

The Lake Constance think tank on global change and feedback from organic carbon dynamics

Defining research visions on how to quantify the molecular-level mechanisms driving soil organic matter turnover



Sponsored by MOLTER: Molecular structures as drivers and tracers of terrestrial C fluxes - An ESF Network Sunday 4. until Wednesday 7. October 2009 Ittingen, Switzerland

Scientific report Program List of participants



The 15 participants in the herbal garden of the old monastery Itttingen, Switzerland.

Dynamic Soil Organic Matter – From black box models to mechanistic predictions

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Abstract – Present soil organic models are empirical, pool-based, black box models, and cannot be applied to simulate soil carbon changes under future atmospheric conditions which never occurred during the observation phase. We propose that to be able to predict how (and how much) soil organic carbon is vulnerable to destabilization within the next decades we urgently need quantitative and mechanistic models. Those models would describe soil carbon cycling by quantifiable mechanisms, which are globally applicable, today and under future climatic conditions. The performance of these models could be tested with manipulative experiments in long-term, lysimeter-like ecotrons.

The "Lake Constance think tank 2009 on global change and feedback from organic carbon dynamics" was held 4.-7. October 2009. The goal was to define research visions on how to quantify the molecular-level mechanisms driving soil organic matter turnover. Fifteen scientists from various disciplines of soil biogeochemistry, including soil chemistry, soil biology, soil biogeochemistry as well as from chemical oceanography and biology, attended the four-day meeting, at the Kartause Ittingen, a former monastery near Zurich, Switzerland. A list of participants and the detailed program are Appendix 1.

Why is it important to quantify the molecular-level mechanisms driving organic matter turnover in terrestrial systems?

Globally, terrestrial systems (including soil) store more organic carbon than is stored in the atmosphere as CO_2 but along with global change, the terrestrial pool becomes vulnerable to destabilization. Thawing permafrost, widespread anthropogenic nitrogen deposition, and increasing summer droughts in Central Europe are just a few examples already observed today. Terrestrial ecosystems could provide a negative or a positive and amplifying feedback in a warming world, and both this direction and its magnitude remain uncertain (Heimann & Reichstein, 2008). To be able to predict future concentrations of atmospheric CO_2 we urgently need a quantitative and mechanistic understanding of how much organic carbon is vulnerable to destabilization to changes in climate and atmospheric conditions within the next decade to century (Trumbore & Czimczik, 2008).

At present, however, we are not able to predict the response of mineral organic matter to future environmental conditions. Existing soil carbon models are primarily empirical. Hence, these empirical models cannot be applied to simulate soil carbon changes under future atmospheric conditions that never occurred during the observation phase. We need to develop a generalizable mechanistic model that describes soil carbon cycling by recognized and acknowledged mechanisms and a common set of first principles, which will be applicable globally, as well as under future atmospheric conditions.

What have we learned from past research efforts?

There are three postulated stabilization processes: recalcitrance, accessibility, and interactions with minerals (Sollins *et al.*, 1996). Some of the postulated processes have been tested extensively, others not. The main results were the following.

In soil, there is no evidence that de-novo abiotic or biotic synthesis of humic substances (termed humic and fulvic acids) is quantitatively important, and could contribute to the recalcitrant pool. As recent examples, the classical humification model is questioned by the following findings. Humic fractions have all the same age in ¹³C natural abundance experiments (Balesdent & Mariotti, 1996), although note that in natural abundance ¹⁴C studies some differences have been observed . Functional group chemistry of soil organic matter can be explained by recognizable biopolymers (Kelleher & Simpson, 2006). In any given location on a large spatial scale, humic substances could not be identified, but rather recognizable biopolymers (Lehmann *et al.*, 2008). Aromaticity can be explained by fire, not by humification (Gonzalez-Perez 2004/2005). Also in aquatic environments, secondary synthesis does not seem to be a quantitatively important process all (Hedges *et al.*, 2000)

Selective preservation of certain recalcitrant organic compounds such as lignin, lipids is *not* a major SOM stabilization mechanism. Organic fractions with slow turnover rates were mostly found when associated with soils minerals, except for fire-derived organic matter (Marschner *et al.*, 2008). In that study [or in a number of studies,] similar-to-average-turnover rates were observed for all analyzed compounds, virtually irrespective of their chemical structure (carbohydrates, lignins, lipids).

Stabilization potentials of soils are specific to individual sites, and even within sites stabilization may vary with pedogenetic horizons (Spielvogel *et al.*, 2008; von Lützow *et al.*, 2008). Processes causing spatial inaccessibility and thus driving organic matter turnover are still poorly understood (von Lützow *et al.*, 2008).

Summary:

Intrinsic chemical recalcitrance is not the mechanism underlying most long-term SOM stabilization

In the long-term (more than a few annual cycles), intrinsic chemical recalcitrance does not seem to play a role. This seems to hold true for individual chemical compounds (including sugars, lignins, plant-derived lipids), and, if they exist, also for *de-novo* synthesis products (humic substances).

What else drives organic matter turnover?

Organic matter persists in soil because the rate of decomposition is slow. But what factors typically drive (limit or promote) organic matter decomposition? If the physico-chemical properties of the organic matter itself have only a short-term importance for decomposition, which environmental conditions and mechanisms modify organic matter turnover? Here follows a brief summary of conditions and mechanisms that warrant investigation.

Input – rate of supply, structre, size, incorporation into larger physical structures, hydrophobicity, oxidation state, density, physico-chemical properties would be better [than what?] because we observe facultative non-utilization as the most important long-term process that controls OM stabilization (Ekschmitt *et al.*, 2008; von Lützow *et al.*, 2006).

Solution characteristics – Important factors limiting getting into solution include: amount of water, compound size and solubility, fauna. Important properties once in solution include reaction kinetics and control byT, pH, and Eh (dissolved O₂), ionic strength, cation speciation, aluminum activity, sorption isotherm characteristics, and transport kinetics.

Chemical reactivity/nature – capacity for forming crosslinks or surfaceinteractions; abiotic polymerization which may occur occasionally under certain circumstances.

Biological – Microbial biomass, density, and spatial distribution, community composition, , types and activities of enzymes produced, temperature, nutrient supply, and energy supply (e.g., as C-compounds).

Transport and mixing – bioturbation, cryoturbation, pedoturbation, leaching, active transport by fungi.

Soil physical structure – preferential flow paths, aggregation, pore size distribution, tortuosity, connectivity (determines transport/diffusion rates, accessibility to enzymes, hierarchical levels that can be co-located), root/rhizosphere location (determines rate of O_2 -supply, energy/substrate supply and types of surfaces in the region of decomposition).

Mineral characteristics – amount, mineralogical composition, surface area, surface charge (zero point charge), crystallinity, chemistry of solution (determines bonding type).

Structure and phase of water – 'structured' water – e.g. in mineral lattices, strongly and weakly bound water layers, Stern layer.

Summary:

In the long-term it probably is not (mainly) the physico-chemical properties of the compound itself which drive its turnover. Rather, it is the environmental conditions and resulting mechanisms, which promote or limit the decomposition.

A new approach

Can we take this information on environmental conditions and resulting mechanisms and combine them in a novel, mechanistic approach to describe SOM turnover? Would this approach be better suited to *predict* organic carbon turnover under future climate conditions than are current approaches? Would it perform better than the classical box model? What if we treat soil organic matter as having only two types of OM? Non-assimilable and assimilable SOM (see Figure 1)?



Figure 1: Conceptual summary of a mechanistic soil organic matter turnover model. *Intrinsic chemical recalcitrance controls decomposition on comparatively short timescales.

Per se all biomass entering the soil is "non-assimilable", unless favorable conditions make it "assimilable". This seems counterintuitive at first. To explain, let us take carbon in a sugar molecule as an example. This sugar molecule is "non-assimilable" if decomposers are physically separated and can't reach it. The molecule could be included in an aggregate, in a small pore, or could be surrounded by other molecules. Next step, if the decomposers are close enough, but the soil has dried out and water is missing, the sugar molecule still would be "non-assimilable". Only if all necessary environmental conditions are just right, the sugar molecule will become "assimilable" and microorganisms will assimilate and use the energy and carbon. The carbon will either be mineralized (leaving the system as CO_2) or build into new biomass (e.g. a cell wall lipid) which first will be "non-assimilable" unless favorable conditions make it "assimilable". And so forth.

Case studies

We could use case studies to test how the mechanistic model performs.

1. Tracing a specific type of compound, e.g. a plant wax *n*-alkane.

Factors that will create "right conditions" that promote more rapid decomposition include high O_2 and energy supplies, low pH, and the appropriate microbial community.

2. Increased moisture in an Oxisol.

We assume the soil is already moist so there was no initial moisture limitation of rates of decomposition. Then climate changes and soil moisture increases. Factors that will influence decomposition rates include (1) lower O₂-supply, and thus reduced decomposition rates of plant material; (2) increased water transport will move more organic matter into deeper soil that has higher available surface area compared to microbes so organic matter stocks would increase; (3) at low enough O_2 you dissolve Fe oxides, potentially releasing OM for decomposition; or moving them around, or altering the form of Fe oxide (goethite/ferrihydrate precipitating somewhere else).

3. Increase the net primary productivity (NPP) in an acid Cambisol

Belowground NPP increases, so the volume of soil influenced by the rhizosphere increases, Organic energy supply (root exudates) increases, allowing increased decomposition rates in the rhizosphere, by fungi; more organic acids will reduce pH. Soil structure would change and increase aggregate strength so decreasing accessibility, and thus decreasing decomposition. On the other hand, earthworm populations could increase, potentially increasing accessibility and increasing decomposition.

Further ideas and research needs

Is our typical time of observation long enough? - Which time scales do matter if we try to assess changes in carbon cycling of ecosystems? Lab experiments typically are carried out for days, weeks or months or in some cases over a year. It is not scientifically defensible to use those short-term laboratory data to predict long-term residue carbon mineralization rates in the field! What eventually matters, though, are increments of at least five years, integrating over natural fluctuations in climate (dry/wet year, long winter/early spring) and plant inputs.

Are we using precise and useful terminology and methods?

Qualitative, poorly defined terms simply are not useful at all, such as recalcitrant, resistant, refractory, inert, labile, resulting in slow, intermediate and fast pools. One example: A sugar molecule (in the right environment chemically very labile) can persist in the soil for decades, be it under anoxic conditions protected in an aggregate or sorbed to an poorly crystaline iron oxide. More accurate ways of describing compounds would include solubility in H_2O (mass per volume), molecular size (Dalton), stoichiometric O_2 -demand (Mol O_2), number of

functionally different bonds within the molecule, and degree of polymerization (number of monomers within polymer). It would be also important to develop procedures and protocols for the determination of molecular-level characteristics of organic substances that influence their degradation by microbes and enzymes in heterogeneous organic matter-mixtures.

Another step forward would be the use of a decomposition standard, used worldwide to calibrate and compare worldwide. One could take advantage of already existing soil decomposition standards, where substrate from different sources is decomposed in a common soil, and a common substrate is incubated in situ in different soils.

Decomposition of charred organic matter (often also called char, pyrogenic organic carbon, biochar, or black carbon) should be studied systematically in (standard) soils. Also here, one should use decomposition standards, either pure, crystalline compounds, or mixtures in environmental matrices (Hammes *et al.*, 2007). When using isotopically labeled materials on could track the fate of decomposing char into soil air, water and microorganisms.

Shared field experiments – A framework is needed where you can make experiments that allow for prediction across different soil types – what is the rate limiting step for decomposition may vary according to whether you are in an Oxisol, a Cambisol, etc. Or does it allow us to predict sensitivities and vulnerabilities to global change? Does it allow us to devise strategies for increasing OM storage in soil?

What happens in the subsoil? – How does a change in soil texture affect SOM degradation? Possibly, the age of soil carbon is related more to the dynamics of ion oxides than nature of SOM. How would the structure of soil in the 10's of microns scale affect SOM degradation? Surfaces of interactions, status of water (liquid, bound, ...)

Visibility and acknowledgement of ESF funding

At all announcements invitations and e-mail contacts it was highlighted that this workshop is funded by ESF. We used presentation slides with ESF logo, program and workshop folders were designed with the ESF logo. Funding by ESF will also be acknowledged in the resulting publication. Submission is envisaged for early 2010.

References

Balesdent, J., Mariotti, A., (1996) Measurement of soils organic matter turnover using ¹³C natural abundance. In: T.W. Boutton, S. Yamasaki (Eds.), *Mass* spectrometry of soils (Ed. by T.W. Boutton, S. Yamasaki), pp. 83-112. Dekker, New York.

Ekschmitt, K., Kandeler, E., Poll, C., Brune, A., Buscot, F., Friedrich, M., Gleixner, G., Hartmann, A., Kastner, M., Marhan, S., Miltner, A., Scheu, S., Wolters, V., (2008) Soil-carbon preservation through habitat constraints and biological limitations on decomposer activity. *Journal of Plant Nutrition and Soil Science*, 171(1), 27-35.

- Hammes, K., Schmidt, M.W.I., et al. (2007) Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochemical Cycles*, 21(3).
- Hedges, J.I., Eglinton, G., Hatcher, P.G., Kirchman, D.L., Arnosti, C., Derenne, S., Evershed, R.P., Kögel-Knabner, I., de Leeuw, J.W., Littke, R., Michaelis, W., Rullkötter, J., (2000) The molecularly-uncharacterized component of nonliving organic matter in natural environments. *Organic Geochemistry*, 31, 945-958.
- Heimann, M., Reichstein, M., (2008) Terrestrial ecosystem carbon dynamics and climate feedbacks. *Nature*, 451(7176), 289-292.
- Kelleher, B.P., Simpson, A.J., (2006) Humic substances in soils: Are they really chemically distinct? *Environmental Science & Technology*, 40(15), 4605-4611.
- Lehmann, J., Solomon, D., Kinyangi, J., Dathe, L., Wirick, S., Jacobsen, C., (2008) Spatial complexity of soil organic matter forms at nanometre scales. *Nature Geoscience*, 1(4), 238-242.
- Marschner, B., Brodowski, S., Dreves, A., Gleixner, G., Gude, A., Grootes, P.M., Hamer, U., Heim, A., Jandl, G., Ji, R., Kaiser, K., Kalbitz, K., Kramer, C., Leinweber, P., Rethemeyer, J., Schaeffer, A., Schmidt, M.W.I., Schwark, L., Wiesenberg, G.L.B., (2008) How relevant is recalcitrance for the stabilization of organic matter in soils? *Journal of Plant Nutrition and Soil Science*, 171(1), 91-110.
- Sollins, P., Homann, P., Caldwell, B.A., (1996) Stabilization and destabilization of soil organic matter: mechanisms and controls. *Geoderma*, 74, 65-105.
- Spielvogel, S., Prietzel, J., Kögel-Knabner, I., (2008) Soil organic matter stabilization in acidic forest soils is preferential and soil type-specific. *European Journal of Soil Science*, 59(4), 674-692.
- Trumbore, S.E., Czimczik, C.I., (2008) An uncertain future for soil carbon. *Science*, 321(5895), 1455-1456.
- von Lützow, M., Kogel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., (2006) Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions - a review. *European Journal of Soil Science*, 57(4), 426-445.
- von Lützow, M., Kögel-Knabner, I., Ludwig, B., Matzner, E., Flessa, H., Ekschmitt, K., Guggenberger, G., Marschner, B., Kalbitz, K., (2008) Stabilization mechanisms of organic matter in four temperate soils: Development and application of a conceptual model. *Journal of Plant Nutrition and Soil Science*, 171(1), 111-124.

Program

Sunday 4. October 2009

Everybody will have a person from our group as a personal local guide assigned, as you can see from the attached file. Most of you already know that person. He or she will contact you directly with details where exactly to meet.

From Zurich airport or railway station it is just 45 km to "Frauenfeld" the nearest city and the meeting site 'Kloster Ittingen'. To avoid heavy road traffic and to take advantage of the famous Swiss railway system, we organized transport by train. Twice an hour, trains commute from Zurich main station (x.07 and x.37 h) via Zurich Airport (x.18, x.48 h) to Frauenfeld, within 30 and 40 minutes respectively. At Frauenfeld station, the local taxi company "Ilg" (red cars, +41 52 720 4444) will take us 4 km to Kloster Ittingen. We just mention "ESF Workshop, University of Zurich at Kloster Ittingen", and do NOT pay directly. The taxi company will charge directly to the seminar hotel.

14 h and later, check in at hotel

20 h Welcome in foyer (just 20 meters from the reception) posters, drinks, snack-dinner (Margaret Torn)

Everybody brings one poster (A0 portrait) visualizing his or her top three research questions which should be solved in the next five years to be able to quantify processes driving organic matter turnover.

Monday 5. October

8.30-10.00 Plenary: Short introduction of participants through session chair, outline of the workshop.

Provocateur input (S. Trumbore, I. Janssens,) "What we think we need to know to model the terrestrial carbon cycle mechanistically" (working title). Discussion. (Michael Schmidt)

10.00-10.30 coffee break

10.30-12.30 Plenary: refining the research questions, forming working groups, naming rapporteurs (Daniel Rasse)

12.30-14.00 lunch
14.15-14.40 group picture
14.40-16.30 working groups (all)
16.30-17.00 coffee
16.30-17.30 Plenary: results from working groups (Johannes Lehmann, Ivan Jannsens)
19.00-20.00 dinner
20.00-23.00 Poster, water, wine and beer (David Manning)

Tuesday 6. October

08.00-09.45 plenary: discussion and formation of new working groups, naming raporteurs
09.45-12.30 working groups (coffee around 10.00)
12.30-13.30 lunch
13.30-15.00 guided tour to Kloster Ittingen
15.00-15.30 coffee
15.30-18.00 plenary: rapporteurs (Susan Trumbore, Johannes Lehmann) present results from working groups, discussion
19.00-20.00 dinner
20.00 Water, wine and beer, and rapporteurs write up one-page statements

Wednesday 7. October

Check Out

09.00-12.30 Plenary: the three rapporteurs present one-page statements on the research priorities for the next six years, synopsis discussion, final statements (coffee around 10.30)

12.30-13.50 lunch

13.50 Taxi to Frauenfeld railway station Train leaves at 14.12 (x.12 and x.42) and reaches Zurich Airport at 14.38, and Zurich main station at 14.51.

More details about the seminar hotel

Ittingen Charterhouse (Kloster Ittingen), is a former Charterhouse monastery with 800 years of history. It feels closely associated with the monastic values lived at this location. These values such as hospitality, care, education and meeting, reflection, spirituality and closeness to nature are also reflected in the operating concept. Ittingen runs a farm estate with its own dairy and viticulture, a market garden and the residential home and workshop for psychologically and mentally impaired persons. <u>http://www.kartause.ch/en</u>

List of participants

To maximize interaction, the number of participants was kept small, i.e. a maximum of about a dozen senior scientists, including ESF MOLTER members

- Daniel Rasse (NOR) <u>daniel.rasse@bioforsk.no</u> <u>http://www.bioforsk.no/ViewPPP.aspx?view=person&id=2416&viewLan</u> <u>guage=English</u>
- Michael Schmidt (CH) (local host, workshop chair) <u>michael.schmidt@geo.uzh.ch</u> <u>www.geo.uzh.ch</u> <u>http://www.geo.uzh.ch/en/units/2b/about-us/staff/michael-schmidt</u>
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- David Manning (GB) <u>david.manning@ncl.ac.uk</u> <u>http://www.ncl.ac.uk/insat/staff/profile/david.manning</u>
- José Gonzalez-Perez (ESP) jag@irnase.csic.es http://www.irnase.csic.es/ingles/geoindi.php

and other specialist

- Paolo Nannipieri (ITA) Soil Microbiology, Dipartimento di Scienza del Suolo e Nutrizione della Pianta, P.le delle Cascine 15, 50144 Firenze, Italy paolo.nannipieri@unifi.it
- Thorsten Dittmar (USA / GER) (USA, after October 2008 Max-Planck-Inst. Marine Chemistry, Bremen, GER) preservation of dissolved organic carbon in marine systems <u>dittmar@icbm.de</u> <u>http://ocean.fsu.edu/faculty/dittmar/dittmar.html</u>
- Georg Guggenberger (GER) guggenberger@ifbk.uni-hannover.de <u>http://www.unics.uni-</u> <u>hannover.de/nhdfjoba/mitarbeiter/wiss_mitarbeiter_bod.htm</u> sorptive stabilization
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