



Oxidation state, bioavailability & biochemical pathway define the fate of carbon in soil

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Numerous experiments under laboratory and field conditions analyzed microbial utilization and mean residence time (MRT) of carbon (C) from plant and microbial residues as well as root exudates in soil. Most of these studies tested the effects of various environmental factors, such as temperature, soil moisture, texture etc. on these parameters. However, only a few studies compared the properties of the substances themselves and there is no conceptual framework based on biochemical pathways. We hypothesize that the fate of C from organic substances in soil strongly depends on the first step of their microbial utilization, specifically, on biochemical pathway and initial C oxidation state, as well as its bioavailability in soils, defined by its hydrophobicity and molecular weight. Here we introduce and evaluate a new conceptual framework based on the following parameters: 1) C oxidation state, 2) molecular weight and hydrophobicity, 3) initial biochemical pathway of a substance class in microbial cells. To assess these parameters, two databases were prepared based on the literature and own studies. The first database included only the studies with ^{14}C or ^{13}C position specific labeled sugars, amino acids, carboxylic acids, phenols and lipids in soil. This database allowed us to analyze microbial utilization and mineralization of organics to CO_2 depending on their C oxidation state (OS) and on functional groups. Additionally, we calculated data on the bond electronegativity of all compounds investigated in these studies. The second data base included the results of ^{14}C and ^{13}C studies with uniformly labeled substances of various classes. This database considered the free enthalpie (Delta H) per C unit from a variety of substrates differing in their aromaticity, hydrophobicity/electronegativity and location of the substance on the van Krevelen diagram. In addition, we calculated the hydrophobicity from the electronegativity of the individual bonds and recorded their molecular weight in our databases. For both data bases the decomposition rates and the MRT of C remaining in soil were calculated by the double first-order kinetics and related to the four parameter groups.

The first database showed high correlation of mineralization rates to CO_2 with the C oxidation state and biochemical pathway. Carboxyl group (OS = +3) was split at first from the skeleton of nearly all substances. In contrast, the methyl group (OS = -3) was mineralized as the slowest and after incorporation into microbial cells remained the longest period in soil. This general pattern reflects a clear preferential oxidation of already highly oxidized, polar functional groups. The initial use of substances within glucolysis (e.g. sugars) lead to a higher portion of remaining C in soil compared to C introduced via citric acid cycle (e.g. carboxylic acids). Concerning substance groups, the mineralization rates were the fastest for amino acids and sugars and the slowest for of the lipids – corresponding to their molecular weight and hydrophobicity. This corresponded well with localization of the substance classes on the van Krevelen diagram. Generally, high oxidation state of the initial substance and consequently its low free enthalpy content lead to faster decomposition. In contrast, low oxidation state (e.g. lipids, aromatics) corresponds to high hydrophobicity and so, slow uptake from soil solution and utilization within microbial cells. Consequently, the optimum for microbial biomass utilization in soil and use for anabolic processes is common for sugars that have the oxidation state close to 0, have medium energy content and are hydrophilic.

We conclude that from the tested substance properties, the oxidation state and biochemical pathway explained well the initial fate of C in soil, i.e. its mineralization to CO_2 and incorporation into microbial biomass. Because the first step and microbial cycling are crucial for its further transformations, the same criteria are pivotal for C stabilization in soil.