PROJECT INFORMATION

Project title: Predicting the impact of redox constraints on soil carbon storage across ecosystem scales

Project ID: 109

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PROJECT DESCRIPTION

Objective(s):

Soil organic matter (SOM) represents the largest active terrestrial pool of carbon and is a critical factor determining soil fertility, water quality, and greenhouse gas emissions. Mineralized SOM enters the atmosphere as greenhouse gases such as methane and CO_2, where the turnover time of SOM (how long deposited organic matter resides in soil) constrains the rate at which an ecosystem releases carbon back to the atmosphere. Currently, our ability to model SOM dynamics is limited by our understanding of the biogeochemical processes controlling SOM cycling. Microbial carbon cycling is traditionally considered to be driven by assimilation of nutrients such as C and N following a particular stoichiometry, allowing limiting resource theory to predict environmental nutrient levels. In this case, 'nutrient limitation' governs the coupled dynamics of C and N. However, anaerobic respiration pathways also drive carbon cycling via mineralization, rather than assimilation, and initiate denitrification under anoxic conditions. Thus, a 'redox limitation' or 'energy limitation' governs C cycling in environments lacking the energetically-favorable electron acceptor, oxygen.
The overall goal of our work is to determine the quantitative importance of energetic constraints on SOM decomposition, and thus soil C storage, across different soil ecosystems based on commonly measured soil characteristics. Specifically, aqueous (and solid state, when available) chemistry of Fe(II), Mn(II), nitrate, sulfate, oxygen, pH and redox potential will be used as predictors of organic carbon in soil and groundwater systems.

Our specific objectives are to:

1) Utilize relationships between total C and dissolved metals (as indicators of anaerobic conditions) and nutrients in soils to predict whether SOM concentrations are predominantly driven by a) redox constraints, or b) nutrient limitations.
2) Develop a statistical model to quantify energetic constraints on soil C turnover using measured dissolved species related to redox potential.
3) Test our model's ability to predict energetic and nutrient constraints on SOM quantities in different soil ecosystems.

The UNECE ICP Forests dataset is the largest and most complete with respect to organic C stocks, pore water chemistry and soil properties. We will use this extensive dataset to calibrate and test the predictive ability of our model under a variety of land cover and soil conditions.

Scientific background:
Terrestrial carbon, over 75% of which resides in soils (Schlesinger 1977), is vulnerable to climate and land use change (Knorr et al. 2005; Davidson & Janssens 2006). Empirical attempts have modeled the decomposition of soil organic matter (SOM) and the resultant fluxes of carbon, mainly as CO_2, from soils (Parton et al. 1987; Jenkinson et al. 1990; Schimel et al. 1994; Skjemstad et al. 2004). These models break SOM into two or more pools of varying accessibility to microbial decomposition based on SOM chemical composition (Kleber 2010). However, recent findings suggest such approaches are mechanistically incorrect (Sollins et al. 1996; Kleber et al. 2011). One potential cause of discrepancy is that these models fail to consider carbon processed by anaerobic respiration. We propose to improve existing models for carbon stocks and turnover in soils by considering the energetic constraints on SOM respiration.
Ecology has a long-standing interest in quantifying resource availability and uptake rates for biological growth (Hutchinson 1948; Hairston et al. 1960). Stoichiometry of elements in biomass has traditionally been used to understand nutrient uptake and nutrient concentrations in the environment- for instance, using the Redfield ratio to understand ocean nutrient cycling (Redfield 1958; Elser & Urabe 1999; Arrigo 2005). Conversely, environmental nutrient levels are used to inform population resource needs and competitive outcomes, as in Tilman resource ratio theory (Bloom et al. 1985; Tilman 1985). However, environmental nutrients are used both for anabolic processes *and* for dissimilatory catabolic processes. Therefore, stoichiometry predicted by limiting resource theory and assimilatory needs of organisms is insufficient to explain the relationships between inorganic nitrogen and carbon levels in certain environments (Helton et al. 2015). Under energy-limited anoxic conditions, microbes will mineralize organic carbon and reduce nitrate as an energy-generating metabolism, resulting in very different C and N fates than predicted based on assimilatory processes alone.
We propose using a model that considers the energetic constraints on respiration of soil organic matter (SOM) to better understand soil stocks and turnover over the full soil depth using routinely obtained soil characteristics. Separation of SOM into two mechanistically distinct pools—aerobic vs. anaerobic/energy-limited—would facilitate empirical modeling of SOM between different saturation states and along a soil

profile. Soils span a large spectrum of redox conditions and host high microbial activity, providing the necessary conditions for us to

1) assess whether energetic or assimilatory needs dominate soil carbon cycling, and
2) correlate the availability of different electron acceptors to carbon cycling under anaerobic conditions. We will use ratios of dissolved organic carbon to dissolved inorganic nitrogen (DOC:DIN) and nitrate to ammonium (NO_3^-:NH_4^+) in soil pore water to evaluate whethernutrient or energy limitation may control SOM cycling in a given environment. Under lowoxygen (energy-limited) conditions, compounds such as nitrate, iron, manganese, and sulfate serve as the electron acceptor for anaerobic microbial respiration and will be used to model C storage.
Helton et al. (2015) suggested that limiting nutrient theory predicts C:N ratios in aerobic environments, where C and N will be assimilated in a molar ratio equal to the C:N molar ratio in microbial biomass. In anaerobic environments, however, nitrogen species such as nitrate can be used as electron acceptors instead of oxygen. Thus, C:N may be lower than expected based on limiting nutrient theory in anaerobic but carbon-rich environments in which nitrate is respired and converted to ammonium, rather than assimilated. We therefore hypothesize the following:

Hypothesis 1:
Relative concentrations of chemical species used as nutrients or for energy metabolism will indicate whether carbon and nitrogen dynamics are nutrient limited (aerobic conditions) or energy limited (anaerobic conditions).
Whether the microorganisms are nutrient or energy limited will subsequently predict whether carbon cycling proceeds via aerobic respiration or via slower, less efficient anaerobic respiration pathways. Dissolved oxygen and redox indicators are less often present in soil water data than DIN and DOC measurements. We will therefore use the relationship between dissolved organic carbon (DOC) and dissolved inorganic nitrogen (DIN), and between nitrate (NO_3^-) and ammonium (NH_4^+), to predict whether carbon cycling proceeds via assimilatory or dissimilatory pathways (Helton et al. 2015). Using nutrient- vs. energy-limitation as a proxy for anaerobic conditions is critical to improve our ability to identify anoxic sites, which should have very different carbon and nitrogen dynamics than oxic sites, over a large range of soil datasets. The relationships of DIN vs. DOC, and nitrate-N (NO_3^--N) vs. ammonium-N (NH_4^+-N) will be tested using linear regression and change-point analysis as in Helton et al. (2015). A change-point between a steep negative and a shallow negative slope for a plot of DIN vs. DOC is indicative of nutrient limitation, which we expect for aerobic soils. Such a system should give a correlation greater than 1 for NO_3^--N versus NH_4^+-N due to the lower energy required for ammonium assimilation. No change-point for DIN vs. OC would indicate energetic limitation. In low-energy anaerobic environments, nitrate is increasingly respired and converted to ammonium, therefore maintaining total DIN levels with increasing carbon.
Under such conditions, a change-point would be expected in the relationship between nitrate and ammonium as a function of DOC. These relationships will be tested for the composite data set, individual sites, and different types of soils represented in the ICP Forests dataset.

After establishing either oxic or anoxic soil conditions, we will create a statistical model relating soil and soil solution parameters to soil carbon abundance and turnover in anaerobic soils. We therefore propose our second hypothesis,

Hypothesis 2: *Under anaerobic conditions, the stoichiometry of redox-active compounds will predict carbon storage.*
Anaerobic conditions should correlate to greater SOM storage that depends on the availability of non-oxygen electron acceptors. For energy-limited environments, we will use the stoichiometry of terminal electron acceptors as predictors of carbon storage in soils and sediments under reducing conditions. Model input will include routinely measured soil solution parameters including nitrate, ammonium, dissolved iron and manganese, sulfate and pH. The ICP Forest dataset encompasses many climates, forest and soil types around Europe that allow for robust parameterization of a globally relevant model. Furthermore, the ICP Forest data have been collected for decades. This time series allows us to look at soil carbon dynamics over time to get residence time estimates in addition to soil carbon stocks.
In summary, we will use the ICP Forest data to create a broadly applicable model predicting soil (and sediment) carbon storage and turnover. This model's novelty arises from its ability to treat aerobic and anaerobic SOM dynamics distinctly, to work over depth, and to account for energetic in addition to nutrient limitations on microbial carbon processing. Our work will improve the ability of ecosystem and climate models to accurately depict terrestrial carbon fluxes and storage in the face of changing climate and feedback mechanisms.

References
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