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Geophysical Research Abstracts
Vol. 17, EGU2015-6260, 2015
EGU General Assembly 2015

The inherent properties of enzymes can only lead to a negative temperature response of soil C decomposition on the long-term.

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More than one century after the pioneer work of Arrhenius on the temperature dependence of chemical reactions, the response of soil C decomposition to global warming remains uncertain. The majority of lab experiments, generally conducted at short term (months to years), suggest that the decomposition of soil C accelerates with temperature. In contrast, long-term (> 5 years) ecosystem warming experiments show that stimulation of soil respiration is only transitory. Moreover, studies on ecosystem C fluxes along a latitudinal gradient even suggest that, for a given amount of C fixed by the ecosystem, the decomposition flux decreases with temperature leading to higher C storage in warmer ecosystems (Giardina and Ryan, 2000; Sanderman, 2003).

To understand this discrepancy between short-term and long-term temperature responses of C decomposition, we re-analysed the thermo-dependence of decomposition in a theory distinguishing enzyme-limited and substrate-limited reactions. Indeed, it is increasingly recognized that decomposition of the largest pool of soil C (humified organic C, HOC) is limited by the amount of soil (extracellular) enzymes.

The substrate-limited reaction and its dependence to temperature were classically modelled with the first order kinetics $dC/dt=-kC$ where reaction velocity k is modelled by an Arrhenius equation. The thermo-dependence of enzyme-limited reactions was studied in models where the reaction velocity depends on the specific activity of enzymes and the dynamics of enzyme pool, each of which may display distinct temperature sensitivities. The dynamics of the enzyme pool depended on (1) the inactivation of enzymes and its dependence to time and temperature and (2) the microbial production of enzymes, which is limited by the energy available to soil microorganisms. These models were analysed mathematically and through simulations using data on thermodynamics properties of enzymes (activation energies) and ecosystem C fluxes.

Our results show that the temperature response of the substrate-limited reaction is systematically positive irrespective of the simulation duration. In the case of enzyme-limited reaction, the effect of temperature is also positive on the short-term whereas it can be positive or negative on the long-term depending on the relative temperature sensitivities of the inactivation and catalysis processes. However, a review of literature showed that the temperature sensitivity (activation energy) is higher for the inactivation than the catalysis reaction for a wide range of enzymes. Consequently, our model predicts that the long-term temperature response of enzyme-limited reaction is negative.

This new theory can resolve the apparent contradiction between short-term and long-term response of soil C respiration to temperature. The immediate increase of soil respiration to warming is explained by the increased specific activity of enzymes. However, warming also accelerates the inactivation of enzymes leading to a slow decrease of the pool of enzymes until a level that is no more compensated by their higher catalytic activity. Consequently, over long-term or at ecosystem steady-state, warming has no or negative effect on soil C respiration.