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Modelling *in situ* activities of enzymes as a tool to explain seasonal variation of soil respiration from agro-ecosystems

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ABSTRACT

Understanding *in situ* enzyme activities could help clarify the fate of soil organic carbon (SOC), one of the largest uncertainties in predicting future climate. Here, we explored the role of soil temperature and moisture on SOM decomposition by using, for the first time, modelled *in situ* enzyme activities as a proxy to explain seasonal variation in soil respiration. We measured temperature sensitivities (Q_{10}) of three enzymes (β-glucosidase, xylanase and phenoloxidase) and moisture sensitivity of β-glucosidase from agricultural soils in southwest Germany. Significant seasonal variation was found in potential activities of β-glucosidase, xylanase and phenoloxidase and in Q_{10} for β-glucosidase and phenoloxidase activities but not for xylanase. We measured moisture sensitivity of β-glucosidase activity at four moisture levels (12% −32%), and fitted a saturation function reflecting increasing substrate limitation due to limited substrate diffusion at low water contents. The moisture response function of β-glucosidase activity remained stable throughout the year. Sensitivity of enzymes to temperature and moisture remains one of the greatest uncertainties in C models. We therefore used the response functions to model temperature-based and temperature and moisture-based *in situ* enzyme activities to characterize seasonal variation in SOC decomposition. We found temperature to be the main factor controlling *in situ* enzyme activities. To prove the relevance of our modelling approach, we compared the modelled *in situ* enzyme activities with soil respiration data measured weekly. Temperature-based *in situ* enzyme activities explained seasonal variability in soil respiration well, with model efficiencies between 0.35 and 0.78. Fitting an exponential response function to *in situ* soil temperature explained soil respiration to a lesser extent than our enzyme-based approach. Adding soil moisture as a co-factor improved model efficiencies only partly. Our results demonstrate the potential of this new approach to explain seasonal variation of enzyme related processes.

1. Introduction

Soil carbon (C) stock is estimated to be >1500 Pg C, significantly higher than atmospheric stock ~750 Pg C (Kirschbaum, 2000; Davidson and Janssens, 2006; IPCC, 2007). SOC, the largest pool in terrestrial C cycling (Kandeler et al., 2005), has the potential to act as a source or sink of greenhouse gases due to its dynamic interactions with the atmosphere (Lal, 2004). A large fraction of C is introduced into the atmosphere as CO_2 through microbial decomposition of organic matter (Frey et al., 2013). Temperature sensitivity of soil organic matter (SOM) decomposition has been given great attention (Davidson et al., 2012) due to the inherent relevance of kinetic theory (Davidson and Janssens, 2006). Expected warming of the earth's climate between 3 and 5 °C over the next century (Bergfur and Friberg, 2012) may accelerate decomposition of SOC (Bengtson and Bengtsson, 2007) through faster processing of SOC by soil biotic communities and, therefore, affect the C source or sink functions of soils. The higher sensitivity of SOM decomposition, and

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in turn soil respiration, to temperature as compared to net photosynthesis makes investigations into the temperature sensitivity of C mineralization very important (Kirschbaum, 2000; Koch et al., 2007).

The temperature response of SOM decomposition depends upon its molecular structure; recalcitrant compounds have higher activation energies (E_a) than labile and, therefore, theoretically higher temperature sensitivity (Davidson and Janssens, 2006). Yet most existing C models consider a uniform temperature sensitivity of decomposition for organic matter pools of different stabilities (Fierer et al., 2005; Todd-Brown et al., 2012). This issue still needs to be resolved due to variations in findings related to the temperature response of different C pools (Zimmermann and Bird, 2012).

Extracellular enzymes (EE), produced by soil microorganisms, perform the rate-limiting step in SOM decomposition as well as nutrient cycling (Sinsabaugh, 1994; Allison and Vitousek, 2005). Most C models do not take extracellular enzyme kinetics explicitly into consideration (Allison et al., 2010). Recently efforts have been made to develop mechanistic models to simulate the combined effect of temperature, moisture and soluble-substrate supply on soil respiration by considering enzyme kinetics (Davidson et al., 2012). As almost half of the CO_2 released from soil is linked to decomposition of SOM by microorganisms and a large fraction of this respired CO_2 depends upon EE activity (Ryan and Law, 2005; Frey et al., 2013), adding enzyme kinetics to C models has the potential to improve climate change predictions (Allison et al., 2010).

Environmental factors, such as soil temperature, pH, diffusion constraints, and substrate availability and complexity modify microbial production, expression and temperature sensitivity of EE (Koch et al., 2007; Burns et al., 2013). For example, by analysing samples collected over different seasons from a forest soil Baldrian et al. (2013) found that seasonal variations in soil temperature strongly influenced SOM decomposition by changing the pool size and activity of EE. Different studies have focused on seasonal variations in the temperature sensitivities of soil enzymes (e.g. Koch et al., 2007; Brzostek and Finzi, 2012). However, it is still unclear which factors drive these seasonal trends (Jing et al., 2014). The complex interactions between enzymes and their environment and high variability of their temperature sensitivities makes it impossible to extrapolate single measurements across different temporal scales (Weedon et al., 2011). The current laboratory assays for measuring EE activities are performed under controlled conditions, which do not represent these complex interactions *in situ* (Henry, 2012). Moreover, this approach neglects the fundamental role of different factors, e.g. temperature and enzyme/substrate diffusion, in controlling *in situ* enzyme activities (Weedon et al., 2011). To illustrate the interactions of enzyme pool size and seasonal temperature sensitivity patterns in controlling *in situ* enzyme activities, Wallenstein et al. (2009) developed a predictive model of *in situ* β-glucosidase activities based on enzyme activities measured at different sampling dates, Q_{10} and daily soil temperature data from an arctic tundra site.

Little information is available on the effects of soil moisture on the temperature sensitivity of organic matter decomposition (Craine and Gelderman, 2011; Steinweg et al., 2012). Limiting soil moisture can cause a decline in diffusion rates of substrates and, therefore, in EE activity (Davidson and Janssens, 2006). As a consequence, increasing temperatures may not result in a positive feedback to climate change when soil moisture is a limiting factor (Allison and Treseder, 2008). Standard enzyme assays are performed in soil slurry (e.g. Poll et al., 2006; Kramer et al., 2013) for estimating enzyme potentials at non-limiting conditions neglecting diffusion constraint. Recently, Steinweg et al. (2012) developed an assay based on the use of fluorogenic substrates, to account for diffusion limitation at low water content and for non-homogeneous distribution of substrate in soil.

Previous studies have predicted the response of EE activity to *in situ* temperature and moisture (e.g. Wallenstein et al., 2009; Steinweg et al., 2012) and have yielded valuable insights into soil carbon dynamics. To date, however, the next step, that of using modelled *in situ* enzyme potentials as an explanatory tool for the seasonal variation of CO_2 respiration, is missing.

The goal of the present study is to explore the role of abiotic controls, i.e. soil temperature and moisture, on SOM decomposition by using modelled *in situ* enzyme activities as a proxy. We modelled *in situ* temperature-based potentials of three different enzymes (β-glucosidase, xylanase and phenoloxidase) targeting organic matter pools of different complexity, at two different study sites, with and without the presence of vegetation (fallow and vegetation plots). The selection of these three enzymes was based on the assumption that the targeted organic matter pools are representative for most of the soil organic matter pools. We also modelled *in situ* moisture-based β-glucosidase potential for both study sites and combined both temperature and moisture functions to illustrate the combined effect of both abiotic factors on enzyme potentials. To identify the similarities in seasonal patterns of modelled *in situ* enzyme activities with soil respiration and to prove the relevance of the modelling approach, we compared the modelled *in situ* enzyme activities with weekly measured soil surface CO_2–C fluxes. We hypothesized that (1) temperature and moisture sensitivity of enzymes targeting organic matter pools of different stability will change during the year. Furthermore, we expected that (2) measured soil CO_2 flux correlates strongly with the modelled *in situ* enzyme potentials, and we expected even stronger correlations with combined controls of soil temperature and moisture on *in situ* enzyme potentials.

2. Material and methods

2.1. Study site description

We investigated two study regions, with different climatic and edaphic conditions, which are part of the integrated research project "Agricultural landscapes under global climate change – processes and feedbacks on regional scale" (https://klimawandel.uni-hohenheim.de/). The first study site (48°31′7″ N, 9°46′2″ E) is located close to the city of Nellingen in the Swabian Alb region, while the second study site (48°55′7″ N, 8°42′2″ E) is located close to the city of Pforzheim in the Kraichgau region. The Swabian Alb (800–850 m a.s.l.) is characterized as an extensively used grassland and croplands region with cool and humid climate (mean annual temperature and precipitation $\leq$ 7 °C and 800–1000 mm, respectively, see Fig. S1a). The Kraichgau region (100–400 m a.s.l.) is characterized by a warmer and drier climate (mean annual temperature and precipitation >9 °C and 720–830 mm, respectively, see Fig. S1b) and intensive agriculture. Swabian Alb is a karst plateau of Jurassic limestone with soils classified as Calcic Luvisol, Anthrosol and Rendzic Leptosol whereas the Kraichgau region has loess parent material with soil developed into Stagnic Cambisol (IUSS Working Group WRB, 2007).

2.2. Experimental setup and soil sampling

To capture a range of soil carbon storage conditions, to investigate soils differing in organic matter input but which are typical for each region and to isolate more recalcitrant organic matter, three fallow plots (5 × 5 m) were installed in three selected agricultural fields in each study region in 2009. These plots were left fallow since 2009 until the time of sampling. Adjacent to fallow plots, vegetation plots (5 × 5 m) were selected in 2012 (vegetation type and period are given in Table S1). Each fallow and vegetation plot