>50–100 cm</td>
<td>4.3 (0.2)</td>
<td>6107 (75)</td>
<td>48</td>
<td>7285 (90)</td>
</tr>
</tbody>
</table>

\(^{a}\)Includes SOC content, mean residence time (MRT), non-hydrolyzable C fraction (NHC), and MRT of the NHC. Data are means (±SE, when applicable).

\(^{b}\)The KBS LTER site is the Deciduous Forest system of the MCSE (Table 5.1) and the other two sites are agricultural row-crop production sites with conventional tillage (CT) and chemical use.

Source: Paul et al. (2001a, b).
Management strongly affects SOM accumulation, especially in the uppermost soil horizons (Robertson et al. 1993, 1997) and is primarily restricted to the top 7 cm of the soil profile (De Gryze et al. 2004, Syswerda et al. 2011). While using concentration (e.g., g C kg⁻¹) to describe SOC content is suitable in many situations, estimates of ecosystem C storage must be made on a surface-area basis (e.g., g C m⁻², kg C ha⁻¹), which incorporates soil bulk density and depth of soil sampling. Changes in both bulk density and distribution of SOC in the soil profile are known to occur in response to changes in land use, including agricultural management (Morris et al. 2007).

Twelve years after establishment of the seven MCSE systems on previously cropped soils at the LTER main site (Table 5.1), the Early Successional system had gained 380 g C m⁻² in the upper 5 cm of surface soil, representing an increase of 61% compared to the Conventional system (Grandy and Robertson 2007). Other systems also gained SOC, in the order Alfalfa (341 g C m⁻², 55% greater) > No-till (264 g C m⁻², 43% greater) > Poplar (229 g m⁻² C, 37% greater) > Biologically Based (148 g m⁻² C, 24% greater) > Reduced Input (107 g m⁻² C, 17% greater). In contrast, the soils of the Deciduous Forest and Mown Grassland (never tilled) systems had about 2.5 times more SOC than the Conventional system in the uppermost 5 cm.

Annual SOC accumulation rates of the MCSE main site systems relative to the Conventional system ranged from 32 g C m⁻² yr⁻¹ in the Early Successional community down to 8.9 g C m⁻² yr⁻¹ in the Reduced Input system. Whether these accumulation rates represent absolute gains of SOC or slower losses of SOC relative to the Conventional system depends on whether Conventional system soils were stable or were losing C over the 12-year study period. In 2006 and 2007, Senthilkumar et al. (2009a, b) remeasured SOC at geo-referenced locations in the MCSE, where SOC had previously been measured in 1988, and in the nearby Interactions Experiment, where SOC had previously been measured in 1986. The studied sites had a common history of conventional agricultural management for at least the prior 70–100 years. In both experiments, SOC content appeared to decline under conventional tillage management (Table 5.3). Carbon losses were less in the No-till and Biologically Based systems, consistent with other studies (Grandy and Robertson 2007; Syswerda et al. 2011) that show SOC gains in these systems relative to the Conventional system.

That C should be lost from these long-cultivated soils is surprising, and may be related to wintertime warming; Senthilkumar et al. (2009a) documented a significant local increase in the number of days per year with above-freezing air temperatures over the 20-year study period (see also Robertson and Hamilton 2015, Chapter 1 in this volume). These findings are consistent with other studies around the world; increasing temperatures are associated with observed soil C losses (Bellamy et al. 2005, Stevens and van Wesemael 2008). However, the contribution of accelerated erosion over this period cannot be ruled out (Wischmeier and Smith 1961), although the adoption of chisel in place of moldboard plowing in 1996 should have slowed...
rather than increased erosion in these well-drained soils. With continued erosion and the projected further increase in global temperature, the adoption of no-till management or the inclusion of cover crops in the crop rotation (Willson et al. 2001) may be necessary to sustain present soil C levels.

Results from KBS show that C losses in near surface soils can be slowed or even reversed with no-till and biologically based farming practices. Rates of SOC accumulation in the top 5–7 cm of no-till relative to conventional tillage are ~22–30 g C m⁻² yr⁻¹ (Robertson et al. 2000, Grandy and Robertson 2007) and are similar to those for the entire Ap horizon (33 g C m⁻² yr⁻¹, Syswerda et al. 2011), indicating that most change occurs in the upper few centimeters. This is consistent with other estimates for U.S. Midwestern cropping systems (West and Marland 2002). There is no evidence for C change in deeper horizons of no-till soils at KBS (to 1 m; Syswerda et al. 2011), which means that whole-profile C change is dominated by changes in surface soils. That coefficients of variation for soil C increase from 7% in Ap to 29% in B/Bt to 92% in Bt2/C horizons (Syswerda et al. 2011) underscores the difficulty with which subsurface soil C change can be detected if it occurs at all (Kravchenko and Robertson 2011).

Table 5.3. Baseline and contemporary SOC content and changes in SOC in the MCSE and Interactions Experiment.

<table>
<thead>
<tr>
<th>System</th>
<th>SOC² (g kg⁻¹ soil)</th>
<th>Change in SOC (g kg⁻¹ soil)††</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1988</td>
<td>2006</td>
</tr>
<tr>
<td>Conventional</td>
<td>9.3 (0.7)ᵃ</td>
<td>8.2 (0.3)ᵇ</td>
</tr>
<tr>
<td>No-till</td>
<td>10.6 (0.5)ᵃ</td>
<td>9.9 (0.5)ᵇ</td>
</tr>
<tr>
<td>Biologically Based</td>
<td>10.0 (0.5)ᵃ</td>
<td>9.8 (0.3)ᵇ</td>
</tr>
<tr>
<td>P value</td>
<td>0.13</td>
<td>0.002</td>
</tr>
<tr>
<td>Interactions Experiment</td>
<td>1986</td>
<td>2007</td>
</tr>
<tr>
<td>Conventional tillage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-fertilized</td>
<td>9.8 (1.4)ᵃ</td>
<td>9.5 (0.5)ᵇ</td>
</tr>
<tr>
<td>Not N-fertilized</td>
<td>9.8 (1.4)ᵃ</td>
<td>8.2 (0.5)ᵇ</td>
</tr>
<tr>
<td>No-till</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-fertilized</td>
<td>7.4 (1.4)ᵃ</td>
<td>8.3 (0.5)ᵇ</td>
</tr>
<tr>
<td>Not N-fertilized</td>
<td>8.7 (1.4)ᵃ</td>
<td>8.9 (0.5)ᵇ</td>
</tr>
<tr>
<td>P value</td>
<td>0.11</td>
<td>0.07</td>
</tr>
<tr>
<td>Mown Grassland (never tilled)</td>
<td>23.0 (0.9)</td>
<td>15.3 (0.6)</td>
</tr>
</tbody>
</table>

¹Mean SOC content (±SE) in 1988 and 2006 for the MCSE (see Table 5.1) and in 1986 and 2007 for the Interactions Experiment and Mown Grassland. Interactions Experiment systems are also corn–soybean–wheat rotations, but either tilled or no-till and N-fertilized or not N-fertilized in a full factorial design (see http://lter.kbs.msu.edu for a description). The Mown Grassland (never tilled) system is part of the MCSE (Table 5.1) and is adjacent to the Interactions Experiment. P values are from an ANCOVA for testing the significance of the factor effects.

²Sampled to 15-cm depth in the MCSE and to 20 cm in the Interactions Experiment.

Within the same column, values followed by the same letter for a given experiment are not significantly different at α = 0.1.

Not: NS = the mean value is not significantly different from zero (P < 0.05).

Source: Senthilkumar et al. (2009a).
The soil C increases of 50 g C m$^{-2}$ yr$^{-1}$ in the Biologically Based system (Syswerda et al. 2011) are particularly intriguing. Syswerda et al. examined SOC in the full soil profile (to 1 m), whereas most studies including the aforementioned one by Senthilkumar et al. (2009a) sampled surface soils (to 15 or 20 cm depth: Table 5.3). The soils in the Biologically Based system received no manure or compost and soil disturbance in this system was more intensive than in the Conventional system because weed populations were controlled with cultivation. Although this system has a legume cover crop, total biomass inputs are not higher than those in the Conventional system, which produces more grain crop biomass. Thus, C accumulation in this system cannot be attributed to reduced soil disturbance or the quantity of biomass or other C inputs, but is instead due to some other factor that is changing the processing of SOM. One possible explanation is that the incorporation of legume cover crops in the rotation cycle (Table 5.1) is altering the decomposition and stabilization of SOM (Willson et al. 2001). Differences in soil communities, the biochemistry of plant inputs, or their interaction may have influenced soil aggregation or other factors that regulate SOM dynamics (Grandy and Robertson 2007). Although the mechanism is not yet clear, the most likely explanation for enhanced aggregation and soil C in the Biologically Based system is related to the red clover cover crop.

Additionally, SOM change in the Biologically Based system appears to vary with topography. On undulating glacial terrain, topography is one of the most influential factors governing spatial patterns of SOM at field scales, while strongly interacting with land use and management. Senthilkumar et al. (2009b) observed a tendency for greater gain in SOC in topographic depressions (“valleys”) of the Biologically Based system than in higher areas of plots (Fig. 5.1). Muñoz et al. (2008) concluded that greater crop biomass inputs together with differences in residue quality contributed to greater SOC accumulation in depressions in spite of higher levels of soil moisture for decomposition. Considering that these results were obtained from small-scale (1-ha) plots of the MCSE, where terrain variations are substantially less than those typical of whole watersheds (e.g., average MCSE terrain slopes are around 1°, ranging from 0–5°), one can suspect that the interactions between management strategies and topographical effects are even more important elsewhere.

Erosion has not yet been explicitly measured in KBS soils, which is an important omission. Voroney et al. (1981), by using the van Veen and Paul (1981) model to predict long-term levels of SOC, found that the inclusion of the universal soil loss equation (Wischmeier and Smith 1961) greatly altered the predicted levels of SOC. Irrespective of topography and historical soil erosion, there are other noticeable differences in the spatial patterns of SOC under different land management practices at KBS LTER (Kravchenko et al. 2006). Semivariance analysis shows that SOC in the MCSE No-till and Biologically Based systems is more spatially autocorrelated than in the Conventional system at scales of tens of meters (Fig. 5.2). Another study observed stronger spatial structure in the Poplar system than in the Conventional system even at 1–2 m scales (Stoyan et al. 2000).

That no differences in spatial patterns among MCSE plot locations were evident in the 1988 spatial analyses (prior to establishment of the experimental plots in 1989; Robertson et al. 1997) indicates that these system-specific patterns have
Figure 5.1. Differences in soil organic carbon (SOC) between the Conventional and Biologically Based systems at two contrasting landscape positions in the KBS Main Cropping System Experiment (MCSE, described in Table 5.1; data represent 0-30 cm depth, indicate mean ± SE. Similar letters indicate similar values (α = 0.05.). Modified from Senthilkumar et al. (2009b).

Figure 5.2. Variograms with model fits (solid lines) for SOC in the Conventional, No-till, and Biologically Based systems of the MCSE. Modified from Kravchenko et al. (2006).
developed since 1988 in response to different management practices. In particular, the reduction in soil disturbance in the No-till and Poplar systems apparently led to more pronounced site-specific variations in factors affecting soil C storage and C and N mineralization (Kravchenko and Hoa 2008). Likewise, replacement of uniform fertilizer applications under Conventional management with cover crops under Biologically Based management may also have led to differences in spatial variability, in this case because of a greater spatial variability of biomass inputs (Kravchenko et al. 2006, Muñoz et al. 2008).

Roots also play a major role in controlling SOM dynamics through their effects on aggregation and the movement of C to depth (Kavdir and Smucker 2005). Crop type and growth habits can potentially affect root-derived SOM, though probably over long time scales. Genetically engineered Bt corn, which is thought to produce litter that decomposes more slowly than traditional varieties, did not alter soil C and N pools relative to that of nonengineered corn over 7 years at the KBS LTER (Kravchenko et al. 2009). In another example, an herbivorous insect infestation of the Poplar system was found to affect the N use and mineralization of the defoliated poplar plants, but did not detectably alter soil N pools (Russell et al. 2004).

Research at KBS LTER has also documented the destabilizing effect of land-use intensification on soil aggregation and SOC mineralization. The conversion of long-term grasslands and other set-aside lands in the USDA Conservation Reserve Program (CRP) to row-crop agriculture (Feng and Babcock 2010) poses a potential threat to stored SOC (CAST 2011). Recent experiments at KBS demonstrated the rapid and destabilizing effect of tilling grasslands on aggregation and the potential implications for SOM dynamics. Grandy and Robertson (2006a, b) plowed a portion of the Mown Grassland (never tilled) community and followed changes in soil aggregation, CO₂ emissions, and microbial activity. They found that after a single spring tillage event, aggregates in the 2000–8000 µm size class declined substantially from 34% to 19% of total aggregates. Associated with these changes, the newly cultivated sites lost an average of 1.4 g C m⁻² d⁻¹, derived from both plant litter inputs and native SOM, between May and October over 3 years. Such results raise concerns about the long-term environmental implications of expanding crop production into CRP and other grasslands to support the biofuel industry (Robertson et al. 2011, Gelfand and Robertson 2015, Chapter 12 in this volume). More work is needed to better understand and perhaps mitigate changes in SOM under different scenarios of land-use change.

Afforestation is another land-use change that impacts the terrestrial C cycle through changes in SOM (Morris and Paul 2003). Soil carbon accrual in afforested former agricultural lands at KBS, at the nearby Kellogg Forest, and at the Russ Forest in Cass County, Michigan—all on the same soil series and with stands of 50–60 years age—are shown in Fig. 5.3 (Morris et al. 2007). Changes were ascertained by comparison with adjacent agricultural fields. In contrast to C, the N content in afforested soils appeared to decrease in the MCSE and Kellogg Forest soils, but increase in the Russ Forest soils. The N accumulation at Russ Forest was in excess of that expected based on localized atmospheric N deposition (Morris et al. 2007). One explanation for the different responses is that afforested soils at KBS may have higher N concentrations because of manure applications when the
land was first cleared, and thus less capacity to accumulate N. Total N content is somewhat higher in KBS soils than on local commercial farms with similar soil C contents (Table 5.4), resulting in a lower C:N ratio for the KBS soils in this comparison. These data further demonstrate the capacity for these soils to accrue C and N during afforestation in most cases, depending on tree species composition and SOM content. That C accrued in these soils indicates that they have not reached C saturation—the concept that a particular soil under a specific set of controls (such as the level of aggregation) can only sequester a specific amount of C. Soil C saturation been observed in both agricultural and forested soils (Six et al. 2002a, b).

Table 5.4. A comparison of SOC, total nitrogen (N), and C:N mass ratio of soils from the MCSE Conventional system and six privately owned sites in Cass County, Michigan.

<table>
<thead>
<tr>
<th>Site</th>
<th>Number of Samples</th>
<th>Profile SOC (Mg ha$^{-1}$)</th>
<th>Profile N (Mg ha$^{-1}$)</th>
<th>C:N Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCSE</td>
<td>6</td>
<td>59.1 (7.3)$^{bc}$</td>
<td>8.7 (0.71)$^{c}$</td>
<td>6.73 (0.24)$^{a}$</td>
</tr>
<tr>
<td>Field 1</td>
<td>5</td>
<td>37.6 (3.6)$^{a}$</td>
<td>4.1 (0.4)$^{a}$</td>
<td>9.1 (0.09)$^{bc}$</td>
</tr>
<tr>
<td>Field 2</td>
<td>5</td>
<td>63.4 (5.0)$^{a}$</td>
<td>6.0 (0.6)$^{a}$</td>
<td>10.6 (0.26)$^{c}$</td>
</tr>
<tr>
<td>Field 3</td>
<td>5</td>
<td>59.7 (9.9)$^{bc}$</td>
<td>5.0 (0.7)$^{ab}$</td>
<td>11.9 (0.66)$^{c}$</td>
</tr>
<tr>
<td>Field 4</td>
<td>5</td>
<td>44.0 (1.7)$^{ab}$</td>
<td>4.6 (0.2)$^{a}$</td>
<td>9.7 (0.43)$^{b}$</td>
</tr>
<tr>
<td>Field 5</td>
<td>5</td>
<td>46.6 (4.6)$^{ab}$</td>
<td>5.0 (0.4)$^{ab}$</td>
<td>9.4 (0.84)$^{b}$</td>
</tr>
<tr>
<td>Field 6</td>
<td>5</td>
<td>73.7 (2.8)$^{c}$</td>
<td>7.1 (0.8)$^{bc}$</td>
<td>10.7 (0.78)$^{c}$</td>
</tr>
</tbody>
</table>

$^{a}$Samples to a soil profile depth of 1 m, corrected for equivalent weights. See Table 5.1 for a description of the MCSE Conventional system. Field sites 1–6 on the same soil type, under conventional till corn–soybean rotation. Data are means (±SE); means followed by similar letters do not differ significantly at $\alpha = 0.05$.

Source: Morris et al. (2007).
When afforestation includes pines (*Pinus* spp.), soil calcium (Ca) content appears to support SOM accrual in a manner not found under deciduous species (Paul et al. 2003). Addition of Ca to soils following afforestation with pines, and with the addition of pine litter, increased the amount of stabilized SOM and decreased its decomposition rate, confirming the importance of Ca in regulating litter decomposition and SOM dynamics (Brewer 2004). Long-term stabilization of SOM through increased Ca on soils planted to pines could improve site fertility on this and other former agricultural sites on similar soil types. Calcium forms bridges between the SOM and the soil matrix such that its interaction with silt and clay-sized particles stabilizes and increases SOM levels (Baldock and Nelson 2000).

**Pools and Fluxes That Control Soil Organic Matter Dynamics**

A number of studies have provided insights into the mechanisms for SOM accrual in agricultural soils, including: (1) physical protection of partially decomposed plant residues found in inter- and intraaggregate fractions of SOM; (2) biochemical protection of SOM due to a molecular structure that is difficult for microbes to metabolize and is therefore recalcitrant; (3) chemical protection due to SOM associations with silt and clay; and (4) differences in soil biota that affect SOM sequestration and turnover.

Whether the plant residues and their associated biota are free or protected within soil aggregates controls their short-term breakdown (Fortuna et al. 2003). The incorporation of plant and microbial-derived C into aggregates protects plant residues (De Gryze et al. 2004), associated microbial C (Smith and Paul 1990), and microbial products (Paul and Clark 1996) for periods of weeks to decades depending on soil conditions (e.g., clay content and water availability) and management (e.g., tillage and crop rotation). Changes in land use that alter patterns of soil disturbance and the quantity and quality of plant residues will influence aggregate formation and stabilization, resulting in long-term effects on SOM dynamics (Willson et al. 2001).

KBS represents a unique environment in which to study soil aggregation because of the diversity of managed and unmanaged ecosystems that occur in close proximity on a common sand- and silt-dominated soil. There are few comparable places where relationships between aggregation and SOM dynamics can be studied in replicated systems that represent a range of management and chemical inputs. Most studies of soil structural processes and organic-mineral interactions have examined soils with high clay content. Differences in SOM across the seven MCSE systems at the LTER main site, developed since its inception in 1989, are closely associated with changes in soil aggregates, particularly the distribution of SOC in different aggregate size fractions, as indicated by an index of aggregation known as the mean weight-diameter (Fig. 5.4). The Biologically Based and No-till systems have more aggregates in the >2000-µm size class. Strong relationships between aggregation and SOM content indicate that physical protection is a key factor controlling short-term SOM dynamics in KBS soils (Grandy and Robertson 2007).

Density, particle size, and incubation-based measurements have been used at KBS to identify fractions enriched in SOM and sensitive to changes in management
These methods have shown that the greatest C sequestration potential lies in the mineral-associated fractions and in fine, intraaggregate particulate C. For example, Grandy and Robertson (2007) found that 82% of the C increase in the 2000- to 8000-µm size class of the No-till system was due to mineral-associated SOM. Incubation-based methods for separating fractions into active, slow, and resistant pools demonstrated the greatest potential C accumulation in the slow pool (6.5 to 21.4 g C m$^{-2}$ yr$^{-1}$) followed by the resistant (0.66 to 16.05 g C m$^{-2}$ yr$^{-1}$) and active pools (0 to 0.24 g C m$^{-2}$ yr$^{-1}$).

Consistent with these results, De Gryze et al. (2004) found that in the Early Successional system, mineral-associated SOM accumulated C at 5- to 13-fold higher rates than did other fractions, while in the Poplar stands the fastest C accumulation rates occurred in the fine intraaggregate fraction. Soil organic matter pools with higher turnover times, such as the interaggregate pool, are extremely sensitive to disturbance and may show large, rapid changes in response to management. However, these pools do not have the long-term sequestration potential of mineral-associated pools with slower turnover times (Six et al. 2002a, b).

Sollins et al. (2009) used sequential density fractionation to separate KBS soil particles collected from 0- to 25-cm depth into “light” predominately mineral-free organic matter from the “heavy” particles associated with the soil minerals. Quartz, alkali feldspars, vermiculite, and kaolinite are major components of the fraction with density < 2.6 g cm$^{-3}$. Quartz dominates the 2.6–2.8 g cm$^{-3}$ fraction, accounting for 73% of soil dry weight. The primary minerals hornblende, hematite, and epidote account for 2% of soil dry weight. The density of the particles was found to depend on the thickness of their SOM coating as well as the density of the mineral particles themselves.

The <1.65 g cm$^{-3}$ density fraction represented 16% of total soil C with a total lignin-phenol content that accounted for 5.5% of total C. The 1.65–1.85 g cm$^{-3}$
density fraction accounted for 8% of soil C and the 1.85–2.00 g cm\(^{-3}\) fraction for 14%. Phenol and lignin concentrations were lower in the higher-density fractions and the C:N ratio decreased with density. The \(^{14}\)C-based MRTs measured by Sollins et al. (2009) ranged from 108 years in the 2.00–2.30 g cm\(^{-3}\) density fraction to 165 years in the <1.65 g cm\(^{-3}\) fraction and 225 years in the 1.65–1.85 g cm\(^{-3}\) fraction. The heaviest densities (>2.80 g cm\(^{-3}\)) had an average MRT of 1050 years. The average MRT for all densities was similar to the MRT of 420 years shown for KBS soil in Table 5.2.

Incubation-based measurements can also identify fractions enriched in SOM and sensitive to changes in management. As noted earlier, Paul et al. (1999a) used long-term incubations to show how only 5 years of MCSE management affected SOM fractions. From 10 to 15% of total SOC was oxidized during their 365-day incubations, with the highest CO\(_2\) production occurring in soils with the higher SOC contents (Table 5.5). The active fraction, as defined by curve fitting of the CO\(_2\) evolved early during incubation (Paul et al. 1995, 2001b; Horwath et al. 1996), represented 1.8–3.3% of the SOC. This is equivalent to half the C content of the interaggregate fraction of SOC isolated by density fractionation, agreeing with the analysis of Haile-Mariam et al. (2008) that the interaggregate fraction contains some nonlabile constituents. The slow pool represented 41–45% of the SOC and serves as the primary basis for soil fertility and ecosystem SOM dynamics. It is made up, in part, by materials in the intraaggregate fraction and by the more labile components of the silt and clay fractions (18–21%) shown to be corn-derived, based on stable carbon isotope ratios as explained in more detail below (Table 5.6). The interaggregate fraction, measured by density gradient fractionation before aggregate dispersion, is also referred to as the light fraction. The intraaggregate fraction, measured by sieving the >53-μm soil fraction after dispersion, is also often referred to as the particulate organic material.

The 6-M acid hydrolysis treatment used to measure the size of the resistant (non-hydrolyzable) fraction of SOC does not remove modern lignin plant

<table>
<thead>
<tr>
<th>System</th>
<th>SOC Pool (g kg(^{-1}))</th>
<th>CO(_2)-C Produced (% of SOC)</th>
<th>Active C Pool (% of SOC)</th>
<th>MRT (days)</th>
<th>Slow C Pool (% of SOC)</th>
<th>MRT (years)</th>
<th>Resistant C Pool (% of SOC)</th>
<th>MRT (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>8.7</td>
<td>10</td>
<td>2.0</td>
<td>45</td>
<td>42</td>
<td>13.1</td>
<td>56</td>
<td>1435</td>
</tr>
<tr>
<td>Poplar</td>
<td>9.1</td>
<td>13</td>
<td>3.3</td>
<td>66</td>
<td>41</td>
<td>11.0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Early Successional</td>
<td>9.0</td>
<td>15</td>
<td>2.5</td>
<td>36</td>
<td>42</td>
<td>9.0</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Mown Grassland (never tilled)</td>
<td>14.6</td>
<td>15</td>
<td>1.8</td>
<td>30</td>
<td>45</td>
<td>9.0</td>
<td>53</td>
<td>170</td>
</tr>
</tbody>
</table>

\(^{a}\) Long-term incubations (365 days) and acid hydrolysis used to determine pools and residence times. See Table 5.1 for a description of MCSE systems.

Note: CO\(_2\)-C = carbon dioxide–C; ND = not determined.

Source: Paul et al. (1999a).
constituents or some microbial cell walls (Paul et al. 2006, Plante et al. 2006), and thus, the non-hydrolyzable fraction contains some young C. However, it contains mostly old C and provides a reasonable estimate of the size of the resistant fraction required for modeling purposes. Carbon dating of this fraction in native KBS forest surface soils yields a MRT of 977 years (Table 5.2). The MRT of bulk soil C in the upper 20 cm of cultivated KBS soil was 546 years (Paul et al. 2001a) relative to 422 years for the native forest soil (Table 5.2), indicating that some labile C had been lost on cultivation and not replaced by more recent plant inputs.

Plants with the C\textsubscript{4} photosynthetic pathway have higher \(\delta^{13}C\) isotope ratios (expressed as \(\delta^{13}C\) in parts per million or ‰) as compared with C\textsubscript{3} plants. Typically, C\textsubscript{4} plants such as corn, sorghum, and switchgrass have \(\delta^{13}C\) values of –10 to –14‰ as compared to values of –22 to –30‰ in C\textsubscript{3} plants such as soybean, wheat, and alfalfa. This difference has been used to measure the dynamics of the inter- and intraaggregate particulate material and the SOM associated with silt and clay fractions. The growth of corn for 10 years on a KBS site adjacent to the MCSE that was formerly dominated by C\textsubscript{3} plants allowed Haile-Mariam et al. (2008) to examine SOM dynamics using \(\delta^{13}C\) analysis of soils from the field before and after 800 days of incubation. The interaggregate fraction, which represents partially decomposed plant residues (as shown by C:N ratios of 21:1), still had 45% non-corn C after 10 years of continuous corn, showing that even interaggregate fractions contain some old C (Table 5.6). This increased to 72% noncorn C by the end of the incubation, showing the difference in lability between the corn and non-corn C. Mid-infrared spectroscopic analysis of this fraction showed that a small

<table>
<thead>
<tr>
<th>Property</th>
<th>Interaggregate</th>
<th>Intraaggregate</th>
<th>Silt</th>
<th>Clay</th>
<th>Whole Soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of soil C</td>
<td>4.5</td>
<td>20.4</td>
<td>17.5</td>
<td>48.5</td>
<td>100</td>
</tr>
<tr>
<td>C:N (by mass)</td>
<td>21</td>
<td>15.2</td>
<td>10.0</td>
<td>8.5</td>
<td>10.4</td>
</tr>
<tr>
<td>(\delta^{13}C) ‰</td>
<td>–18.2</td>
<td>–20.7</td>
<td>–23.5</td>
<td>–23.2</td>
<td>–23.4</td>
</tr>
<tr>
<td>Corn-derived %C</td>
<td>55.7</td>
<td>38.1</td>
<td>18.4</td>
<td>21.2</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Field soil, day zero

Incubated, day 800

| % of soil C                           | 2.9            | 25             | 18.4  | 47.4  | 100        |
| C:N by mass                           | 20.4           | 14.0           | 8.8   | 7.7   | 8.8        |
| \(\delta^{13}C\) ‰                 | –22.2          | –22.9          | –24.4 | –23.6 | –23.2      |
| Corn-derived %C                       | 27.7           | 22.7           | 11.9  | 19.8  | 20.5       |
| Corn C MRT (years)                    | 3.9            | 11.4           | 10.9  | 16.5  |            |
| Non-corn C MRT (years)                | 19.7           | 33.4           | 47.1  | 40    |            |

Table 5.6. Properties of SOC and \(\delta^{13}C\) analysis of soils from continuous corn sites adjacent to the MCSE.\textsuperscript{a}

\textsuperscript{a}SOC fractions determined by long-term incubation.

Note: MRT = mean residence time.

Source: Haile-Mariam et al. (2008).
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The intraaggregate SOC fraction obtained by breaking apart aggregates to release the SOC protected by aggregation showed that only 38% was corn-derived C (Table 5.6). Thus, 62% of the intraaggregate fraction was more than 10 years old. A C:N ratio of 15.2 indicates that accumulation of microbial biomass lowered the C:N ratio from that of the interaggregate fraction. The clay fraction was enriched in SOC relative to the silt fraction and 21% of its C was corn-derived in contrast to 18% in the silt fraction. This indicates that the SOM components of these fractions are primarily composed of materials greater than 10 years old, with a mixture of both young and old SOM components.

Data from this 800-day incubation confirm δ13C field data in that the interaggregate fraction lost nearly half its C during the 800 days (Table 5.6). But there was an increase in the proportion of intraaggregate C, indicating the formation of new aggregates during the incubation. The drop in corn-derived C in the silt fraction during incubation showed turnover in this fraction even though most of it was old. Harris et al. (1997) used δ13C to calculate the MRT of corn-derived vs. noncorn, older C. The MRT of the corn-derived interaggregate C was 3.9 years vs. 19.7 years for the noncorn C (Table 5.6), showing that although older, the noncorn residues were still decomposing. The corn-derived C in the intraaggregate fraction, with an MRT of 11.4 years, is part of the slow SOM pool as defined by incubation and curve fitting for kinetic analysis (Paul et al. 2001b). The 34.4-year MRT of the noncorn C in the interaggregate fraction was older than that of the slow pool determined by incubation (Table 5.6). The MRTs of the corn and noncorn C were determined using δ13C, as described in Harris et al. (1997). The MRTs of the corn-C in the silt and clay fractions (10.9 and 16.5, respectively) reflected the length of time that corn was grown (10 years), while the noncorn C MRT for both fractions was greater than 40 years.

A comparison of Tables 5.2 and 5.6 shows that much longer MRTs are obtained for the soil C from 14C dating than from incubation and δ13C analysis following a C3–C4 plant switch. The radiocarbon dates represent the accrual of SOM over a pedogenic (soil formation) time scale. The δ13C values are a function of the length of time since native C3 plants were replaced by C4 corn. Both dates are correct, but the history of the switch and the turnover of the SOC pools must be taken into account when interpreting and modeling tracer data (Andrén et al. 2008).

The pool size and MRT data in Table 5.5 were used to mathematically model the emission of CO2 from the Conventional system in 1994 (Fig. 5.5). The timing of the CO2 flux was influenced by rainfall and temperature in the field. Predicted CO2 emission based on the data in Table 5.5 and using the CENTURY model corresponded well to measured values during the summer (Paul et al. 1999a). This shows the reliability of the concepts used for modeling and the measurements of pool sizes and their MRTs (Basso et al. 2011) based on long-term incubation and tracers. However, the model did not accurately predict field fluxes for the fall season. This is likely because the model assumes that once harvest is complete, the residue is available for decomposition, whereas in fact aboveground residues are not immediately incorporated into soil; there is also a physical conditioning period before decomposition that is not adequately represented in the models.
A number of approaches are available to examine the molecular-biochemical structure of SOM components (Clapp et al. 2005). Two of the newest and most useful techniques are mid-infrared (mid-Ir) spectroscopy and pyrolysis followed by mass spectroscopy.

Mid-infrared (mid-IR) spectroscopy is a nondestructive measurement of the organic functional groups in both bulk soil and its fractions (Fig. 5.6). Mid-IR spectra show selective absorption by specific SOM functional groups, including OH, NH, aliphatic OH, carboxyl OH stretch, carbohydrates, aromatics, and N compounds, and indicate differences between soil fractions (Calderón et al. 2011). The mid-IR spectra show preferential absorptions of OH, NH, and aliphatic CH bonds in the interaggregate fraction. These are most often associated with partially decomposed plant residues. The intraaggregate and silt fractions show little absorption in these regions, but much higher absorption at 2000–1200 cm\(^{-1}\), indicating a greater presence of carboxylic and aromatic groups. The high, mid-IR absorption in the 1700–1000 cm\(^{-1}\) range is attributable to polysaccharides, phenols, aromatics, and protein amides. Some of the minerals present in clays (particularly silica) also absorb in these regions (Janik et al. 2007, Calderón et al. 2011).

Principal components analysis of the mid-IR signal of soil fractions from KBS, Lamberton, Minnesota, Wooster, Ohio, and Hoytville, Ohio, shows similar

![Figure 5.5](image-url)
differentiation among SOM fractions for all four soils (Fig. 5.7), despite different MRTs across these sites (Table 5.2). The interaggregate fraction was well separated from all others, while the intraaggregate and silt fractions were grouped together. The clays clearly separated from other fractions, and the clay fraction in the prairie-derived SOM from Lamberton separated from the forest-derived clays of KBS, Wooster, and Hoytville. Haile-Mariam et al. (2008) used $\delta^{13}C$ to determine the MRT of the SOM fractions of the Hoytville and Lamberton soils. Their analysis showed that the inter- and intraaggregate C$_3$-derived SOC (i.e., noncorn SOC) of the KBS soil was the youngest, which is consistent with the $^{14}C$ dating data (Table 5.2). The KBS soil also had higher SOM turnover rates than the other soils examined, as determined by incubation, carbon dating, and $^{13}C$ field analysis (Collins et al. 1999, 2000; Paul et al. 2001a). These regional comparisons offer a powerful means for identifying general controls on SOM dynamics in larger landscapes (Fierer et al. 2009, Morris et al. 2010).

Figure 5.6. Fourier transformed mid-infrared spectra of KBS soil, including the whole soil and its various fractions. Absorbance bands of different organic functional groups are shown as vertical bars. From F. Calderón (unpublished data).
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Pyrolysis followed by mass spectroscopy, sometimes with prior separation in a gas chromatographic column, identifies molecular breakdown products following heating in an inert environment. These products can be related back to SOM biochemical structures through the use of standards (Grandy et al. 2007, 2008; Plante et al. 2009). As determined by pyrolysis mass spectrometry, agriculture changes the chemistry of SOM, making it more heterogeneous than the SOM in native soil, and the chemical characteristics of the SOM can be related to both soil type and climate (Haddix et al. 2011). Pyrolysis-gas chromatography/mass spectrometry has been used to determine changes in the chemistry of plant litter during decomposition under various MCSE systems. Wickings et al. (2011) observed changes in litter chemistry and in the composition and activity of the decomposer community during decomposition of corn and grass litter in the Conventional, No-till, and Early Successional systems. After one season in the field, grass litter in the Conventional and No-till systems was enriched in total polysaccharides, whereas in the Early Successional system, it was enriched in N-bearing compounds and lipids. Differences in the soil communities—in particular, microarthropods and

Figure 5.7. Principal Components Analysis of the infrared spectra of unincubated surface soil and particle size fractions from the KBS (Michigan), Wooster (Ohio), Hoytville (Ohio), and Lamberton (Minnesota) sites shown in Table 5.2. The percentages of spectral variance accounted for by each component are in parentheses. Modified from Calderón et al. (2011).
fungal/bacterial ratios—were associated with differences in chemistry, indicating
that the activity and structure of the decomposer community can influence chemi-
cal changes during decomposition (Wickings et al. 2011). Results demonstrate that
efforts to predict long-term SOM turnover and stabilization dynamics may therefore
need to consider the influence of different decomposer communities on changes in
litter chemistry during decomposition.

Plante et al. (2009) used pyrolysis-molecular beam mass spectrometry to iden-
tify carbohydrates, N compounds, lignin derivatives, aliphatics, and sterols in SOM.
They found similar overall constituents for forested and prairie soils. Grandy et al.
(2007, 2008) also found similar chemical patterns in the silt and clay fractions from
different ecosystems, supporting the hypothesis of Fierer et al. (2009) that all soils
share similar overall characteristics that are a function of the biota and their physi-
ological constraints. Much of the N resistant to acid hydrolysis was identified as
amino N, indicating the protected proteinaceous nature of the resistant N. This sup-
ports the conclusions of Di Costy et al. (2003) who, by using $^{15}$N-enriched clover
additions and nuclear magnetic resonance analysis, found that the majority of N in
soil is proteinaceous in nature.

The Role of Carbon Inputs and Microbial Activity in Soil Organic
Matter Dynamics

The Fate of Plant Carbon Inputs

The amount and quality of SOM are dependent on the amount and type of
plant inputs as well as their microbial turnover before stabilization. One of the
best ways to examine these factors is the use of carbon isotope tracers. In pre-
vious sections, we noted the importance of the Poplar system for understand-
ing both sequestration of SOM and aggregate formation. The amount of C that
is provided as litter and from the roots is important in these transformations.
Horwath (1993) and Horwath et al. (1994) used $^{14}$C to observe the distribution
of photosynthesis-derived C in the poplar plant, its movement belowground,
and decomposition by the microbial biomass (Table 5.7). Trees were uniformly
labeled in July or September by exposing the foliage to $^{14}$CO$_2$ for a single day and
the movement of $^{14}$C was traced through the plant–soil system by sampling trees
14 and 372 days after labeling.

Roots that accounted for 18.4% of total-tree C accounted for 9.8% of the $^{14}$C
label (Table 5.7). Some of the photosynthate was stored in coarse roots and moved
to fine roots the following spring. During the 3-week labeling period, belowground
respiration accounted for 7.7% of the label taken up by photosynthesis. Microbial
biomass C, accounting for 1.5% of the soil C, received 0.4% of the $^{14}$C, showing
significant turnover during the labeling period. The 0.3% of the label present in the
biomass after 328 days shows a slow turnover of root and microbial C during the
period after labeling, with some transfer to the soil C component. Labeled litter,
added to the soil in a separate experiment, lost 67% of its $^{14}$C content during the first
year, and 73% over a 2-year period (Horwath 1993; Horwath et al. 1994).
The uptake of $^{14}$CO$_2$ by photosynthesis and its later distribution in the plant–soil system in a laboratory-grown sorghum crop showed results quite similar to those found for poplars in the field (Calderón 1997). Fifty percent of the $^{14}$C remained in the aboveground biomass, 30% in the roots, and 6% was transferred to the soil in a 24-day period. Belowground respiration accounted for 12% and shoot respiration for 5% of the label in plants with symbiotic, mycorrhizal fungi. Non-mycorrhizal plants had more aboveground allocation and less allocation to the roots and soil respiration. The mycorrhizal plants did not quite compensate for the needs of their microbial partners by increased photosynthesis, indicating that the fungi can act as both symbionts and parasites (Calderón et al. 2011, 2012).

The Role of Microbial Biomass and Composition

Microbial biomass is an important component of SOM and, in particular, the active fraction that is so important to soil fertility (Paul et al. 1999a, b). Microbes also provide the enzymes required for decomposition and the microbial products that interact with the soil matrix to stabilize SOM (Paul and Clark 1996). Microbial biomass in KBS soils was measured from 1993 to 1996 (Horwath and Paul 1994, Horwath et al. 1996). The bacterial and fungal biomass of the Deciduous Forest soils constituted, on average, 107 mg C kg$^{-1}$ soil and 179 mg C kg$^{-1}$ soil, respectively. In MCSE agronomic systems, the biomass of the bacteria and fungi was nearly equal at 85–89 mg C kg$^{-1}$ soil. The microbial biomass represented 1.2–1.8% of the total soil organic C, and MCSE systems with greater SOM accumulation (No-till and Biologically Based) had higher percentages of microbial biomass.

These values are similar to the 1.5% of soil C measured as microbial biomass in the Poplar system (Table 5.7). Fungal and bacterial biomass in this system were similar during the first few years of growth, but this changed as Poplar
mycorrhizal associations switched from endomycorrhizal (AM) to a mixed endomycorrhizal-ectomycorrhizal (AM-EM) symbiosis. Fungal biomass increased with the addition of extra-radical mycelia associated with ectotrophic mycorrhiza. When the trees were sampled in 1997, both AM and EM fungi were present. Kosola et al. (2004) showed the differential response of these symbionts to environmental conditions: N fertilization reduced AM colonization of roots from 16% to 14% and increased EM colonization from 15% to 18%.

Bacterial communities are also affected by environmental conditions (Schmidt and Waldron 2015, Chapter 6 in this volume) and can be influenced by SOM differences associated with aggregates. Blackwood et al. (2006), for example, found greater inter- than intraaggregate variability in bacterial community structure in a comparison of soils from KBS and Wooster, Ohio. They found a higher number of active bacteria (as indicated by a cell volume greater than 0.18 µm³) within aggregates than elsewhere, indicating potentially higher microbial activity within aggregates. The number of bacteria and the proportion of large, active cells were not affected by the cropping system; the larger bacteria accounted for 30–50% of the number of cells, but composed 85–90% of the biomass (Blackwood and Paul 2003).

The fungi showed more microspatial variability than bacteria (Horwath et al. 1994, 1996). They were larger and more often associated with plant residues than the bacteria. And whereas bacterial biomass varied by a factor of 50% during the growing season, fungal biomass varied by a factor of 100%. Fungi, however, tend to have cytoplasm-free cells, and thus the DNA content of soils may be 80% bacterial even though the two populations may have similar biomass. Harris and Paul (1994) used the incorporation of 3H-thymidine to measure bacterial growth rates and found that the bacteria of the Conventional system soils doubled every 160 days, while those in soils of the Mown Grassland (never tilled) community, which have a higher SOM content, doubled every 107 days.

High seasonal variation in bacterial and fungal biomass during the growing season (Horwath and Paul 1994, Horwath et al 1996) indicates that the microbial biomass is a significant proportion of the active pool of SOM and changes in microbial biomass might be used to manage SOM dynamics and N fertility (Fortuna et al. 2003). This could be especially important when combined with the catalytic effect of rhizosphere microbiota on SOM decomposition. In the KBS Living Field Lab experiment (Snapp et al. 2015, Chapter 15 in this volume), Sánchez et al. (2002, 2004) found that cover crops such as clover increased both intraaggregate SOM and microbial biomass. A corn crop that followed soil N enrichment by a clover cover crop mineralized 168 kg N ha⁻¹ from SOM pools, whereas wheat mineralized only 116 kg N ha⁻¹, and bare soils with roots excluded mineralized 108 kg N ha⁻¹ from SOM pools (Table 5.8).

A corn crop after a clover cover crop contained 168 kg N ha⁻¹ mineralized from SOM pools, as compared to 108 kg N ha⁻¹ of mineralized N in microplots where roots were excluded and 116 kg N ha⁻¹ of mineralized N in a wheat crop (Table 5.8). Soil planted with corn mineralized more C than bare soil with roots excluded. This suggests that microbes stimulated by labile C from the corn rhizosphere specifically degraded N compounds. The role that legumes and cover crops (Harris et al. 1994),
including clover, play in SOM accumulation was described earlier in this chapter. Their ability to provide N for subsequent crops indicates that such rotations should continue to be a dominant component of sustainable cropping systems.

Summary

Twenty years of KBS LTER research have produced a remarkable consensus about controls on SOM dynamics and has furthered our general understanding of long-term changes in SOM in agricultural ecosystems. This understanding includes the concept that although SOM takes many years to develop and includes a continuum of young and old materials, it is sensitive to management changes that can either improve or hinder its role as one of the major controllers of soil fertility and ecosystem functioning. Differences in SOM levels within the soil profile and across landscapes can foster greater biological diversity both above- and belowground, but the high spatial variability of SOM makes it especially difficult to interpret data collected at low frequencies, particularly from only one or two sampling points in time. Thus, long-term studies that allow resampling of the same locations across time offer one of the best opportunities to detect gradual changes in SOM levels, characteristics, and dynamics relative to vegetation influences, cultivation, fertilizers, and cover crops (Robertson and Paul 2000). These will all be affected by global environmental change and the need for increased production of food and biofuel crops in the future.

Results from KBS show that variation in SOM content and dynamics occurs across the landscape even on relatively flat terrain with only shallow depressions. Lower, wetter areas accumulate SOM most rapidly. Soils in these areas receive higher inputs of crop residue and also receive eroded materials from upper slopes, thus increasing their SOM content and water-holding capacities. Soils in so-called steady state after many years of cultivation can continue to slowly lose SOM. Both erosion and the change in SOM, with consequent alterations in aggregation, can significantly affect soil bulk density, an important soil physical property. Changes in bulk density can introduce uncertainty into estimates of soil C change when measurements made from soil cores are compared across time.

Table 5.8. Effect of corn and wheat roots on nitrogen (N) uptake during crop growth and nitrogen and carbon (C) mineralization subsequent to cropping.

<table>
<thead>
<tr>
<th></th>
<th>N Supplied by Soil (kg ha⁻¹)</th>
<th>N Mineralized after Crop (mg N kg⁻¹ soil)</th>
<th>C Mineralized after Crop (mg C kg⁻¹ soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare soil</td>
<td>108</td>
<td>70</td>
<td>525</td>
</tr>
<tr>
<td>Corn</td>
<td>168</td>
<td>22</td>
<td>780</td>
</tr>
<tr>
<td>Wheat</td>
<td>116</td>
<td>45</td>
<td>680</td>
</tr>
</tbody>
</table>

*The field study was conducted at the KBS Living Field Lab, adjacent to the MCSE.

Note: Bare soil = microplots with roots excluded.

Source: Sánchez et al. (2002).
The complex, multistructured, multicomponent pool of organic materials constituting SOM includes: (1) decomposing plant residues, (2) associated microorganisms and their products, and (3) the biochemically transformed (“humic”) fraction. KBS LTER studies have shown that all these components can be associated with Ca, minerals, and sesquioxides that greatly increase their MRTs. Long-term incubations to allow microorganisms to metabolize labile components, together with stable isotopic tracers to identify sources and acid hydrolysis to quantify the resistant fraction, have provided a useful framework to interpret SOM dynamics at KBS.

Interpretation of the long-term incubation results distinguishes three pools for modeling purposes—the active, slow, and resistant fractions—although SOM is known to represent an oxidation continuum (Paul et al. 2001b). The active pool representing the most labile components is small at ~5% of the SOM, and is composed of some of the interaggregate plant residues measured by physical fractionation. The active pool also contains a portion of the microbial biomass and has MRTs of months to a few years. This pool is important in the management of nutrients on a growing season basis. The slow pool, with MRTs ranging from months to decades, accounts for ~40% of total SOM. This is the major source of soil nutrients that change with management, often requiring 6 to 7 years to show measurable differences in yield and soil sustainability. The dynamics of the slow pool are controlled by aggregation (intraaggregate SOM) and the association of microbial products with Ca, as well as the silt and clay fractions. The intraaggregate fraction measured by physical separation also has young and old constituents, but on average has MRTs of decades. The silt and clay SOM fractions and the nonacid hydrolyzable residues have the longest turnover times. They also contain the largest concentrations of aluminosilicate minerals and sesquioxides. The actual mechanism of stabilization of the oldest SOM in soils (the resistant pool) has yet to be determined.

Soil organic matter is a dynamic system with some components that can change rapidly with changes in management and environmental and biotic controls, while other components respond very slowly. The fractions we have identified, while reflecting these controls, are not discrete. For example, in young fractions, such as those protected by aggregates, there is a small amount of old C, possibly charcoal. The older component, such as the SOM associated with clays, can also have a small amount of young C, such as that coming from absorbed microbial biomass constituents. The MRTs and pool sizes we have measured have been useful for interpreting the effects of management practices, as well as providing fundamental knowledge of the basic controls affecting SOM dynamics.

The recent use of molecular-structure analysis to measure the biochemical composition of SOM provides insights into SOM dynamics (Paul et al. 2008). The major components derived from plant and microbial products such as carbohydrates, proteins, and related N compounds, lignins, sterols, aromatics, and fatty acids are readily identified by pyrolysis-mass spectrometry. These constituents vary with ecosystem type and management. However, they also illustrate the effect of microbial processing under unifying controls in that the molecular structure of SOM also shows significant similarities among different soils. In addition, there are some unidentified organic components that have century-to-millennia turnover rates.
The old, resistant SOM fraction, identified by its resistance to acid hydrolysis, consists of some aromatics and long-chain aliphatic materials as well as protected carbohydrates and proteins closely associated with sesquioxides and clays. Mid-IR spectroscopy that identifies functional groups in both the organic and inorganic soil constituents clearly shows different functional groups in the inter- and intraggregate fractions, with higher plant residue components in the interaggregate fraction. Clay and silt components are also clearly differentiated. Principal Components Analysis of KBS soil fractions, relative to other soils in our landscape comparison, shows more similarities within fractions than between soils, except that the prairie-derived clays were clearly separated from those in the forest-derived sites, such as those from KBS.

Microbial biomass, shown in our studies to represent approximately 1.5 to 3% of the soil C, plays a major role in decomposition and provides the intermediate products that are stabilized as organic matter. Fungi, which are equal in biomass to bacteria in many of our agricultural systems, are more variable over time and in their management responses. They provide a larger proportion of the biomass in the forested sites, where ectomycorrhizae are important. The soil biota, together with their breakdown products, are especially significant in the legume-based systems. Our studies have shown that the use of a clover cover crop in rotation results in a greater active SOM pool (Nannipieri and Paul 2009). This SOM pool can be accessed by the rhizosphere organisms of corn, and to some extent wheat, to provide much of the N required for plant growth. Clover cover crops should thus continue to be studied and used for their capacity to both fix N and release available N to succeeding crops (McSwiney et al. 2010).

The challenges of providing a sustainable food supply and a variety of resilient ecosystem services (Paustian et al. 1996, 1997; Robertson and Paul 1998; Bhardwaj et al. 2011) in the face of global climate change are closely related to the molecular composition of SOM and its interactions with physical, biotic, and chemical controls. The studies summarized in this chapter have laid an important baseline for many years to come as interacting processes and controls continue to be elucidated.

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