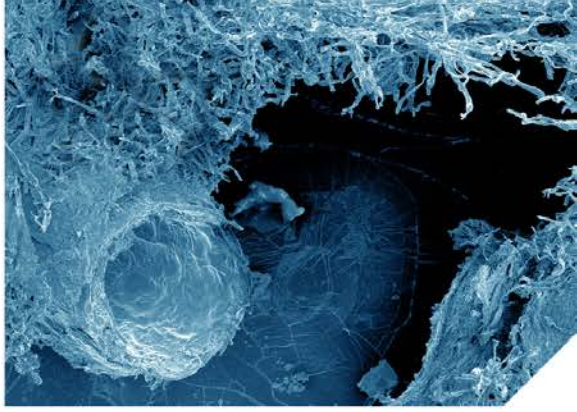
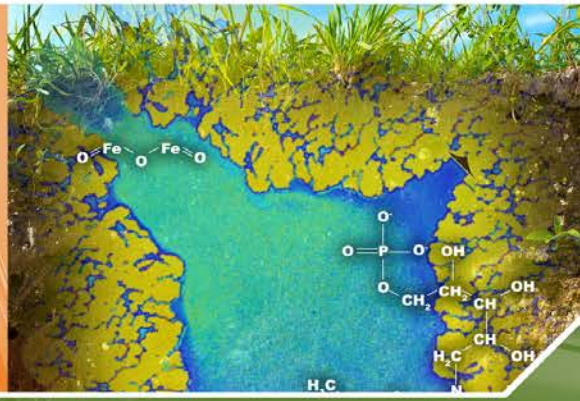
Belowground Carbon Cycling Processes at the Molecular Scale



Science Theme Advisory Panel Workshop



Workshop Date: February 19-21, 2013

Report: October 2013

EMSL

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Belowground Carbon Cycling Processes at the Molecular Scale

An EMSL Science Theme Advisory Panel Workshop

Workshop Date: February 19-21, 2013

Prepared for the U.S. Department of Energy's Office of Biological and Environmental Research under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

As part of the Belowground Carbon Cycling Processes at the Molecular Scale workshop, an Environmental Molecular Sciences Laboratory (EMSL) Science Theme Advisory Panel meeting, attendees discussed critical biogeochemical processes that regulate carbon cycling in soil. They concluded by offering recommendations for future EMSL activities:

1. Representation of soil organic matter (SOM) in terrestrial carbon cycle models as a fast, slow, and stable C pools is recognized as flawed. Soil C persistence, in general, is not solely a function of its chemical resistance to biological degradation. Rather, it depends on its situational context. EMSL's current work and investments in the characterization of SOM using high-resolution mass spectroscopy (HR-MS) and nuclear magnetic resonance (NMR) already have helped to redefine soil processes. Continued investments in this area, the integration of nano secondary ion mass spectrometry (nanoSIMS) capability, and the high-resolution mass accuracy capability (HRMAC) are encouraged and should lead to improved mechanistic models of soil C stability under changing climatic conditions.
2. There is a fundamental gap between molecular and nanoscale research on the biogeochemical interactions between soil C, minerals, and microbial ecosystem and field-scale measurements and modeling. EMSL's pore-to-intermediate scale capabilities are ideally and uniquely suited to bridge this "mesoscale gap" and look at the impact of pore geometry, soil water, and oxygen availability on biogeochemistry. There are no other institutions equipped to approach this challenge. EMSL's efforts to model water flow in unsaturated, porous media at fairly small scales could contribute enormously to characterizing how dynamic soil water content affects microbial habitat, substrate supply, and activity.
3. Fine root dynamics are poorly understood and represented in current models. Yet, they have large impacts on the origin of soil C. There is potential to integrate several EMSL tools to address this problem, including x-ray and magnetic resonance tomography, spatially resolved HR-MS, and advanced fluorescence microscopy techniques.

Acronyms and Abbreviations

BER	Office of Biological and Environmental Research
CESD	Climate and Environmental Sciences Division
CESM	Climate and Earth System Modeling
CLM	Community Land Model
DOE	U.S. Department of Energy
DOM	dissolved organic matter
EcM	ectomycorrhizae
EMSL	Environmental Molecular Sciences Laboratory
FACE	Free-Air CO_2 Enrichment
FTICR	Fourier transform ion cyclotron resonance
GT	gigatons
HR	hydraulic redistribution
HR-MS	high-resolution mass spectroscopy
MS	mass spectroscopy
nanoDESI	nanospray desorption electrospray ionization
NMR	nuclear magnetic resonance
NOM	natural organic matter
NPP	net primary production
PNNL	Pacific Northwest National Laboratory
SC	Office of Science
SIMS	secondary ion mass spectrometry
SOM	soil organic matter (materials)
STAP	Science Theme Advisory Panel
STXM	scanning transmission x-ray microscopy
TES	Terrestrial Ecosystems Science

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1.0 Workshop Background and Purpose

The Environmental Molecular Sciences Laboratory (EMSL), a Department of Energy (DOE) scientific user facility located in Richland, Washington, provides premier experimental and modeling/simulation capabilities for molecular-level research on energy and environmental needs facing DOE and the nation. By periodically engaging experts from the scientific community, EMSL identifies opportunities for future investments in capabilities that will lead to impactful scientific results in targeted research areas to address programmatic priorities within DOE's Biological and Environmental Research (BER) program. Recently, BER's Climate and Environmental Sciences Division (CESD) issued a strategic plan for all of the research programs and user facilities within the division. One of the five goals articulated in the CESD Strategic Plan is to develop, test, and simulate process-level understanding of atmospheric systems and terrestrial ecosystems, extending from the bedrock to the top of the vegetative canopy.

This Science Theme Advisory Panel (STAP) workshop—*Belowground Carbon Cycling Processes at the Molecular Scale*—identified opportunities for future investments in capabilities that will help researchers funded by CESD programs address this specific CESD goal. The workshop was aimed at identifying key biogeochemical processes that regulate carbon cycling in the subsurface biosphere because one objective of CESD's Terrestrial Ecosystem Science program is to gain: "a mechanistic understanding of the role of subsurface processes (e.g., microbiology, geochemistry, root/rhizosphere, soil processes) in the terrestrial carbon cycle."[1]

Improved representation of the processes that control carbon allocation and fluxes at the terrestrial/atmospheric interface in landscape and regional climate models ultimately will lead to reduced uncertainty in global climate models. As a user facility, EMSL can provide the tools and expertise needed to elucidate the molecular foundation that underlies mechanistic descriptions of these biogeochemical processes. Consequently, the goal of this workshop was to identify the science gaps that hinder either development of mechanistic description of critical processes or their accurate representation in climate models.

[1] DOE-SC 0151. 2012. *Biological and Environmental Research Climate and Environmental Sciences Division Strategic Plan*. Available online at: http://science.energy.gov/ber/news-and-resources/.

2.0 Belowground Carbon Cycling

In the terrestrial ecosystem, approximately 120 gigatons (GT) of carbon are removed by photosynthesis annually. Nearly half is returned to the atmosphere by plant respiration and another half via microbial respiration and biomass decomposition. However, soil stores approximately 2300 GT that is potentially vulnerable to release into the atmosphere, and these are primarily concentrated in arctic regions (DOE/SC-108; IPCC 2007). Understanding the processes involved in this delicate balance and how they will respond in future climatic conditions is a major objective for multiple government agencies.

Earth system scientists and policy makers rely on large-scale terrestrial ecosystem models, such as the Community Land Model (CLM) (Oleson et al, 2010; Lawrence et al, 2011) to make predictions of carbon cycle responses to climate change decades into the future. The large uncertainties associated with future predictions limit the acceptance and utility of these models' results, and efforts are underway to identify and minimize the origin of these uncertainties. However, model development and validation have proven difficult for two major reasons. First, some belowground processes (such as hydrologic and geochemical impacts on C cycling) are inadequately or not at all represented in these models. Second, the belowground processes that impact C allocation and cycling are inherently complex and operate on spatial and temporal scales spanning several orders of magnitude. The issue of how complex, multiscale processes may be represented in next-generation C cycle models—in a way that significantly improves predictive power—remains to be resolved.

Belowground ecosystems are diverse and heterogeneous. The processes and mechanisms that operate belowground are complex, often coupled, and vary widely on temporal and spatial scales. The study of belowground biogeochemical processes is especially difficult because they are concealed from direct, *in situ* observation and measurement. Despite the complexity and ecosystem-dependent variability, there are critical elements and processes that impact the C cycle common to most belowground ecosystems (see Figure 1). However, the relative importance may vary from ecosystem to ecosystem.

How the C cycle is perturbed by changes in atmospheric carbon dioxide concentration, temperature, and rainfall is of particular interest. Some key elements of the belowground C cycle include:

- Microorganisms including bacteria, archaea, and fungi
- Root life cycle, structure, and function
- Mycorrhizal associations
- Soil structure
- Soil mesofauna
- Soil C chemistry
- Soil mineral geochemistry
- Soil water dynamics.

Each of these elements is complex enough in its own right to be separate research fields or considered in widely separated research fields. Likely, limited communication between research communities has been an impediment to the development of a comprehensive understanding of the belowground C cycle across disciplines.

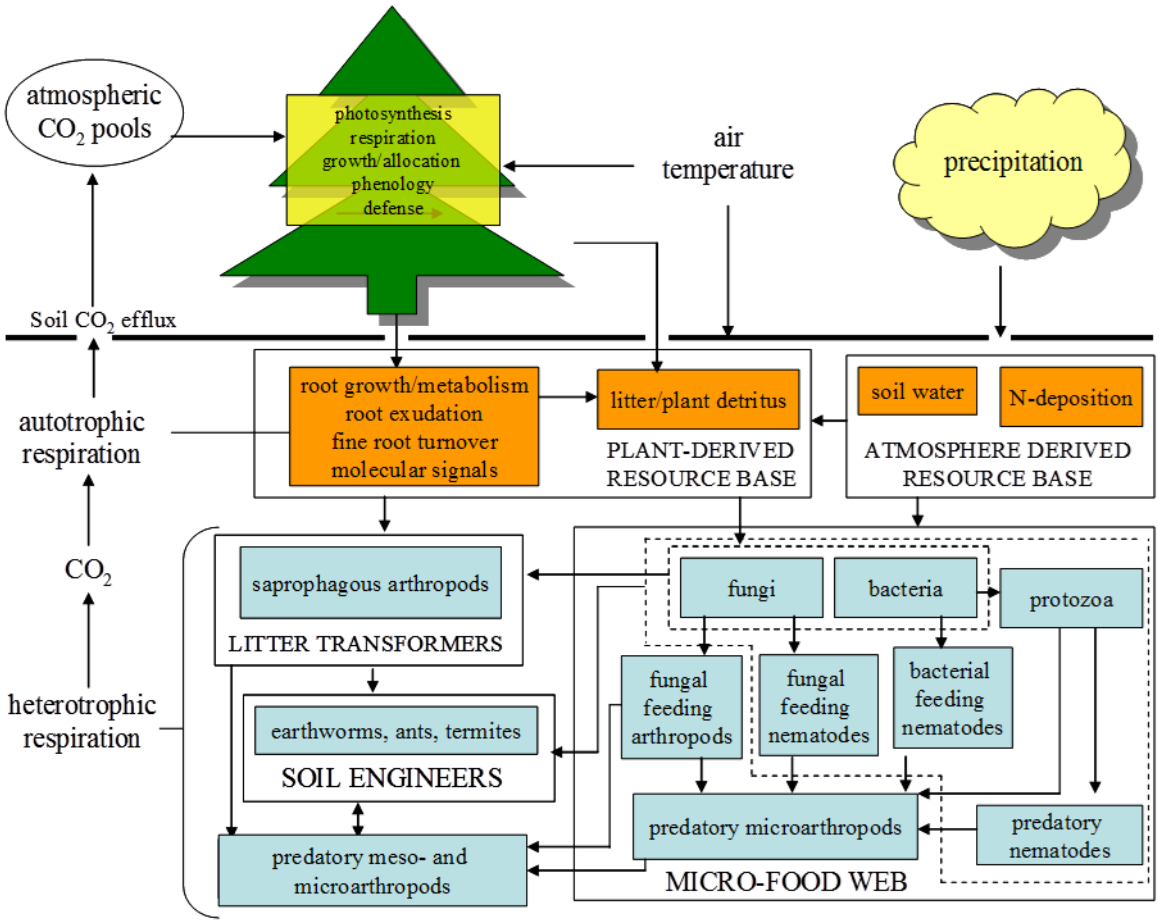


Figure 1. Schematic representation of some key elements and processes of the belowground terrestrial ecosystem that impact C cycle (from Pritchard 2011).

At all scales, system functionality and belowground processes result from the interdependencies, feedbacks, and linkages between many, if not all, of these system components. Furthermore, common words and terms can evolve to have nuanced meanings, sometimes complicating communication between research communities. For example, "mineralized" in geochemistry implies the formation of a mineral, while "mineralization" in soil ecology implies the conversion of the organic form of a nutrient, such as nitrogen in amino acid into one of its "mineral" forms, NH_4^+ or NO_3^-.

Discussions at the Belowground Carbon Cycling workshop focused on two main areas: 1) soil C and 2) roots and their influence in the belowground C cycle. The discussion in each of these topical areas is described in greater detail herein. Science gaps that align with EMSL capabilities and expertise were identified as were recommendations for EMSL investments.

Terrestrial Carbon Cycle Models

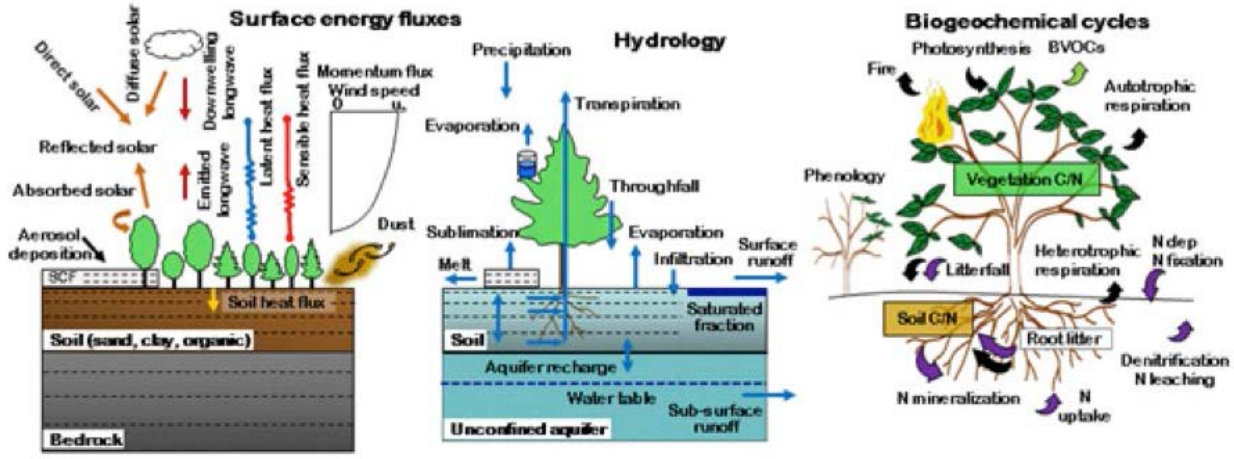


Figure 2. Major components of the Community Land Model

Terrestrial C cycle models range in complexity and scale from empirical annual time-step models to full representations of the land-surface integrated within Earth system models capable of representing complex feedbacks resulting from climate, land-use history, CO_2 fertilization, disturbance, and nutrient cycling. The latter model categories continue to increase rapidly in process complexity and spatial resolution, usually requiring high-end computing facilities to run global simulations. This continual push for model improvement has advanced the state of the science considerably and has been supported both by substantial funding commitments and exponential growth in computational power. Yet, as seen in multi-model intercomparisons (e.g., CMIP5 or the North American Carbon Program interim syntheses), uncertainties in key global variables of interest (e.g., the net carbon land-atmosphere exchange in the Year 2050) remain high (Friedlingstein et al. 2006). Regional uncertainties are even higher, seriously complicating planning for decision makers at local and national scales. Such model intercomparisons provide useful diagnostics, but they seldom provide definitive answers about which model processes or parameters drive the large uncertainties. In addition, danger exists that these ensembles portray overconfidence in their predictions despite already large uncertainties because these models share many similar components or may all be missing essential processes. Thus, they may fail to account for the full range of uncertainties.

Recently, there has been more focused efforts to better integrate a wealth of data from observation networks and experiments for model development, uncertainty quantification (UQ), and validation. Clearly, new model-data fusion studies are vital toward answering questions about model parameters, as well as structural and driver uncertainties. However, the infrastructure to perform these studies currently is lacking. One first step is an inventory and synthesis of existing data sets. Can these data be used for model testing? If not, then either the model or data may need to be rescaled for a more direct comparison. For example, the model may be missing a required process or data may need to be scaled temporally or spatially. As models begin to be tested simultaneously against data constraints across multiple scales, they will provide more realistic predictions and uncertainty estimates. New observations and experiments then could be prioritized by testing them within models for their ability to constrain and reduce uncertainties about key processes.

Key questions:

1. What is the current strength of the terrestrial C sink and/or source and how will this sink evolve over decadal-to-century timescales due to feedbacks between the C cycle, socioeconomic factors, and changing climate?

2. What are the best land management strategies to maximize both the sink strength and the lifetime of stored C to mitigate potential climate change effects?
3. Are there critical tipping points in the climate/C system, and are these related to processes that are not well represented in current models?
4. How can variables in C cycle models best be constrained with existing observations from molecular to grid cell (100 km^2) scales?
5. What processes need to be added to models to take advantage of molecular-scale data, and how can these data be scaled or transformed to match existing model processes?

These questions are directly relevant to belowground processes. In particular, an assessment of the strength of the terrestrial C sink requires knowledge of the processes that transfer reduced C into soil and allow C to persist belowground and how those processes will be impacted by climate change. This concept is explored in more detail in Section 4 regarding soil C, which addresses soil C characterization, the formation and distribution of soil C, and soil C persistence.

3.0 Soil Carbon

Soil organic matter (SOM) has been studied intensively for over a century. However, within the last one to two decades, many of the foundational concepts concerning SOM have come under intense scrutiny. Recent review articles by Schmidt et al. (2011) and Conant et al. (2011) provide excellent perspectives on how the conceptual framework for soil C has moved toward a more process-based understanding. Many details of the processes that form and stabilize soil C remain to be understood and incorporated into numerical terrestrial C cycle models.

SOM is composed of hydrocarbon compounds that can include other elements, such as nitrogen and phosphorous, as well as metal cations. Traditionally, SOM has been functionally described in terms of soil C pools with different decomposition rates or residence times. However, there is growing recognition that SOM is a continuum of decaying organic compounds stemming from direct biological origin without any acquired or inherent stability. This perhaps is best encapsulated in the following from Hedges et al. (2000):

> *Organic matter is a thermodynamic anomaly atop a free energy precipice that drops off on all sides to dispersed, stable ingredients such as carbon dioxide, water, nitrate and phosphate*.

The persistence of soil C results from its situational ecosystem context rather than any inherent chemical property. This emerging perspective is illustrated in Figure 3.

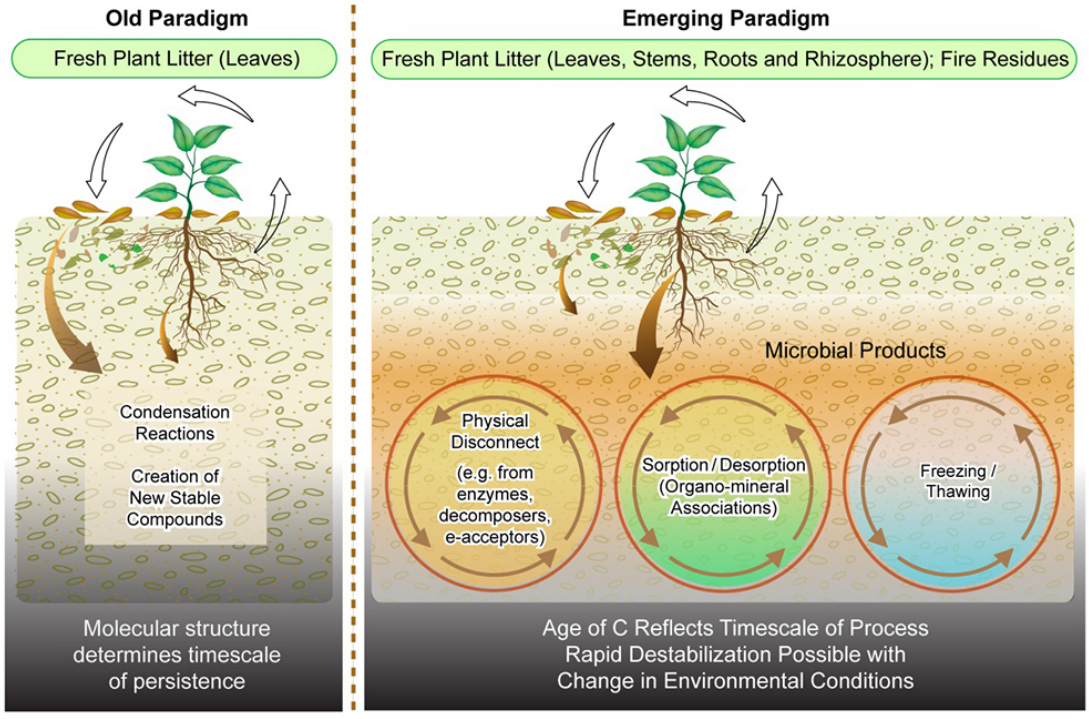


Figure 3. Comparison of old and emerging paradigms for C cycling belowground. Leaf litter was the primary source of SOM in the old paradigm and decomposed by a series of condensation reactions to form increasingly persistent C pools. Multiple sources are considered in the emerging paradigm and persistence is related to the situational environment (from Schmidt et al. 2011).

SOM traditionally is thought of as being composed of recognizable, non-humic substances (e.g., lipids, carbohydrates, proteins) and polymeric, highly aromatic, "recalcitrant" macromolecules (humic substances) produced by secondary

metabolism but of unknown molecular structure. Alternatively, SOM has been viewed recently as a highly heterogeneous mixture of biomolecules in various stages of defragmentation, depolymerization, and oxidation (Schmidt et al. 2011; Kleber 2010; Kleber et al. 2007; Wallenstein et al. 2013).

Both traditional and modern perspectives agree that SOM is complex. Recent characterization using ultra-high resolution mass spectrometry (HR-MS) has shown SOM to be composed of identifiable classes of organic molecules of biologic origin, including lipids, carbohydrates, proteins and lignin, and biochar, which may or may not contain a high content of aromatics (Baldock et al. 1992; 1997). However, they also can be present as complex hybrids of biomolecules, such as polyphenol-protein complexes, lignocelluloses, glycoproteins, lipoproteins, polyphenol-polysaccharide complexes, cutins, suberins, and thermally transformed products thereof.

Models such as CLM must be modified to reflect the evolving understanding of belowground processes leading to soil C formation and stability. To affect these changes, improved soil C characterization techniques are needed, as well as better understandings of soil C formation, vertical distribution, and persistence.

Soil C Characterization. Bulk characterization techniques commonly used for SOM analyses do not provide sufficient molecular detail to discern the processes that form or stabilize soil C or to test hypotheses that have been recently introduced (Schmidt et al. 2011). In fact, the limitations of standard methods likely have hindered the development of process-based conceptual models (see sidebar, "Limitation of SOM Characterization"). Advanced characterization methods have not been applied to SOM because SOM is difficult to isolate from soils. Other than the O (organic) horizon, which is largely composed of organic matter, deeper horizons typically contain more than 95% mineral components. Organic matter in these horizons can be tightly associated with mineral particles or complexed with metal ions. Extracting SOM from these horizons is difficult, and no known separation technique achieves full separation between the mineral and organic matter. In addition, the extraction processes themselves can result in altered or transformed SOM complexes not found in the natural environment. Often, the resulting characterization of SOM in a given soil is assembled from results from sequential extraction (dissolved organic matter (DOM), alkaline extracts, etc.) or analysis of SOM association with different mineral fractions (polycyclic organic matter (POM), silt/clay associated, etc.) that may result in incomplete analyses because of strong bonding to the mineral surface. The question remains whether the resulting assembled characterization is adequate to provide the needed information and if the characterization technique provides unbiased representation of the SOM constituents.

SOM Extraction Protocols

- Alkaline extraction
- Water extracts (DOM)
- Organic solvent extraction
- Acid hydrolysis
- Wet oxidation
- Mineral dissolution
- Density separation

The intrinsic heterogeneity of SOM at nearly any spatial scale is a prominent challenge to SOM characterization. The composition and distribution of SOM within soils also will vary temporally in response to environmental and ecosystem changes. However, the heterogeneity observed in SOM reflects the intimate relationship between SOM and the processes that form and degrade it. Thus, characterization of SOM has the potential to elucidate those processes and form the basis for a conceptual framework of SOM formation and stabilization once molecular characterization techniques are routinely used.

Assessing the functionality of chemical moieties is equally important to the identification of individual molecules of SOM. Both measurements have merit, and the level of detail relevant is most likely linked to the scale of the observation and science question. For example, the identification of specific organic molecules pre- and post-microbial inoculation can provide valuable information about the consumption and production of metabolites in a system, whereas understanding the impact of pH on organic molecules adhered to a clay surface may only require knowledge of the change in the type or distribution of binding ligands. Fortunately, recent advances in spectroscopic imaging and mass

spectrometry techniques have the potential to make significant advances in both of these areas. These approaches and their application to specific research problems are discussed in Appendix A.

Vertical Distribution. Simplistically, the vertical distribution of SOM in the soil profile encompasses three discrete and functionally distinct compartments in mineral soils: 1) the litter layer, 2) topsoil, and 3) subsoil. Figure 4 summarizes the characteristics of each compartment. The litter layer contains leaf litter and other surface materials that are not considered SOM until they start to decompose. Within this layer, there is high concentration of mesofauna (earthworms, insects, nematodes, etc.) that physically and chemically begin the decomposition process. The underlying topsoil has the highest concentration of organic matter and microorganisms per gram of soil. Thus, it is a zone of high biological activity. The underlying subsoil, which reaches to the regolith, may contain as much organic matter as the topsoil, but it is distributed over a greater volume of mineral soil.

While much is known about how climate, litter quality, and decomposer community composition affect the rate at which plant litter is decomposed, litter decomposition rates are of little importance to the long-term net ecosystem C and N balance (reference). Instead, what really matters is the proportion of plant litter C and N eventually incorporated into SOM and further stabilized by spatial inaccessibility in small aggregates or interactions with minerals. Hence, both empirical studies and predictive C cycle models need to address the controls on soil formation and stabilization rather than overly focusing on decomposition and C loss. An improved basis for determining the proportion of net primary production (NPP) sequestered over different time scales is necessary to predict how it may be affected by global climate change.

Limitation of SOM Characterization

Our current understanding of soil C is largely based on batch extraction approaches. These approaches underpin many historical advances in soil science. However, they also have two limitations: 1) they reveal nothing of how C and its chemical forms are organized in the soil fabric, and 2) these approaches may alter the intrinsic chemistry of the C. For instance, the classic pH-based extraction procedures used for quantifying soil humic, fulvic, and humin fractions result in soluble and precipitated C pools that reveal little about where these C pools are located, nor do they identify discrete compounds present in the soil.

Recent advances in chemical imaging, spatially resolved mass spectroscopy tools, and other integrated approaches are improving descriptions of native soil C. This is advancing soil science beyond describing how soil C changes with depth toward the development of models of how soil C compounds associate with different mineral microsites. One benefit of such findings will be to consider soils in terms of the types of microbial habitats they host. This may allow us to differentiate between chemically recalcitrant and physically protected C and then predict quantitatively the vulnerability of soil C under different environmental conditions.

Still, the wide spatial variation in local C chemistry within a soil and among different soils will hinder these advances. However, it may be possible, with a focused and interdisciplinary effort, to develop an understanding of factors that contribute to the organization of C within the soil fabric that may transcend sites. These factors probably are system-wide and include local climate, plant associations or root types, soil texture, and disturbance history.

Vanessa Bailey

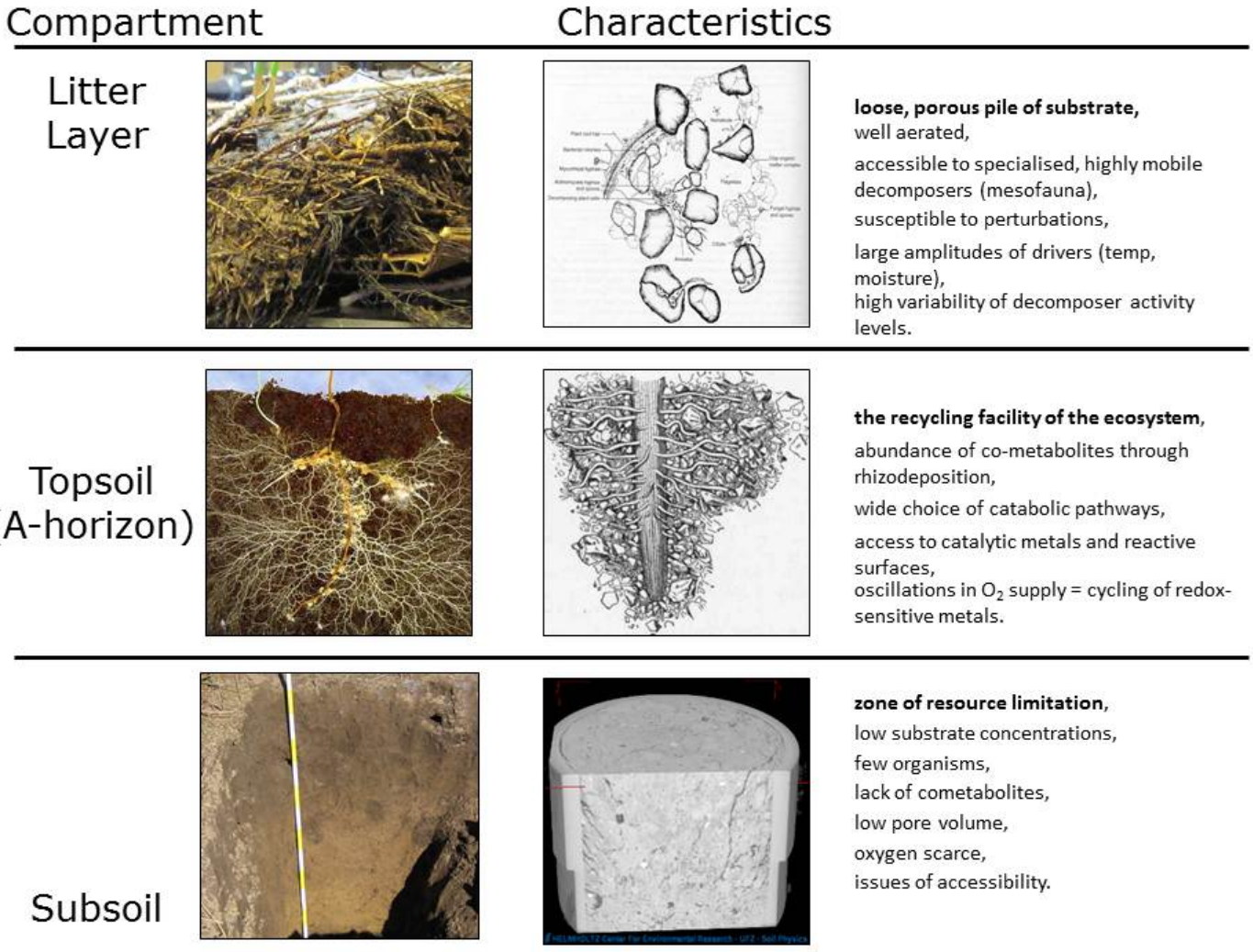


Figure 4. Vertical distribution of SOM. The three layers can be distinguished by SOM concentration and biological activity (from Kleber, unpublished).

SOM Formation. SOM formation rates are controlled by both biotic and abiotic processes. First, soil organisms affect the rate at which detritus is depolymerized, and the transformation of detritus into novel metabolites. In turn, the soil organism community composition and metabolic efficiency is controlled by long-term abiotic and ecological drivers and short-term fluctuations in temperature, moisture, and substrate availability. SOM stabilization rates are controlled via the interaction of microbial products with the soil mineral matrix and through biologically influenced soil aggregate formation. Figure 5 depicts the interdependencies of these soil formation and stabilization processes.

In most ecosystems, the highest concentrations of organic matter per gram of soil occur at shallow soil depths, and much of the current understanding of SOM formation comes from shallow soils. However, it also is important to understand the occurrence of SOM in the subsoil. First, more than 50% of the belowground ecosystem C stores are located at depths greater than 30 cm from the surface (Rumpel et al. 2011). Second, SOM at depth tends to be more persistent. As a result, deep SOM may represent the long term portion of the soil C pool in terrestrial ecosystems. For these reasons, it is important to understand deep soil SOM formation, transport, and degradation processes so they can be represented in terrestrial C models.

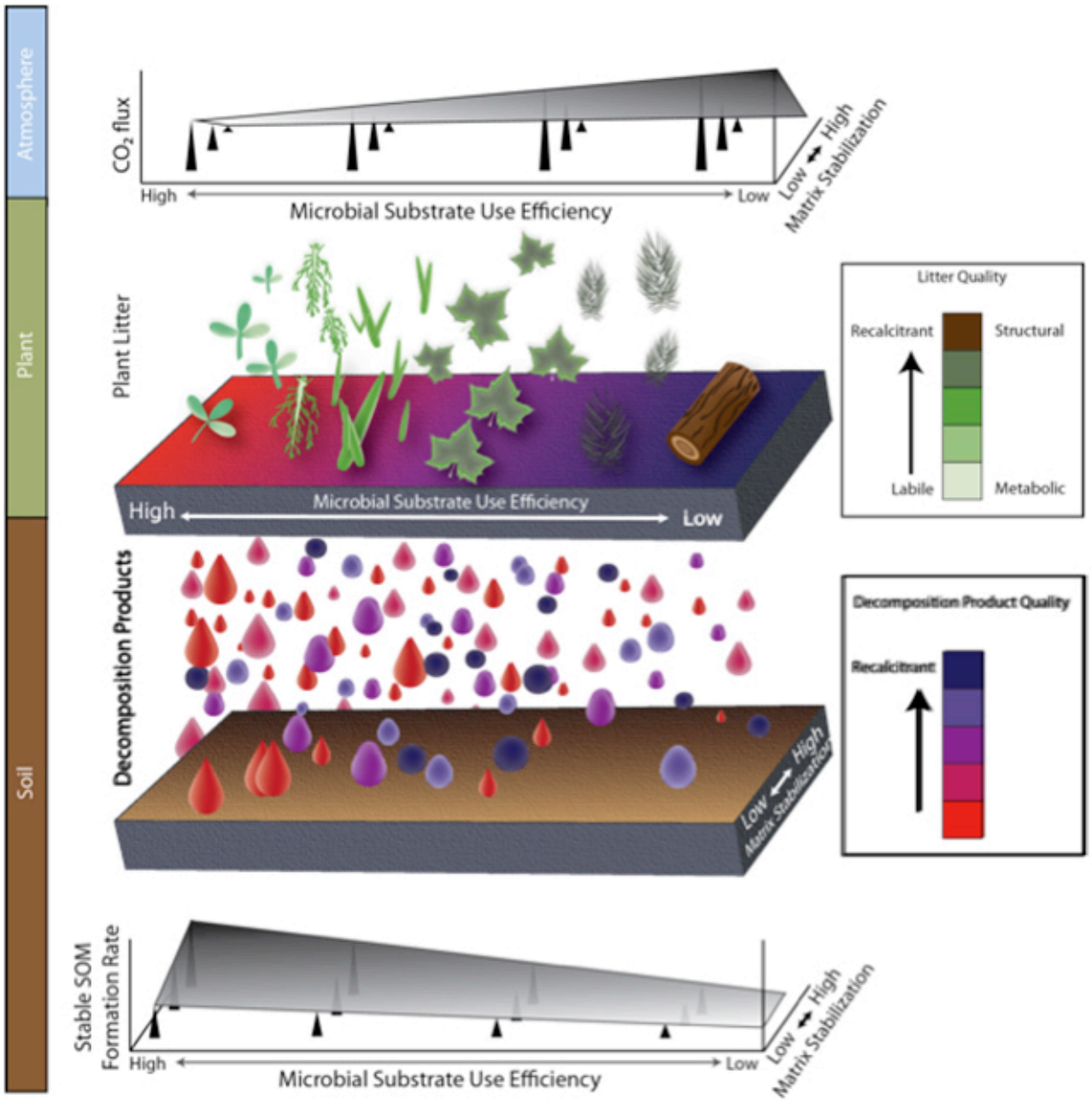


Figure 5. Representation of the effects of plant litter quality on CO_2 efflux and SOM stabilization in the Microbial Efficiency-Matrix Stabilization (MEMS) framework (from Cotrufo et al. 2013).

The flow of organic matter from roots to belowground soil and the extent that this varies by environmental and soil factors to alter SOM are not yet fully understood. As shown in Figure 6, the magnitude of this knowledge gap increases with depth in the soil profile (Sollins et al. 2007; Rumpel et al. 2011). Deep SOM has been characterized at a number of local, regional, and global scales. However, large gaps in the knowledgebase about the cycling and residence time of deep SOM related to plant-microbial-environment interactions still exist (Jobbagy and Jackson 2000).

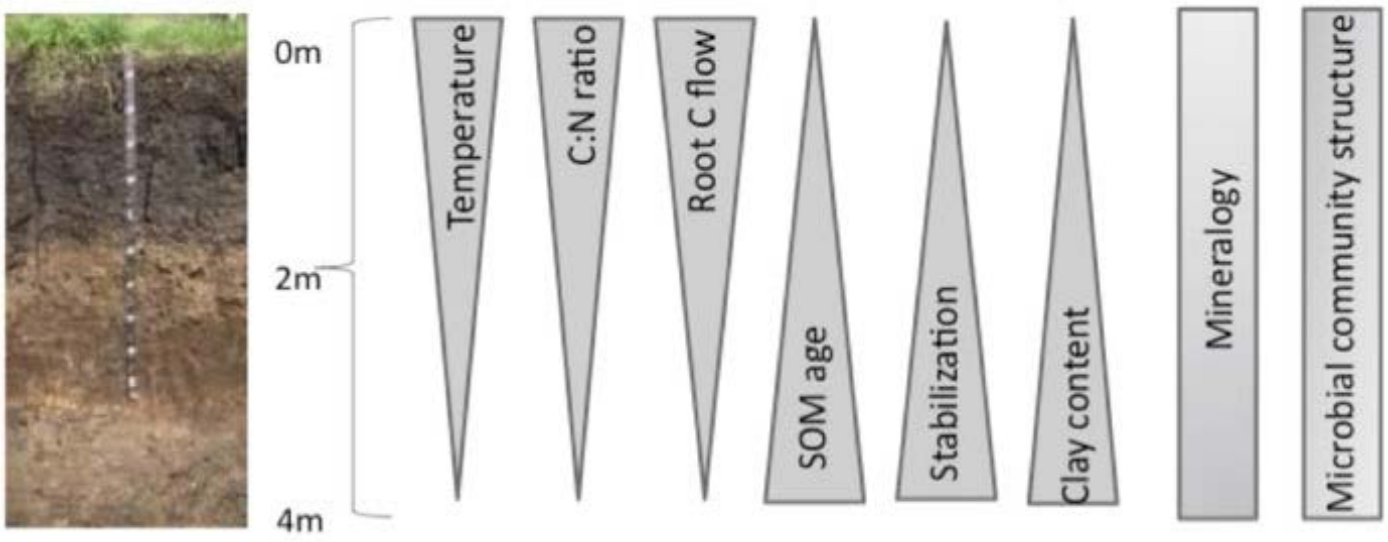


Figure 6. Depiction of the parameters that impact SOM formation and stabilization as a function of depth in the soil profile. Wedge width indicates reflects current understanding of the change in the magnitude of that parameter with depth (from Williams, unpublished).

SOM Persistence. The amount of time organic matter spends in the subsurface biosphere is a function of mineral protection (adsorption), accessibility (physical separation from the decomposer), the presence or absence of a decomposer organism with a matching catabolic capability, and the availability of resources that the decomposers need to function (oxygen, nutrients, co-metabolites). This contrasts with the traditional view that SOM persists in soil because some of it forms very complex molecular structures that are "biochemically protected" and able to resist the decomposer organism. In this regard, "biochemical protection" means organisms are unable to degrade this type of organic matter because of the complex nature of the chemical structure or composition. Common measures used to assess the degree of biochemical resistance to decomposition include: degree of solubility in aqueous solution; bond energy; average carbon oxidation state; number of functional different C bonds; and amount of C remaining after oxidative, hydrolytic, and solubilizing treatment of the original soil C. Large molecular size and activation energy are other assumed attributes.

The correlation between molecular size and decomposition rate has been studied by Fierer et al. (2005). They have shown that for some organic molecules with nearly the same molecular mass, degradation rates can vary by an order of magnitude, whereas those with similar degradation rates can have molecular masses that differ by more than order of magnitude (see Figure 6). The correlation between molecular structure of organic matter, its origin, and its residence time in soil also has been investigated using stable isotope methods. While some chemical compounds are particularly short-lived in soils (e.g., glucosamine), there are no classes of chemical compounds, other than black carbon, that can explain the long lifetimes of 100 to 500 years measured for natural SOM based on stable isotope measurements (Amelung et al. 2008; Schmidt et al. 2011).

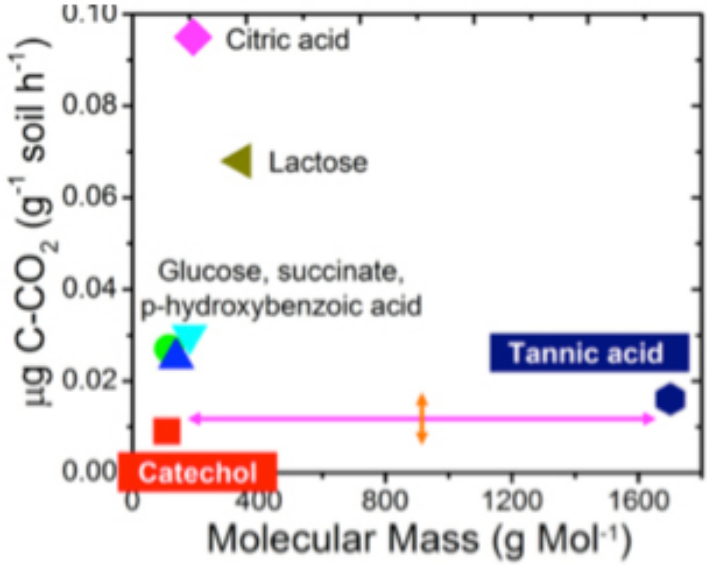


Figure 7. Graphical representation illustrating the lack of correlation between decomposition rate and molecular size (from Fierer et al. 2005).

As a result of these new findings, a competing hypothesis to explain SOM dynamics is based on the concept that soil architecture, pore structure, and pore connectivity, together with soil logistics, can have a significant influence on SOM degradation processes. "Soil logistics" that vary with soil depth and can impact SOM dynamics include: presence and activity of mesofauna; large amplitude variations in temperature, soil moisture, and microbiota (microbes, fungi, mycorrhizal associations); abundance of co-metabolites; and geochemistry of soil minerals. For example, the rate of SOM oxidation can be limited by the O_2 diffusion in soil pores. With soil depth, the pores become more O_2 limited. As a result, some SOM molecules may persist longer due to reduced O_2. In addition, the overall composition of SOM likely will vary with depth because some SOM components (e.g., carbohydrates) require less O_2 for complete oxidation to CO_2 than others (e.g., lipids). Particularly important in wetlands is the inactivation of phenol oxidases under anoxic conditions and the accompanying inhibition of the decomposition of aromatic compounds and buildup of inhibitory phenolic substances (Freeman et al. 2001; Limpens et al. 2008). For more information, refer to "SOM in Peatlands" sidebar.

The "decomposability" of a substrate is best assessed within its situational context which is a function of: 1) its accessibility within the soil pore space; 2) the decomposer community makeup (mesofauna, fungi, bacteria, archaea, etc.); and 3) the availability of catalysts (enzymes) and other resources (O_2, H_2O, mineral nutrients, catalytic mineral surfaces)As a result, research on SOM stability in the terrestrial ecosystem needs to move away from focusing on solely on chemical characteristics of SOM and instead consider the "design" or assemblage of the belowground ecosystem. Then, these new insights must be incorporated into numerical models of the terrestrial C cycle. Six important mechanisms that can impact the residence time of C in soils are described briefly (as follows).

Composition and activity of the decomposer community. Decomposers (mesofauna, fungi, bacteria, archaea) evolve with the ecosystem and usually are most efficient in decomposing substrates they are adapted to, a frequently reported phenomenon called "home field advantage" (e.g., Wallenstein et al. 2013). Adaptations exist for all naturally occurring substrates, including lipids and aromatic compounds in lignin (termites, white rot fungi, and ligninolytic bacteria can all depolymerize lignin, for example). A mismatch between substrate properties and available decomposer adaptations will slow or even inhibit decomposition. The availability of catabolic tools (enzymes) that match the available organic substrate properties is another closely related mechanism. Enzyme production by decomposer organisms is regulated by complex feedback mechanisms. These have been described by Schimel and Weintraub (2003) among others.

Accessibility of organic substrates within the pore system of the soil architecture. The accessibility of organic substrates can be restricted in two ways. The organic substrates may become physically separated from decomposers by incorporation into soil aggregates, or they also may be separated from decomposers when the architecture of the pore system inhibits diffusive mass transport or migration of decomposers.

Interactions with mineral surfaces. The adsorption of substrates to mineral surfaces is known to reduce decomposition rates (Kalbitz et al 2005; Kleber and Johnson, 2010). The energetic stability of mineral-organic interactions is a function of mineral surface properties and organic molecular features and plays a role in controlling the decomposition rate of adsorbed organic compounds.

Availability of co-metabolites. Decomposition of complex organic compounds, such as lignin, has been shown to rely on the availability of co-metabolites, which may serve as a C source, energy source, or complexing agents to enable the increased metabolic effort that often seems required to initiate the decomposition process.

Availability of other resources (O_2, H_2O, mineral nutrients, catalytic surfaces/metals, etc.). Metabolic pathways and strategies among decomposer organisms in the soil are manifold and strongly dependent on electron acceptor type, nutrient availability, soil moisture content, and other resources.

Freezing conditions. A huge part of global C stocks are contained in permafrost soils (Tarnocai et al. 2009). Once the permafrost thaws, this organic matter will become available for decomposition.

SOM in Peatlands

Recent research in upland ecosystems questions the importance of chemical recalcitrance of organic matter and emphasizes the dominant role of mineral-organic complexes in the protection of SOM. However, many wetlands accumulate very high levels of organic matter, which, at its extreme, results in peatlands with very little mineral matter to stabilize SOM. Wetlands contain about 33%—peatlands about 27%—of the global soil C pool, so the factors that control SOM dynamics in these ecosystem is of particular concern. The ability of wetlands to accumulate C has been variously ascribed to waterlogged and anoxic conditions, low pH, low temperatures, and the chemical recalcitrance or inhibitory effects of the SOM derived from some plant species. Dissolved organic C and the solid organic phase in peatlands both have very high concentrations of aromatic substances. Moreover, many wetland plants have high concentrations of inhibitory compounds (phenolics and various cell wall components of *Sphagnum* mosses), suggesting a role for organic matter chemistry beyond the traditional concept of chemical recalcitrance. The enzyme-latch hypothesis suggests that the inactivity of phenol oxidase exoenzymes due to anaerobic conditions allow this accumulation of phenolic and aromatic compounds, and, as a consequence, SOM accumulates over millennia in peatlands.

However, it is a facile answer to suggest that peatlands exist simply because they are waterlogged. So, why do all wetlands not become peatlands? If they are completely drained, all peatlands eventually have their SOM oxidized, although this can take a century or more. Still, moderate drainage of some peatlands has led to increased SOM accumulation because of increased plant productivity. Many peatlands have a seasonally aerated zone (the "acrotelm") that can be up to a meter deep during a substantial portion of the warm growing season. The ericaceous shrub vegetation of some peatlands makes for very high phenolic concentrations in peat, regardless if it is waterlogged, that have well documented inhibitory effects on many biogeochemical processes. Many bogs have very low potential to make methane and accumulate the fermentation product acetate, even under permanently anaerobic conditions. Thus, the (at least) seasonal anaerobic conditions characteristic of all wetlands must interact with other factors to allow for peat accumulation. Furthermore, SOM also has been demonstrated to be an important electron acceptor under anaerobic conditions in peatlands.

It is difficult to imagine that the general principles emerging from the terrestrial literature about the limitations of the concept of chemical recalcitrance of SOM do not apply to peatlands. Clearly, peat, under the appropriate artificial conditions, can be decomposed rapidly as any SOM, but it is not degraded in nature, even under prolonged conditions of drought or partial drainage. Under anaerobic conditions, it still can make very little methane, a potent greenhouse gas. Peatlands provide an example of the multiple roles that SOM can play: it simultaneously is a microbial substrate, an antibiotic, and an electron acceptor. The relative roles that SOM plays in any particular peatland depend on the specific set of biotic and abiotic conditions. The hydraulic properties of peat also control the development and persistence of peatlands on the landscape in a highly dynamic process. Given the large amounts of soil C stored in these ecosystems and their importance as a global source of methane, much greater research needs to be focused on these questions. Until their underlying dynamics are better understood, prediction of climate change effects on their C dynamics by models will be inherently limited.

Scott Bridgham

Key questions and recommendations for future research:

1. Soil C protection mechanisms
   - How chemically distinct are the organic molecules found inside micro- and macro-aggregates from those found outside of aggregates?
   - How do small molecular weight, multifunctional organic molecules order on mineral surfaces?
     - Do ordered multi-domain layers, such as those proposed herein, exist on surfaces?
     - Do they order spontaneously to a low energy state out of a mixture of these molecules, or do they arise from the "depositional history" of this surface?
     - What conditions cause them to re-order or not, e.g., wet/dry cycles, changes in ionic strength?
2. Soil C formation and stabilization
   - What controls the accessibility of substrates to extracellular enzymes, and what are the approaches to model them?
   - What are the controls on microbial substrate use efficiency, and what are the approaches to incorporate this concept into models and parameterize them?
   - Can we easily identify measurable traits of microbial communities that improve the ability of models to predict C cycling?
   - Can we elucidate the chemical transformations that occur during decomposition and transformation of litter and SOM and how they vary under differing conditions?
   - How does deep SOM form, and what fraction of SOM forms at depths relative to the fraction that is transported to depths?
   - Do the same mechanisms that result and modulate SOM formation in shallow soil operate at depth, or do the processes that oxidize SOM operate more slowly at depth?
   - Are there mineral associations protecting SOM, or subclasses of SOM, that are more prevalent at depth, such as the abundance of clay and silt?
   - How do these processes vary across local, regional, and global scales, and can they be represented in C cycle models?

4.0 Plant Roots and the Carbon Cycle

Roots are an important component of the global C cycle because nearly half of the biomass of most plants resides belowground and because most SOM is derived from root derived inputs. There is much unknown about controls of belowground C allocation; magnitude and heterogeneity of root production and senescence (turnover); and root exudates' impact on rhizosphere interactions, including mycorrhizal associations—are all of these details important, and how do they scale in terrestrial C cycle models?

In the CLM, roots are represented using a fixed, prescribed depth distribution based on plant functional type. There are different root pools for fine and coarse roots or for live structural or juvenile roots. The C allocation to roots is a fraction of NPP, which decreases slightly as NPP increases. Roots do not play an active role in driving above-ground growth beyond meeting the plants' demand for water and nutrients. Roots also supply C for heterotrophic respiration. Root turnover is linked entirely to leaf turnover. As a result, in evergreen plants, the portion of roots that turnover is a fixed constant fraction of root biomass. Meanwhile, in deciduous plants, fine root turnover increases with leaf turnover during senescence. Hence, when there are no leaves, there are no fine roots. Mycorrhizal associations are not explicitly represented.

It is recognized that terrestrial C models, such as CLM, should have a more realistic representation of root dynamics and function. Some key improvements include root phenology; the allocation of C; and realistic representations of the growth of fine and coarse roots, especially in response to changes in atmospheric CO_2 concentrations (see sidebar "Root Distributions in Response to Elevated CO_2"). However, before these improvements can be made, there are many details of root processes that must be better understood. These include fine root senescence; C:N ratios; and quality of C variation with root depth, age, function, and order, as well as with mycorrhizal associations. Some of these topics are discussed in more detail herein.

Fine roots. Historically, fine roots have been defined as those roots with a diameter smaller than 2.0 mm. These roots are extremely numerous compared to larger-diameter roots and may account for 99% of total root length and 20% to 30% of total root biomass in some forests (Lynch et al. 2013; Taylor et al. 2013). These small-diameter root modules are a key component of the global C cycle because their frequent turnover accounts for 10% to 60% of total forest NPP (Jackson et al. 1997; Ruess et al. 2003) and results in the transfer of large amounts of organic C into the soil. For example, fine root turnover was the source of 75% to 80% of soil organic carbon and nitrogen accumulated in a sweetgum plantation, and the remaining 20% to 25% was derived from canopy litter and turnover of roots >2 mm in diameter (Lynch et al. 2013). The movement of reduced C into the soil through fine roots can take several pathways including: 1) exudation of organic molecules of variable molecular weights; 2) sloughing of root cap, epidermal, and cortex cells during root growth and aging; 3) direct transfer of carbohydrates to mycorrhizal fungi, where they either respire C or exude low-molecular-weight organic molecules; and 4) death of entire root modules. Despite their importance, only a rudimentary understanding exists of how endogenous (i.e., phenological and ontogenetic) and exogenous (temperature, soil moisture, atmospheric CO_2 concentrations, soil nutrient availability) factors interact to control soil carbon flow through fine roots into SOM pools.

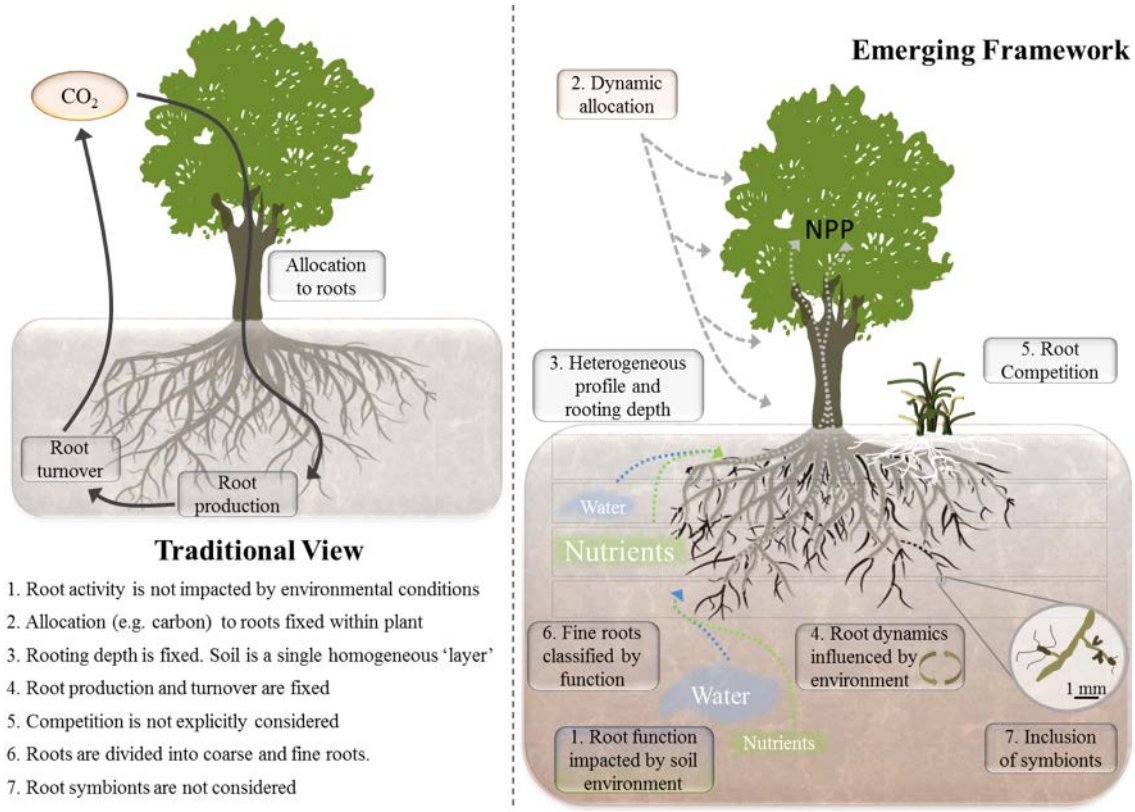


Figure 8. Schematic illustrating the differences between the traditional representation of roots in terrestrial C cycle models and the emerging understanding (from Smithwich et al., unpublished).

Not only do fine roots quantitatively transfer significant amounts of organic matter into soil, they also represent the nexus between C, N, and phosphorus biogeochemical cycles (Yuan et al. 2011). For example, a large share of a plant's carbohydrate budget is expended to construct and maintain fine roots to acquire N and P from soil pools.

The fine-root-mediated exchange of C for N is a highly regulated process influenced by the stoichiometry of plant photosynthate production to plant-available mineral nutrients (Finzi et al. 2007). For instance, when carbohydrates are plentiful relative to soil nutrients, allocation belowground to support nutrient acquisition by fine roots and their mycorrhizal fungi generally increases. Therefore, fine root processes exert significant control over the fate of SOM pools because the influx of root-derived materials controls the expansion of soil C stocks (sequestration), while, simultaneously, stimulation of saprophytes by labile root exudates or sloughed root structures can lead to depolymerization/oxidation of

Root Distributions in Response to Elevated CO_2

Ecosystems have rooting distributions that vary from shallow- to deep-rooted (Jackson et al. 1996). How this rooting distribution changes in response to elevated CO_2 was one focus of the Free-Air CO_2 Enrichment (FACE) experiments. At Oak Ridge National Laboratory's FACE Sweetgum plantation, elevated atmospheric CO_2 resulted in the increased production of fine roots and distribution of roots at greater depths. Deeper roots may result from increased competition between roots and microbes for N. However, rooting depth and distribution also can be notably impacted by the depth to water table (shown in SPRUCE FACE experiments in a black spruce bog) (Iverson et al, 2011; 2012). In arctic ecosystems, the rooting distribution may have an important influence on the soil C:N ratio and ecosystem C and N cycling.

Colleen Iversen

SOM and contraction of total C pool sizes. Subtle changes in the balance of these activities will determine if soils function as sinks or sources of C in the future.

Mounting evidence indicates the understanding of global soil C cycling is significantly hindered by the lack of comprehension regarding which roots within the <2.0 mm category function as ephemeral modules and which function as long-lived structural elements (Strand et al. 2008; Chen and Brassard 2012). Based on observations that Orders 1–3 exhibited no secondary growth, had the shortest lifespans, and were the site of mycorrhizal colonization, Xia et al. (2010) suggested the existence of ephemeral fine root modules, analogous to leaves above the ground (see Figure 8). In contrast, higher-order fine roots (4th- through 6th-order roots) probably turnover very slowly, primarily fulfill structural and transportation rolls, and are expected to contribute significantly less toward the formation of SOM pools (Guo et al. 2008; Xia et al. 2010). Studies based on modeling data from ^{13}C tracer and ^{14}C depletion experiments suggest that 10% to 20% of the fine root pools turnover multiple times per year, while the remaining 80% to 90% turnover much more slowly (from years to decades) (Gaudinski et al. 2010).

5.0 Areas for Future Work

Root Order and Function. Although recent work has highlighted the importance of fine root heterogeneity for modeling C cycling (Lynch et al. 2013) and empirical data have hinted at the presence of multiple root pools with different turnover times (Gaudinski et al. 2010), a mechanistic biological explanation for the differential behavior of roots from different developmental orders or diameters is lacking in the literature.

Fine Root Senescence. Fine root decay makes important contributions to SOM. Yet, much remains unknown about fine root senescence and what processes initiate it. For example, it is unknown if senescence is triggered by signaling from the plant, if it is synchronized with leaf senescence, or if it can be initiated by mycorrhizal or other microbial organisms in the rhizosphere.

Mycorrhizal Associations. Mycorrhizal fungi are central to soil C cycling because they are the most direct link between reduced C supplied by the plant canopy and nutrients present in SOM. As much as 10% to 20% of NPP may be diverted from plants directly to mycorrhizal fungi to support colonization of roots and exploration of bulk soil by fungal mycelia (Vogt et al. 1982; Cairney 2012). In exchange, mycorrhizal fungi provide nutrients to their host plant—as much as 80% of a plant's N may be derived from symbiotic fungi (van der Heijden et al. 2008). Ectomycorrhizae (EcM), which primarily colonize woody species, may prove especially important because of their ability to directly absorb plant photosynthate from roots while accessing organic forms of N contained in SOM pools (Phillips et al. 2013). A growing body of evidence suggests that EcM fungi may be able to access organic N in soil by depolymerizing N-containing litter.

In forest ecosystems, as much as 30% in the microbial biomass consists of EcM fungi, which contributes as much as 15% of the NPP. Of note, as much as 25% to 35% of soil CO_2 efflux is derived from EcM activity. Yet, mycorrhizal associations are not explicitly represented in terrestrial C cycle models. Instead, the C flowing through the mycorrhizal fungi is considered in an aggregate fashion as part of either the autotrophic or heterotrophic CO_2 response. This assumption is only reasonable as long as allocation to the mycorrhizal component remains linear or proportional in response to changes in environmental factors, such as temperature, elevated CO_2 concentrations, or soil moisture. There are few studies that attempt to separate the mycorrhizal response (refer to sidebar: "Response to Rising CO_2 Since the Last Glacial Period."

Plant Responses to Rising CO_2 Since the Last Glacial Period

Major shifts in global conditions over geologic and contemporary time scales have likely impacted plant physiology and productivity with further effects on belowground processes. For example, there is solid evidence that low CO_2 during the last glacial period negatively affected leaf level physiology, producing major C limitations within plants and altering C allocation to above- and belowground structures. Over time, rising CO_2 has alleviated those constraints in modern ecosystems. However, recent work suggests that some glacial plants may have been acclimated or adapted to low CO_2 of the past, and that a legacy of plant adaptation to low CO_2 may constrain potential responses to future CO_2 increases.

The availability of key soil resources and the presence of soil microbes likely impacted plant responses to low CO_2 during the last glacial period and to rising CO_2 over more contemporary times. For example, recent evidence indicates that major shifts in global N cycling resulted in decreased N availability during periods of low CO_2. Because N is involved in RuBisCO production and photosynthesis, these shifts in N availability likely influenced plant productivity under low CO_2. Moreover, mycorrhizal fungi are hypothesized to influence plant responses to changing CO_2 over both geologic and contemporary time scales by altering plant C and nutrient dynamics as well as through above-belowground feedbacks. Recent work suggests that the effects of mycorrhizal fungi on plants may not always scale linearly with rising CO_2.

Incorporating potential legacy effects and plant-microbe interactions into existing climate change models will be critical for predicting the effects of rising CO_2.

Katie Becklin

Hydraulic Redistribution. Hydraulic redistribution (HR) is the movement of water from moist to dry soil using plant roots as conduits. HR has been demonstrated in seasonally dry ecosystems worldwide, and it can exert strong effects at physiological and landscape scales (Neumann and Cardon 2012; Prieto et al. 2012). Water redistributed upward from deep, moist to shallow, dry soils at night (often called "hydraulic lift") can contribute as much as 50% of the water lost by plant transpiration the following day, affecting latent heat flux and supporting stomatal opening that potentially enhances plant C gain during dry seasons. At landscape scales, Ryel et al (2003) estimate that more than two-thirds of the water that falls on the dry Rush Valley, Utah landscape during monsoon rains is rapidly redistributed downward by HR through plant roots, potentially reducing runoff and surface evaporation.

In the future, a major factor that will influence the response of terrestrial ecosystems toward increasing atmospheric CO_2 is the expected warming-induced increase in atmospheric evaporative demand and resulting soil drought, which may be further intensified by altered precipitation regimes. Although HR is considered an important mechanism buffering plant productivity against drought and has the capacity to affect fluxes of energy and C, the current generation of standard dynamic global vegetation models and Earth system models do not include a representation of HR. To date, those researchers who have added HR into their individual modeling efforts (Lee et al. 2005; Baker et al. 2008; Wang et al. 2011) have included only the "direct effect" of HR on evapotranspiration and plant C gain, an effect exerted via increased shallow soil moisture, amplified stomatal opening, and, potentially, increased C gain (refer to "Considering Hydraulic Redistribution" sidebar). For example, using the Community Atmosphere Model 2, or CAM2, and the CLM modified to include HR, Lee et al. (2005) estimated that evapotranspiration could be increased by up to 0.8 mm day^{-1} and surface temperatures decreased by as much as 2°C as HR occurs in tropical forest regions. Using CLM3 modified with HR, Wang et al. (2011) points out that at longer time scales, HR-supported plant transpiration (and associated soil moisture depletion) early in drought in the Amazon may lead to critically, even fatally, low soil water contents later during very prolonged drought.

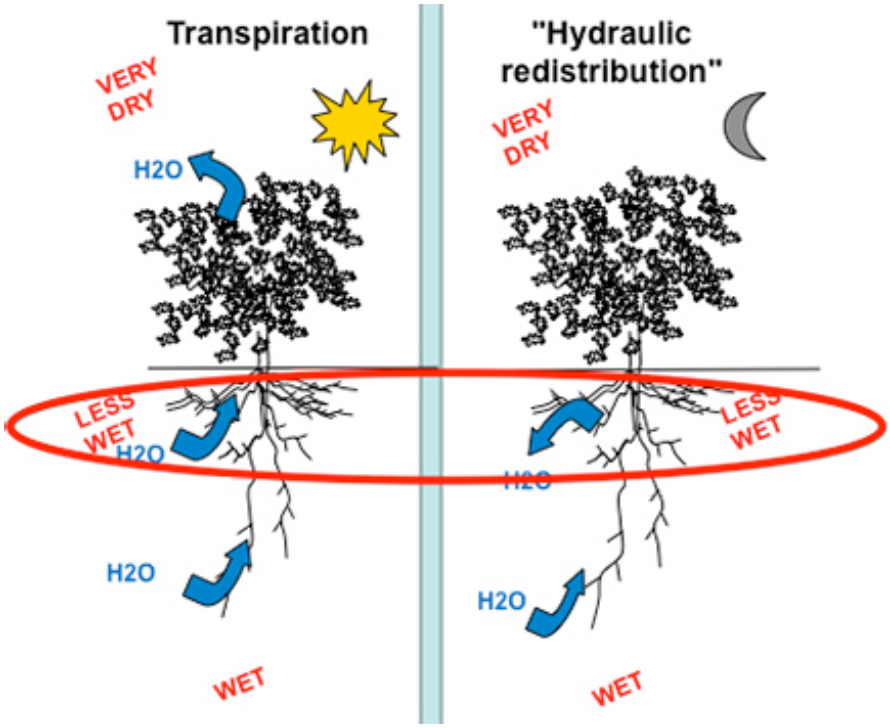


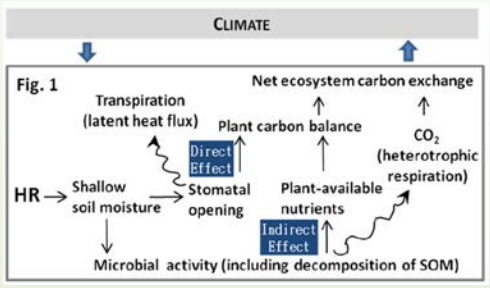
Figure 9. Comparison of transpiration that occurs during the day where water is drawn from the entire root zone and lost to the atmosphere and the hydraulic redistribution that occurs at night where water from deep roots rewets the soil in the fine root zone (courtesy of Zoe Cardon 2013)

Beyond these "direct" effects of HR on ecosystem energy and carbon exchange, it has been hypothesized for decades that hydraulic lift also may support enhanced shallow soil microbial activity, nutrient availability to plants, and enhanced productivity in the field. This hypothesis highlights a potential "indirect effect" of HR on plant C gain (see sidebar: "Considering Hydraulic Redistribution"), with implications for heterotrophic respiration. To date, no large-scale modeling has captured the biogeochemical "indirect effect" of HR on terrestrial ecosystem carbon balance.

Considering Hydraulic Redistribution

In the rhizosphere (the volume of soil around plant roots, influenced physically and/or chemically by those roots), interacting carbon and nutrient cycles are strongly affected by fluctuating soil water content driven by transpiration stream and hydraulic redistribution. The rhizosphere is a fundamental commodities exchange in terrestrial ecosystems, where C moves from roots to the microbial community, and the microbial community uses readily available C for energy and to build biomass, influencing availability of N and P to plants in the process. A large body of literature now suggests that it is dominantly root-derived (rather than shoot-derived) C sequestered as organic matter in soil. Thus, understanding the fate of dying roots and rhizodeposits (e.g., sloughed root cells, exuded and secreted solutes) and C sequestration requires a focus on the rhizosphere environment affecting microbial activity and access to organic matter. Soil moisture content and its fluctuations are important controllers of available habitat and microbial activity, acting through direct effects on the microbes themselves, on solute diffusion, and on microhabitat availability associated with soil wetting and drying.

Capturing how dynamic water potential (water content) controlled by plants in unsaturated soils affects microbial activity and processing of root-derived organic C will be an important step toward capturing key controls of belowground processes, including C sequestration, in terrestrial ecosystems.



Hydraulic redistribution of soil water through plant root systems, a well-known phenomenon demonstrated in multiple seasonally dry ecosystems worldwide, is particularly important. During HR, soil water flows along the water potential gradient from wetter rhizosphere soil into roots, through the root system, and out of roots into drier rhizosphere soil—exactly where the C and nutrient commodities exchange potentially is most active. The current generation of dynamic vegetation and Earth system models do not include HR, and individual efforts to incorporate HR into large-scale models center solely on water and its "direct effects" on stomatal behavior and plant C balance (see image inset). Yet, fluctuating water, nutrient, and C cycling are linked in the rhizosphere, and that linkage may be a critical control over dry-season nutrient availability to plants and heterotrophic respiration (inset). It has been hypothesized for decades that hydraulic "lift" (upward HR moistening surface soil layers at night) may stimulate surface soil microbial activity, nutrient availability to plants, and enhanced plant productivity in the field. This "indirect effect" (inset) results because fresh litter and SOM available for decomposition by microbes are dominantly found in upper soil layer. However, water content of those upper soil layers is depleted most rapidly as plants transpire, limiting microbial activity. Water provided at night by hydraulic lift moistens the thin sleeve of soil around plant roots for hours, providing a slightly wetter nighttime niche for rhizosphere microbes in surface soil layers. Whether or not net ecosystem exchange will shift positive or negative as a function of HR depends, in part, on the relative strengths of direct and indirect pathways, the signs and strengths of their component processes, the intensity of future drought, and the time scale over which HR's effects are considered.

Zoe Cardon

Key questions and recommendations for future work:

1. Chemistry, structure, and signaling in fine roots
   - What is the biological basis for defining "fine roots" (i.e., ephemeral roots that make the greatest contribution to resource uptake and soil C inputs)?
   - What is the variation in structure, function, and longevity among fine roots of different orders/modules?
   - How can a mechanistic understanding of molecular signaling that mediates development of symbioses, control of fine root system architecture, exudation, and allocation to mycorrhizal fungi be developed and incorporated into terrestrial C cycle models?
   - What are the transcriptomic, proteomic, and metabolomic variations that occur as ephemeral fine roots transition from a living to dead state?
   - Are there generalizable patterns in the chemistry, structure, and signaling in fine roots that can be applied to community-level ecology scales?
2. Modeling belowground processes at the pore scale
   - Are there critical scales of observation, i.e., scales that must be considered while smaller /larger scales can be neglected?
   - Which processes/features exhibit "scale invariance," or do not change when observed at different scales?
   - What happens when subsystems (two or more pores, two or more aggregates, etc.) are coupled? Does this generate interactions and new emergent behavior? If so, which?
   - How can rigorous mathematical procedures be developed to deal with nonlinearities and heterogeneity when upscaling/downscaling from the pore/Darcy scale?
3. There is a great need for field-deployable instrumentation for *in situ* characterization of the growth and function of roots.

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Appendix A: Advanced Soil Carbon Characterization

Advanced Soil Carbon Characterization

There has been significant progress in applying complementary spectroscopic techniques for the identification of functional moieties of the carbon molecules present in soil. Standard experimental techniques include Fourier transform infrared (FTIR); ^{13}C-nuclear magnetic resonance (NMR); and, less routinely, synchrotron-based techniques such as near edge x-ray absorption fine structure (NEXAFS) and scanning transmission x-ray microscopy (STXM) (Figure A1). However, there have been recent exciting applications of ultra high-resolution mass spectrometry (HR-MS) techniques to provide molecular characterization and assignment of chemical formulas to individual molecular organic species found in dissolved organic matter (DOM). Furthermore, spatially resolved, ultra HR-MS techniques have the potential to describe of the spatial organization of soil C within soil architecture. Several of these advanced techniques are described in this appendix.

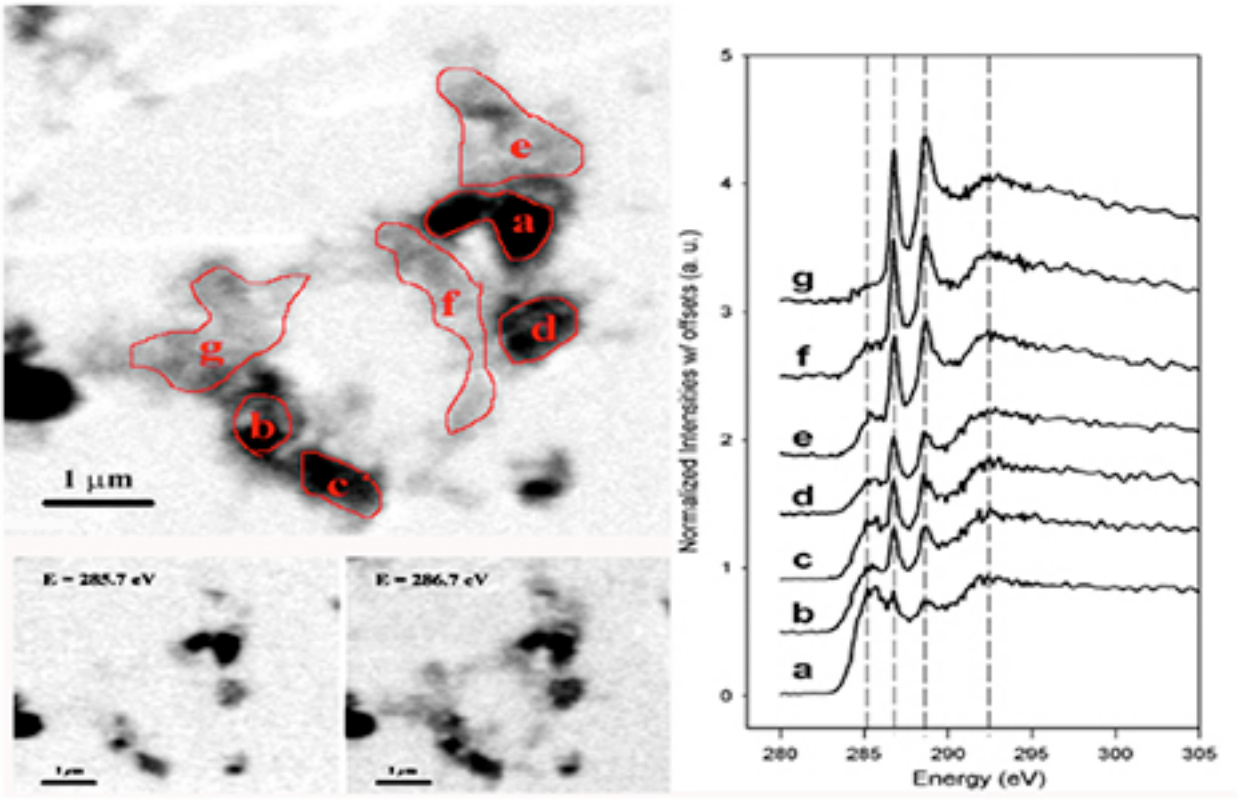

Figure A1. Carbon STXM image (Yoon et al. 2006).

Complementary Experimental Approaches to Soil Organic Matter Characterization – Peter Nico, 2013

Even at the pore scale, the belowground environment is heterogeneous in terms of the microbial community's composition, the chemistry and bioavailability, and the physical structure. Figure A2 shows the potential diversity of soil pore composition. Experimental approaches to study the complex interplay between these components at the pore scale require using high-resolution imaging, spatially resolved chemical speciation, and spatially resolved isotopic analysis.

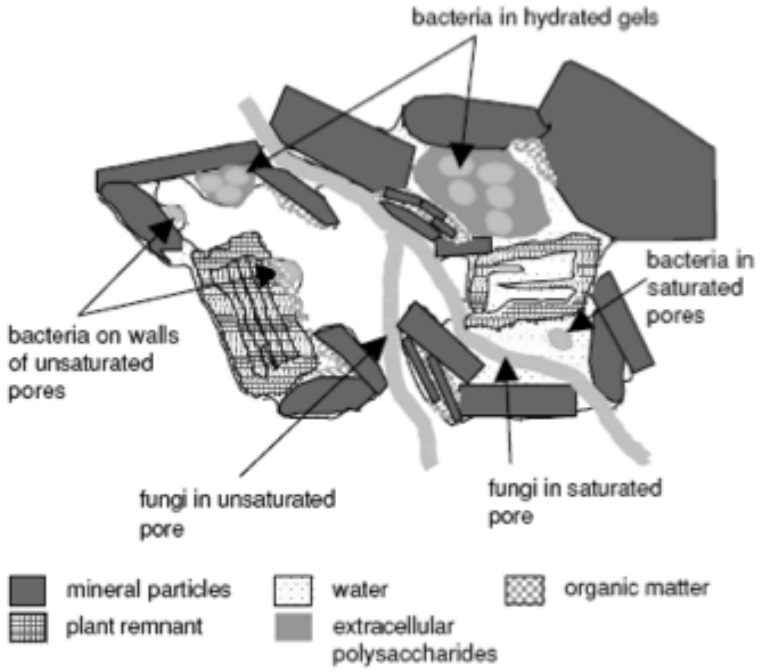

Figure A2. Heterogeneity in local environmental found in soil pores and local environments (from Chenu and Stotsky 2002).

Complementary techniques, such as scanning electron microscopy (SEM), nano secondary ion mass spectrometry (nanoSIMS), and synchrotron-based spectromicroscopy (e.g., STXM and NEXAFS) are ideally suited to visualize the spatial associations (SEM), as well as characterize the diversity of organic compounds from fungal hyphae to microbial biomass (STXM) to the flow of metabolites using labeled substrates (nanoSIMS). Keiluweit et al. (2012) recently demonstrated these techniques in their study of C,N-cycling and interaction between iron mineralization, organic matter, and mycorrhizal mats in the O-horizon of Pacific Northwest forest soils. Using C NEXAFS and STXM, they can distinguish between fresh and decaying fungal hyphae and map that distinction at the submicron length scale (shown in Figure A3). By using ^{15}N-labeled substrate, they can measure the relative uptake of the substrate in four different biomass pools.

Characterization of Dissolved Organic Matter – Rose Cory, 2013

Terrestrial and aquatic organisms produce biopolymers that are degraded in the water column and mainly in the sediments by diagenesis to fulvic and humic acids plus humin and finally by catagenesis to kerogen. Simultaneously, microbial and photochemical degradation in the water column produces DOM, which then is further degraded to more oxidized forms of DOM and finally to CO_2. If the rates of this degradation sequence are fast, the DOM is considered "labile." In marine systems and overall, it is important to note that of all the net primary production (NPP) on Earth, about 0.1% of it is eventually stored as organic matter. This means that all of the primary production must pass through the DOM pool on its way to being converted to CO_2. Thus, because all primary production on Earth passes through DOM on different time scales and there are large pools of DOM, the transformations and fluxes of this DOM are important to the net changes in the global C cycle.

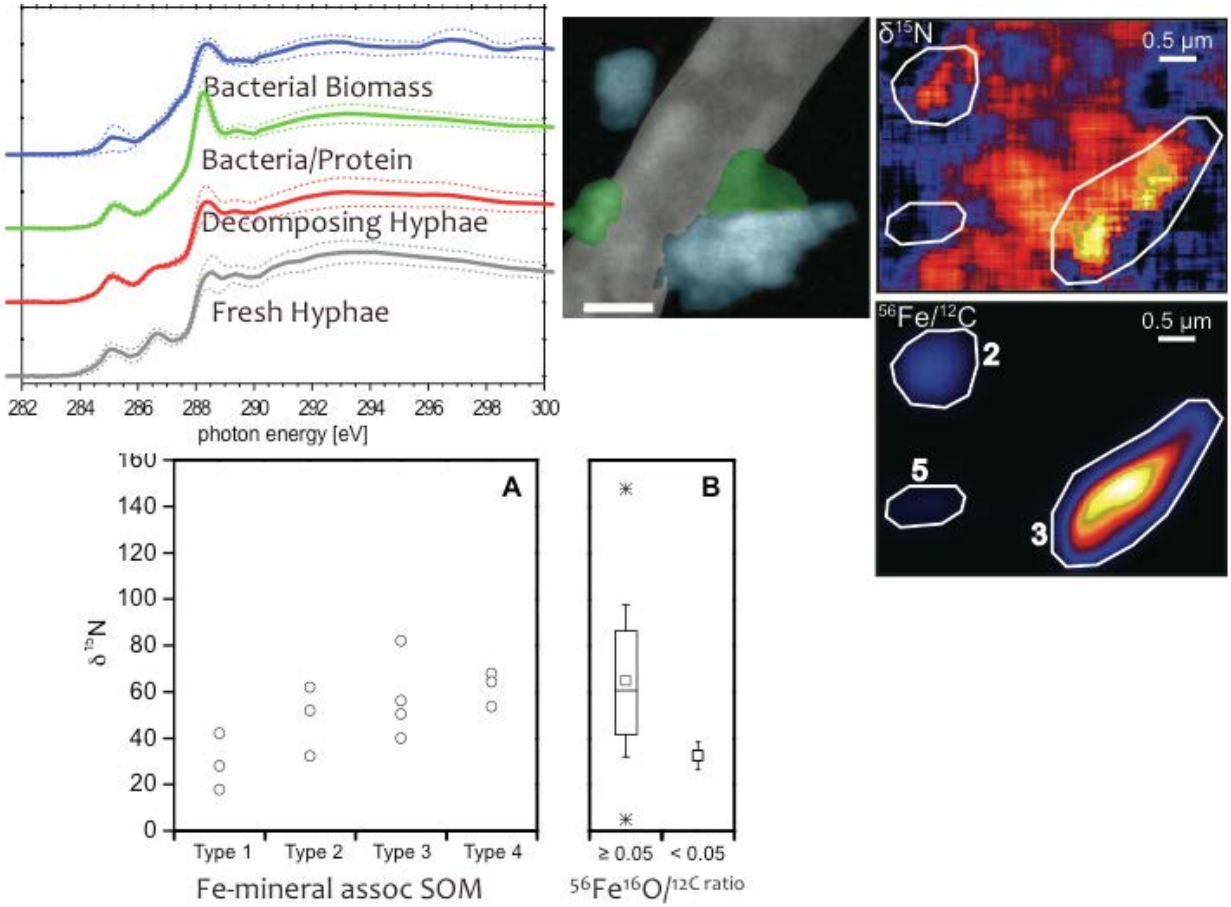

Figure A3. Multi-modal imaging techniques used to understand C,N flow in mycorrhizal fungi associated with iron mineralization in Pacific Northwest forest soils. Upper left panel, C STXM; upper right panel, SEM and nanoSIMS; bottom panel, nanoSIMS results (from Keiluweit et al. 2012).

Although soil organic matter (SOM) is protected from sunlight, the dissolved fraction of SOM (e.g., DOM) is transported from land to sunlit surface waters, where the light absorbing properties of soil-derived DOM often control photochemical processes and the depth of ultraviolet (UV) and visible light penetration in surface waters. This land-water transfer of DOM is important for C budgets, especially in the Arctic where C fluxes from Arctic surface waters to the atmosphere and from land to ocean could represent up to 40% of the net land-atmosphere C exchange—maximum flux of ~0.16 Pg C y^{-1} and a net terrestrial sink of 0.4 ± 0.4 Pg C y^{-1} (McGuire et al. 2009). Once it has been exported to surface waters, the nexus point of soil DOM fate is the oxidation to CO_2 or its partial oxidation and export in rivers to oceans. The lability and fate of soil DOM depends, in part, on photochemical reactions in surface waters (Cory et al. 2013).

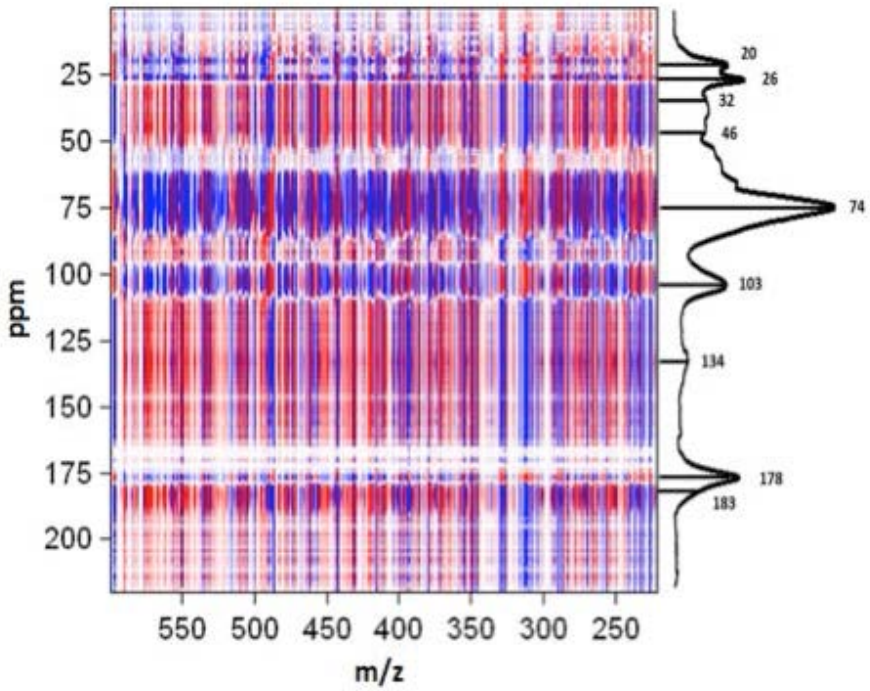

Figure A4. ^{13}C NMR and Fourier transform ion cyclotron resonance mass spectroscopy (FTICR-MS) data to extract the MS peaks that correlate (red) or anti-correlate (blue) with the emergence of signals along a salinity gradient (from Abdulla et al. 2013).

However, while quantifying the bioreactivity or susceptibility of DOM to bacterial degradation in streams and rivers is of critical importance to global change studies, a comprehensive understanding of DOM bioreactivity has been elusive, in part, due to the stunningly diverse assemblages of organic molecules within DOM in transport. This is one of the most complex organic mixtures on Earth. Currently, only the composition is understood, meaning the amounts of C, H, O, and N are known, but not the way they are put together. Presently, the lack of structural information regarding DOM limits the ability to relate the chemistry of DOM to its susceptibility and rates of degradation.

One of the best tools available to resolve the composition of DOM is ultra HR-MS (e.g., FTICR-MS), which confirms that DOM is a complex, heterogeneous mixture composed of thousands of different molecules. FTICR-MS provides molecular formulas for most of the thousands of ions detected. Still, even when using FTICR-MS, only the composition (the amount of carbon, nitrogen, oxygen, phosphorous, and sulfur content of the compounds in known and not the way in which each atom is arranged (e.g., structure). This means the ability to predict *a priori* the susceptibility of DOM compounds to bacterial degradation is limited. Because so little is known about the molecular features of bioreactive DOM compounds, a way to organize and quantify the detailed molecular-level data that provides insights into this important C pool must be determined.

One approach is to couple analytical methods (FTICR-MS, NMR, and optical proxies) so that, at a minimum, the strengths of one can shore up the weaknesses of another. At best, one method will facilitate the improvement of another (refer to Abdulla et al. 2013). For example, two-dimensional correlations of NMR and FTICR-MS are critical to constrain the chemical structure and assess how that structure relates to bioreactivity (see Figure A4). However, while FTICR-MS provides the best resolution of DOM composition, it is not yet feasible to use HR-MS or NMR to capture the often rapid dynamics of DOM degradation in the environment. For that, optical characterization, such as fluorescence spectroscopy and parallel factor analysis, is used.

Using these tools to understand C cycling is especially important in the Arctic, where thawing permafrost soils may release tremendous stores of organic C to participate in the modern C cycle. Recently, it was determined that once this C is exposed to sunlight upon export to surface waters, photodegradation stimulates bacterial respiration of this C to CO_2 by 40% compared to if it remained in the dark. To predict the fate of this C—whether it will end up in the atmosphere as CO_2 or exported to the Arctic Ocean as partially oxidized, more slowly cycling DOM—the synergy between photochemical and biological degradation of DOM and how these processes depend on the chemistry of DOM must be understood. Obtaining a mechanistic knowledge of DOM bioreactivity constitutes one of the grand challenges in environmental geochemistry. Thus, such an accomplishment would be transformative in advancing a new frontier, where geochemistry, biogeochemistry, and ecosystem science meet.

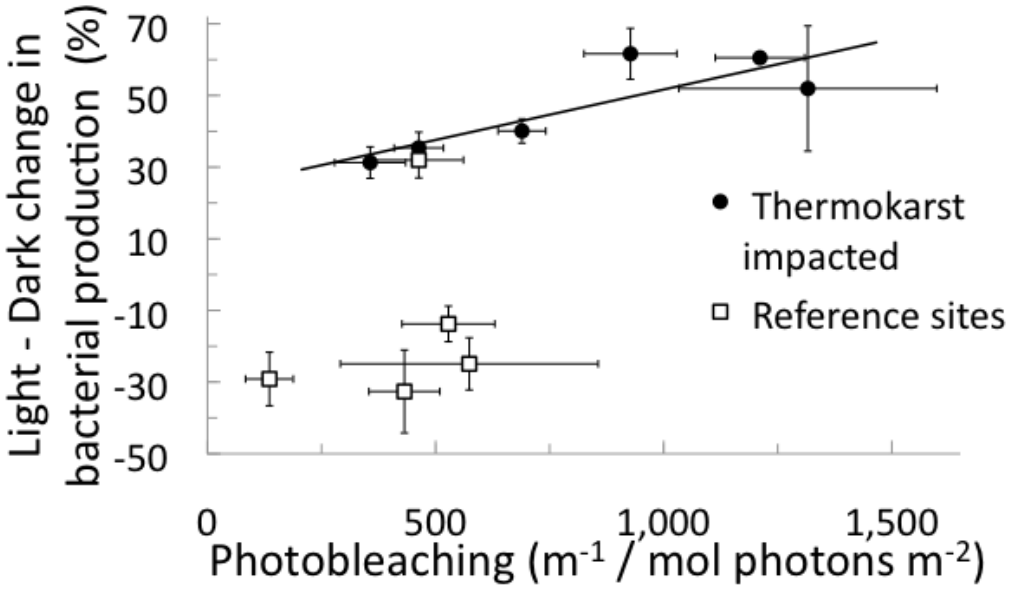

Figure A5. Light exposure of DOM from thermokarst-impact lakes increases bacterial activity by 40% (from Cory et al. 2013).

For other examples of the application of advanced experimental techniques for soil C characterization, refer to these publications and reviews:

Behrens S, A Kappler, and M Obst. 2012. "Linking environmental processes to the *in situ* functioning of microorganisms by high-resolution secondary ion mass spectrometry (NanoSIMS) and scanning transmission X-ray microscopy (STXM)." *Environmental Microbiology* 14(11):2851-2869.

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Appendix B: Workshop Agenda

Workshop Agenda

Belowground Carbon Cycling Processes at the Molecular Scale
February 19-21, 2013
EMSL, Richland WA

AGENDA

February 19, 2013

6:00 pm **Twigs Bistro and Martini Bar (all internal attendees will pay for their own meals)**

Workshop scope

i) What are the greatest needs for molecular level understanding of soil organic matter chemistry and what are the experimental resources and funding opportunities in those areas?
ii) What is the contribution that EMSL should/could uniquely provide?
iii) How do existing EMSL capabilities impact that need and should they be deployed differently?
iv) What new capabilities need to be developed?

February 20, 2013

7:30 am **Badging/Breakfast refreshments - EMSL Lobby/ EMSL Boardroom**

8:00 am **Welcome and plans for the day – EMSL Boardroom**

- EMSL Future Vision – Allison Campbell, Sherry Cady
- Comments from BER/TES program managers – Dan Stover and Paul Bayer
- Review of workshop objectives – Nancy Hess, Gordon Brown

8:30 am **Terrestrial Carbon Cycle Models**

- **Dan Ricciuto - ORNL**

9:00 am **Plant Response to Climate Change**

- **Katie Becklin-Atkinson – University of Kansas**
- **Colleen Iversen – ORNL**
- **Vanessa Bailey – PNNL**

10:30 am **Break Out Groups**

11:30 am **Break Out Group Report**

12:00 pm **Lunch (provided) + EMSL investments in SOM analysis**
NanoDESI – Julia Laskin
LA-AMS – Liz Alexander
Deep fractionation of SOM – Robby Robinson

1:00 pm **Rhizosphere Processes**

- **Scott Bridgham – University of Oregon**
- **Zoe Cardon - Marine Biological Laboratory, Woods Hole**
- **Seth Pritchard – College of Charleston**
- **Matt Wallenstein – Colorado State University**
- **Mark Williams – Virginia Tech**
- **Group discussion**

3:00 pm **Break Out Groups**

4:00 pm **Break Out Group Report**

4:30 pm **EMSL Tour**

6:00 pm **Catered Dinner / EMSL 1077**

- **Tim Scheibe, PNNL, TBD**

February 21, 2013

8:00 am **Breakfast refreshments/EMSL Boardroom**

8:30 am **SOM Mineral Interfaces/Redox and SOM characterization – EMSL Boardroom**

- **Markus Kleber – Oregon State University**
- **Peter Nico – Lawrence Berkeley National Laboratory**
- **Rose Cory – University North Carolina**
- **Gordon Brown – Stanford University**

10:30 am **Break Out Groups**

11:30 am **Break Out Group Report**

12:00 pm **Lunch (provided) + EMSL capabilities**
NWChem – Niri Govind
Future Major Investments – Ljiljana Pasa-Tolic, James Evans

1:00 pm **Workshop Panel Recommendations and Break Out for writing assignments**

4:00 pm **Reports from Breakout Session/Final comments**

5:00 pm **Adjourn**

Appendix C: Workshop Attendees

Workshop Attendees

Attendees

Vanessa Bailey	Pacific Northwest National Laboratory
Scott Bridgham	University of Oregon
Zoe Cardon	Marine Biological Laboratory, Woods Hole
Seth Pritchard	College of Charleston
Matt Wallenstein	Colorado State University
Mark Williams	Virginia Tech
Dan Ricciuto	Oak Ridge National Laboratory
Daniel Stover	DOE-BER
Paul Bayer	DOE-BER
Katie Becklin-Atkinson	University of Kansas
Colleen Iversen	Oak Ridge National Laboratory
Markus Kleber	Oregon State University
Peter Nico	Lawrence Berkeley National Laboratory
Rose Cory	University of North Carolina
Gordon Brown	Stanford University *(Workshop co-Lead)*

EMSL/PNNL Staff

Liz Alexander, Laser Ablation-Aerosol Mass Spectrometry scientist
Don Baer, Science Lead, Science of Interfacial Phenomena
Scott Baker, Science Lead, Biological Interactions and Dynamics
Mark Bowden, Capability Lead, Deposition and Microfabrication; Subsurface Flow and Transport
Sherry Cady, EMSL Chief Science Officer
James Evans, High-resolution Transmission Electron Microscopy scientist
Niri Govind, Computational Chemistry
Nancy Hess, Science Lead, Geochemistry, Biogeochemistry and Subsurface Science (*Workshop co-Lead*)
Dave Koppenaal, EMSL Chief Technology Officer
Ian Kraucunas, Deputy Director, Atmospheric Science and Global Change Division
Alex Laskin, EMSL, nanoDESI scientist
Julia Laskin, PNNL, nanoDESI scientist
Scott Lea, Capability Lead, Electron Microscopy
Christine Mahoney, nanoSIMS scientist
Galya Orr, Capability Lead, Cell Isolation and Systems Analysis
Ljiljana Pasa-Tolic, Lead Scientist, Mass Spectrometry
Robby Robinson, Capability Lead, Mass Spectrometry
Kevin Rosso, PNNL, Geochemistry

Tim Scheibe, PNNL, Multi-scale Reactive Transport Modeling

Bill Shelton, Assistant Lab Director, Molecular Science Computing Facility

Ray Teller, Assistant Lab Director, Scientific Resources Division

Theva Thevuthasan, Capability Lead, Spectroscopy and Diffraction

Tamas Varga, X-ray Tomography scientist

Nancy Washton, Capability Lead, NMR

Mike Wilkins, Microbiology

John Zachara, Battelle Fellow

Appendix D: EMSL Capabilities

EMSL Capabilities

Belowground Carbon Cycling Processes at the Molecular Scale

EMSL capabilities and contact information
for a complete list go to: http://www.emsl.pnl.gov/contacts/

Molecular Science Computing
Doug Baxter (Consulting)
Bert de Jong (High-Performance Software Development)
- Chinook Supercomputer
- NWChem
- ECCE
- ParSoft

Cell Isolation and Systems Analysis
Galya Orr
- Cell and organelle isolation
- Fluorescence Microscopy/Spectroscopy
- Transcriptomics

Mass Spectrometry
Robby Robinson
- Proteomics
- Metabolomics
- Organic macromolecule analysis

Alex Laskin
Julia Laskin
- Nanospray Desorption ElectroSpray Ionization (nanoDESI)

Liz Alexander
- Laser Ablation Aerosol Mass Spectrometry (LA-AMS)

Microscopy
Scott Lea
- TEM
- SEM
- Helium ion microscopy

NMR and EPR
Nancy Washton
- 300 to 900 MHz NMR for solids, liquids, imaging
- Metabolomics
- Pulsed EPR

Spectroscopy and Diffraction
Theva Thevuthasan
- XPS
- NanoSIMS
- SIMS
- SFG/VS

Tamas Varga
- Computed X-ray Tomography

Mark Bowden
- Mossbauer
- XRD

Subsurface Flow and Transport
Mark Bowden
- Microfluidics
- Intermediate Flow Cells