Introduction
Soil carbon is one of the most poorly understood global carbon pools. This is partly due to the difficulty and expense of current techniques available to measure soil organic matter (SOM) components and changes and partly due to spatial variability and the difficulty of obtaining representative samples. As a result, the uncertainty in SOM knowledge is so great that opposition exists to giving credit for soil carbon sequestration in international greenhouse gas negotiations. The perception is that it will be difficult, if not impossible, to verify claims that carbon is actually being absorbed and retained in soils, a problem that is compounded by the fact that the dynamics and chemistry of SOM are not well understood. The work described here begins to address the need to develop and demonstrate analytical techniques that can rapidly provide information on soil carbon concentration and chemistry, information that is crucial to verifying carbon uptake and storage in the largest terrestrial pool—soil.3,4

A primary component of soil organic matter comes from the decomposition of biomass-derived materials. The resulting humic substances vary greatly in their decomposition rates, and when accurately measured, provide a foundation for estimating the uptake of carbon in soils. Separating and measuring these components with classical techniques is both difficult and complex. Most soil analyses require mechanical preparation, extraction and one or more chemical analyses; processes which are time consuming and labor intensive. Moreover, some analyses may not be representative of the original material due to the harsh chemical separations used.

We have developed the py-MBMS technique for analyzing a wide range of large and complex biomolecules that include lignins, cellulosic materials, plastics, and polymers. Schulten details the application of pyrolysis field ionization mass spectrometry to identify SOM components. This work applies MBMS analyses to whole soils. At each of the sites, only mineral soil was sampled and 5-cm cores were taken as a function of depth. Samples were dried and sieved through a 2-mm screen prior to MBMS analysis. Soil samples (~0.1 g) were weighed in quartz boats in triplicates and pyrolyzed or combusted in a reactor consisting of a 2.5 cm quartz tube with helium flowing through at 5 L/min (at STP). The reactor tube was oriented so that the sampling orifice of the molecular-beam mass spectrometer (Figure 1) was inside the end of the quartz reactor. We used a molecular beam system comprised of an ExterITM Model TQMS C50 mass spectrometer for both pyrolysis and combustion vapor analysis. The reactor was electrically heated and its temperature maintained at 500°C or 800°C. Total pyrolysis time was 5 minutes and combustion time 2 minutes. The residence time of the vapors in the reactor pyrolysis zone was estimated to be ~75 ms. This residence time is short enough that secondary cracking reactions in the quartz reactor are minimal. We used a soil reference material (Carbosba, Milan, Italy, PN 33840026) containing 3.55 wt% C and 0.37 wt% N to calibrate the m/z 44 (CO2) and the m/z 30 (NO) mass spectral peaks.

![Figure 1. Schematic representation of the molecular beam sampling mass spectrometer (py-MBMS) system. The soil samples were introduced into the heated quartz reactor for pyrolysis and combustion analysis.](image)

Mass spectral data from 15-350 amu were acquired on a Teknivent Vector 2M data acquisition system using 22eV electron impact ionization. Data acquisition was continuous, through digitization of electron-multiplier signals from the arrival of positive ions and programmed storage in an IBM PC computer. Repetitive scans (typically one 300 amu scan/s) were recorded during the evolution of a pyrolysis or combustion wave from each soil sample. The stored spectra could be manipulated to give average spectra, subtracted spectra, or time evolution of different masses. Using this system, both light gases and heavy molecules are sampled simultaneously and in real time. We used multivariate data analysis (pattern recognition) to handle mass spectral data sets and identify trends to discover the underlying chemical changes that may not be obvious by comparison of such complex mass spectra.5,6

Results and Discussion
Figure 2 shows the weight percentages (wt%) of total carbon and nitrogen obtained from combustion-MBMS data from agricultural soils managed for hybrid poplar production. Hybrid poplars, which
grow rapidly, are biomass energy crops. Three sites were sampled in depth increments of 0-5, 5-10, and 10-20 cm. Total carbon (C) and nitrogen (N) contents are the average of two separate samples per site. Site 1 is fallow after one rotation of hybrid poplar, site 2 is currently in a second rotation of hybrid poplar, and site 3 is adjacent unmanaged sagebrush. All samples exhibited decreasing C and N contents with increasing depth. The fallow soil contained the least total carbon and nitrogen likely because of soil disturbance from harvesting the rotation. The soil in the second rotation of poplars contained about twice as much C and N as the fallow site and the amounts were approximately equal in the deeper increments. The unmanaged sagebrush contained the most C and N in the 0-5 cm increment and C and N contents in the 5-10 and 10-20 cm increments were about equal to those of the second rotation. The high C and N content in the 0-5 cm sagebrush increment may be attributed to the presence of dense fine roots from the sagebrush. These preliminary results show the utility of combustion-MBMS method for rapidly determining total C and N contents.

Figure 2. Total carbon and nitrogen contents of soils from a hybrid poplar plantation. Soil cores were taken in depth increments of 0-5, 5-10, and 10-20 cm. The first site (left 3 samples) was fallow after one rotation of poplar had been harvested, the middle 3 samples come from a site in a second rotation of poplar, and the 3 samples on the right are from adjacent unmanaged sagebrush.

Figure 3 shows mass spectra from the pyrolysis of soil samples taken from the Tionesta Scenic and Research Area in northwestern New York. These forest soils, which come from a site vegetated with 600-year old virgin beech hemlock, were chosen for maximum SOM carbon content. Figure 3a shows the pyrolysis mass spectrum for the 0-5 cm depth increment and Figure 3b the spectrum from the 15-30 cm increment. Comparison of the spectra shows that the shallow increment contains pyrolysis products characteristic of more recent biomass decomposition (carbohydrates, lignin) and the deep increment contains more degraded forms of biomass (phenolics, nitrogen-containing compounds).

These preliminary results show that py-MBMS can distinguish the chemical changes that occur with depth. Recent biomass is characteristic of shallow samples and more aromatic species, representative of more degraded biomass, are found in the deeper samples. This technique can also distinguish among samples of different ecological sites. With continued development, this rapid analytical technique offers the opportunity to greatly increase our understanding of the role of SOM in carbon sequestration and carbon cycling, and to assess how forest and agricultural management practices can enhance that role.

References