INTRODUCTION

# Stabilization and destabilization of soil organic matter—a new focus

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Interest in soil organic matter (SOM) is ramping up as concern mounts about steadily increasing levels of atmospheric $CO_2$. There are two reasons for this. First, there is hope that improvements in crop, forest, and soil management may allow significant amounts of $CO_2$ to be removed from the atmosphere and sequestered in soil. Second is the possibility that increased soil respiration rates, associated with climate change, will unleash a positive feedback in which temperatures rise even faster than now expected. Other reasons have long existed for understanding SOM dynamics, such as SOM as the source of most of the non-fertilizer N needed for plant growth, but the specter of run-away climate change seems to have now overtaken these other justifications.

Much of the work on SOM triggered by climate change has involved measuring pools over large areas and, especially, changes in those pools over time (Smith 2004; Bellamy et al. 2005). Other work has sought to measure changes in soil C and N stores under elevated $CO_2$ regimes (Lin et al. 1999; Six et al. 2001; Jastrow et al. 2005). But it is widely recognized that measuring such changes is not enough. We have to understand the mechanisms underlying soil organic matter stabilization if we are to predict the course of $CO_2$ flux between atmosphere and soil under a changing climate and a steadily increasing demand for agricultural and forest products.

A 6-year project led by Prof. Ingrid Kögel-Knabner (Soils as Source and Sink for $CO_2$—Mechanisms and Regulation of Organic Matter Stabilization in Soils, funded by Deutsche Forschungsgemeinschaft) was arguably the first major formal effort in this direction. The project also hosted the First International Conference on Mechanisms of Soil Organic Matter Stabilization as part of a mid-term project review. The conference (Munich, October 2003) was attended by about 140 people from 12 countries. Several American SOM scientists asked if a follow-up conference in the US was warranted. The response was enthusiastic and funding was secured from US sources including the National

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Science Foundation (Ecosystems Cluster), USDA NRI (Soil Biology Program), Lawrence Livermore National Laboratory (Center for Accelerator Mass Spectrometry), Kearney Foundation of Soil Science, NASA (Applied Earth Science Program, Carbon Management), and Oregon State University (College of Forestry). The Second International Conference on Mechanisms of Soil Organic Matter Stabilization was held at the Asilomar Center, near Monterey, California in October 2005, and was attended by about 120 people from 13 countries. The papers presented in this special issue of Biogeochemistry derive from presentations made at this 2005 conference. Because of the success of the second conference, a third is scheduled for Adelaide, Australia, in September 2007 to be hosted by Jan Skjemstad, Jeff Baldock, and Evelyn Krull, of the Australian Commonwealth Scientific and Industrial Research Organization (CSIRO). The Adelaide conference will specifically include both soils and aquatic sediments.

The Asilomar presentations, both oral and poster, covered topics ranging from soils to riverine sediments, from kinetics of extracellular enzymes to mechanisms of OM sorption on mineral surfaces, and from charcoal to microbial surface-active proteins. What follows highlights major scientific findings and questions that emerged from the Asilomar conference, then considers scientific and logistical obstacles to further progress in this field and opportunities for addressing those obstacles.

## Conference themes and highlights

One conference thread was the viability and usefulness of the "humic" theory of SOM (e.g., Stevenson 1994; Essington 2004). The "humic" paradigm holds that over time, plant debris is transformed into very large polyaromatic structures, largely via abiotic condensation mechanisms. In addition to "humic substances", SOM includes "non-humic substances": carbohydrates, lignin, proteins, amino-sugars and other compounds that are still recognizable as plant and microbial metabolites. Proteins are thought to be involved in formation of humic substances via reactions with sugars, tannins and lignin degradation products, but the resulting products are not thought to play a major role in binding of SOM to mineral surfaces.

Kleber et al. (this volume), following on work by Wershaw et al. (1996), Piccolo (2001), and Sutton and Sposito (2005), offer an alternative view. Briefly, SOM is viewed as consisting of organic molecular fragments of varying degrees of amphiphilicity in intimate contact with mineral surfaces of variable chemical reactivity and a polar solvent (water). The second law of thermodynamics then dictates that the organic fragments and mineral surfaces will arrange themselves in structures that maximize entropy, which leads these authors to propose a layered structure for mineral–organic associations. This layered structure is fundamentally different from earlier "humic-substances" based concepts for organo–mineral interactions in that the organic molecular fragments are seen as degradation products derived from the depolymerization and oxidation of standard biomolecules, and not as large resynthesized polyaromatic structures as postulated by the various pathways of classical humification theory.

The same work strongly emphasizes proteins as the organic compounds with the greatest functional versatility. Unlike other organic moieties, proteins can bind to almost any kind of surface over a wide range of pH conditions. This is because of their multifunctional nature, that is, their ability to develop positive as well as negative charge as well as their ability to gain entropy by conformational changes, which reinforces any electrostatic bonding to mineral surfaces.

The theme of the importance of soil N in controlling soil C dynamics is taken up and developed in more detail by Rillig et al. (this volume) who review information on the nature and amounts of soil protein, especially microbial surface-active proteins. Despite controversy as to precise amounts of such compounds in soil, and their role in aggregation, it is clear that they are

ubiquitous in soil and exceptionally stable, which is only reasonable since N is so often strongly limiting to microbial activity in soils. After all, why would microbes have evolved attachment compounds that can be readily degraded? In fact, recent work by Amelung et al. (2006) uses amino-acid racemization rates to suggest that soil protein may have residence times measured in centuries rather than decades.

The paper by Rillig et al. (this volume) also reinforces a second conference theme that the majority of the organic N atoms, and even to some extent the organic C atoms, are likely to have undergone microbial processing since last having been part of plant tissue. Although virtually all soil C derives ultimately from vascular-plant photosynthesis, a major tenet of the poly-phenol "humic" theory is that lignin-derived aromatics provide the structural framework for soil "humic" substances. The $^{13}$C-NMR evidence to date suggests, however, that aromatics account only for a relatively small portion of SOM and that alkyl C, rather than aromatic C, accumulates over the time scale of soil formation (e.g., Baldock et al. 2004). This finding is supported by the spatial association of alkyl C with kaolinite functional groups determined by synchrotron-based FTIR and the alkyl-rich coatings on min-eral surfaces shown with X-ray spectroscopy (Lehmann et al., this volume). Direct measure-ment in soil of lignin monomers and their degradation products further confirms a relatively rapid turnover for lignin compounds (e.g., Kiem and Kögel-Knabner 2003; Nierop and Filley 2006; Sollins et al. 2006).

A fourth conference theme was the role of aggregation in stabilization of SOM. Johannes Lehmann et al. (this volume) use synchrotron-based spectroscopy to map not only element distributions, but even molecular speciation in individual microaggregates ($< 5$ μm) from a variety of soils. They found little systematic variation in C levels from the outside to inside of these aggre-gates, suggesting that organic debris do not form a nucleus around which such microaggregates then develop. Certain classes of organics, however, did vary systematically from aggregate exterior to interior, in keeping with the multilayer theory proposed here by Kleber et al. (this volume). In general, these synchrotron-based techniques (both NEXAFS and FTIR) offer unprecedented oppor-tunities for 2-d mapping of both elements and compounds across the soil microfabric.

Much of the work presented at Asilomar refers to topsoil. This reflects in part the assumption that deep-soil SOM does not cycle or change as rapidly as the topsoil SOM. An additional factor is simply the enormous work required for careful deep-soil sampling. Baisden and Parfitt (this volume) go deeper and find that subsoil SOM in New Zealand is accumulating bomb carbon at a substantial rate suggesting that it is more dynamic than previously assumed. This idea that even SOM pools that yield long $^{14}$C mean residence times (MRTs) may still be very dynamic fits well with the multi-layer model of Kleber et al. (this volume): The multi-layer model includes an outer kinetic zone in which molecules and even cell fragments can be bound rapidly but also exchange readily with the soil solution. Such rapid incor-poration of labeled material into an organo-mineral heavy fraction has also been noted by Strickland et al. (1992) and Swanston et al. (2005).

SOM fractionation procedures, and density-based fractionation in particular, were used in many of the studies presented at Asilomar. Crow et al. (this volume) review the development of the density fractionation methodology and its limita-tions. They also include new experimental evi-dence that a large amount of C and N is mobilized in the fractionation medium (SPT). This SPT-solubilized fraction is discarded in most studies and not typically reported or explicitly discussed. Moreover, the SPT-solubilized fraction is func-tionally distinct from both heavy and light frac-tion in ways that are not consistent across soils—clearly an important consideration and intriguing opportunity for further work.

Lastly, the role of black carbon (char and soot) continues to receive attention, especially well-deserved given the likelihood of increased wild-fire under a warming global climate. Knicker (this volume) reviews the nature of black carbon and possible modes of formation. She concludes that polyaromatics do form the core of these materials but that molecular weights (number of benzene rings) are much less than previously assumed.

This relatively small size raises interesting questions about the recalcitrance of such materials and thus their potential to be degraded microbially, especially under a warmer climate. Char research is also suggesting that most of the heterocyclic N in soils is pyrogenic, although the extent to which some is inherited from organic-rich sedimentary parent materials has not yet been quantified.

## Future SOM research needs

The Second Conference highlighted not just results but also major gaps in both our knowledge and in our research efforts. Clearly, soil organic N dynamics have received much less attention that those of soil organic C. With the advent of ^{15}N-NMR in the 1990s, it became clear that most of the organic N in soils is in amide form. Seemingly lost in this wave of NMR data, however, was a large wet-chemistry literature on protein in soils and sediments, some papers dating back to 1940s (see Rillig et al. this volume). Moreover, clays have been used to remove protein in industrial applications for decades (e.g., Kleber et al. this volume), and further review of this literature is needed. In any case, it seems possible now that N dynamics in large part drive soil C stabilization, rather than the other way around, and that this occurs via at least two mechanisms, possibly interrelated: strong sorption of proteins on mineral surfaces and accumulation of recalcitrant surface-active proteins in the soil. If true, this shift in thinking would have major implications, especially for attempts to model soil C and N dynamics.

The Second Conference, like the first, emphasized stabilization mechanisms over destabilization, which comprises processes that decrease stability and thus promote turnover and degradation (Sollins et al. 1996; Baldock and Skjemstad 2000). Presenters, however, did discuss kinetics of enzyme-mediated substrate degradation (J. Schimel) and temperature dependence of microbial degradation processes (S. Frey). Less well covered were processes of desorption of organics from mineral surfaces and of increases in substrate accessibility due to decreases in aggregation. Destabilization processes, however, may

ultimately be even more important to global C dynamics than stabilization processes, if the long-term net flux of C between soil and atmosphere turns out to be toward atmospheric $CO_2$ rather than soil C.

Given the complexity of the soil, modeling provides the only way to link mechanisms to future fluxes. Unfortunately, little of the work presented at the Asilomar conference is reflected in current models of SOM dynamics (Lützow et al. 2006). One major class of SOM models focuses on substrate ''quality'' (Ågren and Bosatta 2002; Currie 2003) and assumes that the dynamics of C and N in mineral soil and plant litter are identical. Given that organic substrates as well as the microflora and the enzymes they produce all interact with mineral surfaces in ways that greatly affect their behavior, this assumption greatly limits the applicability of these models. A second class of SOM models relegates soil organo–mineral interactions to parameters that must be set empirically for sites of different mineralogy. Moreover, most of these models (e.g., Century, Trace, and Biome-BGC) are built around pools that cannot be separated physically or chemically, or even quantified directly (Kelly et al. 1997; Currie et al. 1999; Thornton and Rosenbloom 2005). A few approaches do make use of pools that can be quantified. For example, several models distinguish between plant debris (either a light fraction or a particulate organic matter pool) and mineral-associated OM (Hassink and Whitmore 1997; Skjemstad et al. 2004; Nadporozhskaya et al. 2006). A third group (e.g., GEM) assumes that ''proximate analysis'', an approach developed for food and fiber and used for many years to model litter dynamics, is meaningful when applied to mineral soil (Rastetter et al. 1991; McKane et al. 1997), but these again do not consider organo–mineral interactions.

Unique perhaps is Terraflux (Neff and Asner 2001), which builds directly on Century but includes a soluble C pool and allows sorption/desorption reactions out of and into that pool. The authors review the C sorption/desorption literature in relation to soil mineralogy, especially extractable Fe and Al, and subsume that information into two parameters. Their appendix table lists these parameter values for a wide range of

soils, but the authors do not explore further how those values might relate to soil mineralogy or texture. Nonetheless, organo–mineral interactions are widely recognized as of crucial importance in SOM stabilization, and the modeling community must begin to incorporate more of this thinking into its work. Moreover, all SOM models that include N use C:N ratios to link fluxes of C and N. As already discussed, this assumption may not apply if indeed nitrogenous and non-nitrogenous organics play fundamentally distinct roles in SOM stabilization.

Perhaps part of this reluctance to include organo–mineral interactions in SOM models, stems from a disconnect between what might be termed ''decomposition'' and ''SOM'' research. ''Decomposition'' research, as the term is used here, focuses on the breakdown of plant and microbial substrates by microbes and higher trophic-level organisms. Perhaps because most of the research deals with organic horizons rather than mineral soil horizons, such ''decomposition'' research tends to leave out the organo–mineral interactions entirely. A small group of people are studying microbial/mineral interactions directly (e.g., Omoike and Chorover 2006) but there continue to be two highly disconnected literatures and corresponding research communities: a ''litter decomposition community'' (often forest ecosystem oriented) and an ''SOM community'' (often agriculturally oriented). These groups need to interact more effectively if there is to be efficient progress on SOM dynamics.

SOM science spans a huge array of disciplines, perhaps even uniquely so. The authors of the papers included in this issue cited papers in a 172 peer reviewed journals. Of these Soil Biology & Biochemistry ranked first (54 citations), followed by Soil Science Society of America Journal (48), Organic Geochemistry (28), European Journal of Soil Science (25), Soil Science (25), Geoderma (24), and Global Biogeochemical Cycles (20). An additional 24 journals were cited between 6 and 19 times, while 135 journals were cited 5 times or fewer. An informal survey indicated that the conference attendees hold membership in at least 10 professional societies, not counting general science societies such as AAAS. Is there another environmental-studies field that is so widely dispersed? Thus, meetings that focus on specific areas such as SOM and allow time for extended discussion occupy a niche not filled by meetings of professional societies in that they bring together people from all the relevant fields and they do so with much less distraction. This is not to in any way denigrate the importance of professional societies, their meetings and journals. They are necessary but not sufficient. We sincerely hope that funding agencies and societies worldwide will join together to support the Third International SOM Conference, which is now scheduled for Adelaide, Australia, as well as subsequent efforts.

The broad interdisciplinary nature of SOM research also affects funding. NSF Ecosystems Cluster increasingly funds landscape and global-level studies, not detailed process studies of the sort needed to understand SOM dynamics. The USDA NRI Soil Processes Program does fund this area but its budget is excruciatingly small. NASA's increased focus on space exploration has decreased the funding available for earth-science research including all terrestrial process-level studies. The DOE Office of Biological and Environmental Research, especially the Terrestrial Carbon Processes program, invests in carbon research at multiples scales, including studies of mechanisms of SOM stabilization. Yet even this DOE program suffers from a static and increasingly strained budget, with much of its yearly budget dedicated to infrastructure support of $CO_2$ exchange and FACE experiments. In short, the possibilities for funding mechanistic SOM research, never extensive, are getting steadily smaller, at least in the US. If this trend continues we may slide into a major global crisis that we lack the information to even fully understand, much less solve. Carbon cycle science in general and SOM research in particular must get higher priority than they do now if we are to understand and mitigate the consequences of fossil fuel emissions for the climate and ecosystems of the Earth.

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