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# Sorption affects amino acid pathways in soil: Implications from position-specific labeling of alanine

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## ABSTRACT

Organo-mineral interactions are the most important mechanisms of long-term C stabilization in soils. Nevertheless, a part of the sorbed low molecular weight organic substances (LMWOS) remains bioavailable. Uniformly labeling of substances by <sup>14</sup>C or <sup>13</sup>C reflects only the average fate of C atoms of an LMWOS molecule. The submolecular tool of position-specific labeling allows to analyze metabolic pathways of individual functional groups and thus reveals deeper insight into mechanisms of sorption and microbial utilization.

Alanine labeled with <sup>14</sup>C in the 1st, 2nd or 3rd position was adsorbed to five sorbents: two iron oxides with different crystalline structure: goethite and haematite; two clay minerals with 2:1 layers – smectite, and 1:1 layers – kaolinite; and activated charcoal. After subsequent addition of these sorbents to a loamy haplic Luvisol, we analyzed <sup>14</sup>C release into the soil solution, its microbial utilization and <sup>14</sup>CO<sub>2</sub> efflux from individual C positions of alanine.

All sorbents bound alanine as an intact molecule (identical sorption of 1st, 2nd or 3rd positions). The bioavailability of sorbed alanine and its microbial transformation pathways depended strongly on the sorbent. Goethite and activated charcoal sorbed the highest amount of alanine (~45% of the input), and the lowest portion of the sorbed alanine C was microbially utilized (26 and 22%, respectively). Mineralization of the desorbed alanine peaked within the first 5 h and was most pronounced for alanine bound to clay minerals. The initial mineralization to CO<sub>2</sub> of bound alanine was always highest for the C-1 position (–COOH group). Mineralization rates of C-2 and C-3 exceeded the C-1 oxidation after 10–50 h, reflecting the classical biochemical pathways: 1) deamination, 2) decarboxylation of C-1 within glycolysis, and further 3) oxidation of C-2 and C-3 in the citric acid cycle. The ratio between two metabolic pathways – glycolysis (C-1 oxidation) versus citric-acid cycle (oxidation of C-2 and C-3) – was dependent on the microbial availability of sorbed alanine. High availability causes a peak in glycolysis C-1 oxidation followed by an abrupt shift to oxidation via the citric acid cycle. Low microbial availability of sorbed alanine, in turn, leads to a less pronounced, parallel oxidation of all three positions and to a higher relative incorporation of alanine C into microbial compounds. Modeling of C fluxes revealed that a significant portion of the sorbed alanine was incorporated in microbial biomass after 78 h and was further stabilized at the sorbents' surfaces.

Position-specific labeling enabled determination of pathways and rates of C utilization from individual molecule positions and its dependence on various sorption mechanisms. We conclude that position-specific labeling is a unique tool for detailed insights into the submolecular transformation processes, mechanisms and rates of C stabilization in soil.

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## 1. Introduction

Soil organic carbon (SOC) represents a major terrestrial carbon (C) sink. This makes studies on the transformation of organic substances in soils important for understanding the C cycle in terrestrial ecosystems. Plant residues, rhizodeposits and pyrogenic

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organic matter are the main sources of organic matter in soils (Knicker, 2011a; Kuzyakov and Domanski, 2000; Rasse et al., 2005). Accordingly, many studies have focused on decomposition, microbial utilization and stabilization of C from these sources in soils (Rasse et al., 2005; von Luetzow et al., 2006; Dungait et al., 2012).

During litter decomposition, all macromolecular compounds are split by enzymes into low molecular weight organic substances (Cadisch and Giller, 1996). Thus, transformation of LMWOS is a key step in biogeochemical processes in soils: all high molecular substances pass this stage during their degradation. Microorganisms determine the fate of LMWOS in soil because they either decompose them to CO<sub>2</sub> (catabolism) or incorporate them into cellular compounds (anabolism). Both main branches of metabolism occur in parallel and C partitioning between them depends on environmental conditions.

Within the LMWOS, amino acids play an important role because they are the quantitatively most important compound class coupling the C and N cycles. In topsoils, amino acid N – mainly bound in proteins – constitutes 7–50% of the total organic N (Knicker, 2011b; Stevenson, 1982), and concentrations of free amino acids range from 0.5 μM in root-free bulk soil up to 5 mM directly next to bursting cells (Jones and Hodge, 1999; Fischer et al., 2007). Thus, many recent studies focused on the fate of N-containing LMWOS (Kuzyakov, 1996, 1997; Lipson et al., 2001) and investigated the three major pathways of amino acid in soil: 1) sorption (Jones, 1999), 2) microbial utilization (Vinolas et al., 2001a, 2001b), and 3) plant uptake (Nasholm et al., 1998; Lipson and Nasholm, 2001). Whereas the importance of plant uptake strongly depends on the type of ecosystem (especially its N limitation) (Lipson and Nasholm, 2001; Jones et al., 2005; Sauheitl et al., 2009), sorption and microbial utilization are significant in all ecosystems and are competing processes. They lead either to a stabilization of amino acid C and N in soils or to their decomposition.

Many studies on the microbial utilization of free amino acids showed that their metabolization occurs mainly intracellularly after uptake by transport systems (Anraku, 1980; Hediger, 1994; Hosie and Poole, 2001; Dippold and Kuzyakov, 2013). Based on the uptake kinetics of some single amino acids, microbial uptake outcompetes sorption in soils (Jones and Hodge, 1999; Vinolas et al., 2001a; Fischer et al., 2010). Nevertheless, sorption is thought to be the most relevant long-term stabilization mechanism for amino acids in soils. This is even more relevant for their amino acid polymers – te proteins – which accumulate at mineral surfaces (Duemig et al., 2012; Spence and Kelleher, 2012). However, neither the exact processes nor the relevance of amino acid sorption compared to stabilization by inaccessibility in micropores or aggregates has been analyzed (Sollins et al., 1996; von Luetzow et al., 2006).

The lack of accumulation of strongly sorbed amino acids in ecosystems (Stevenson, 1982) supports the idea that sorption does not completely protect amino acids from biodegradation. They do, however, remain at least partially bioavailable (Gonod et al., 2006). Jones and Hodge (1999) demonstrated that sorption strength of three amino acids (lysine > glycine > glutamic acid) behaves contrary to microbial utilization (glutamic acid > glycine > lysine). These results support the idea that the presence of substrate in solution and consequently sorption is key driver regulating the fate of amino acids. Furthermore, both the quantity of microbial uptake and the metabolization pathways of LMWOS are affected by sorption (Schneckenberger et al., 2008; Fischer and Kuzyakov, 2010; Dijkstra et al., 2011a).

Broadly, amino acids can be adsorbed by three types of functional groups (Jones and Hodge, 1999): 1) ion exchange by the positively charged amino groups, 2) ligand exchange by the carboxyl groups and 3) hydrophobic interactions by the alkyl

groups. In addition, weak electrostatic interactions (H-bondings, dipole-dipole-interactions, van-der-Waals bondings) are possible by the C skeleton (Brigatti et al., 1999) and intercalation into the clay mineral interlayer has also been discussed (Wattel-Koekkoek et al., 2003). There is strong evidence that soil properties (Kemmitt et al., 2008) such as soil mineralogy (Strahm and Harrison, 2008) influence the microbial utilization of LMWOS, but detailed studies comparing sorption on various mineral phases and their effect on microbial utilization of amino acids are rare (Dashman and Stotzky, 1982).

Here, we use the approach of position-specific labeling to elucidate the shifts in microbial amino acid transformation pathways caused by sorption. This tool, commonly used in biochemistry to reconstruct metabolic pathways, has increasingly been applied in soil science in recent years (Dijkstra et al., 2011a, 2011b, 2011c; Fischer and Kuzyakov, 2010). It overcomes the limitations of uniform labeling because it helps differentiate between cleavage of a molecule vs. utilization of the entire molecules.

Our model amino acid – alanine (one of the most abundant amino acids in soil) – occurs under soil conditions as a dipolar ion: it has a positive charge, a negative charge and a hydrophobic methyl group – enabling different sorption mechanisms. As a representative subset of sorbents common in soils and representative for three basic sorption mechanisms, we chose a three- and a two-layer clay mineral (smectite and kaolinite), two iron oxides (goethite and haematite) and activated charcoal. Thus, we present here a submolecular approach to elucidate LMWOS stabilization on sorbents and effects of sorption on amino acid transformations in soil. We assume that alanine interacts differently with various mineral phases and that interaction strength and mechanism strongly affects its subsequent microbial utilization, e.g. we assume a preferred allocation of LMWOS-C into the anabolic pathways of maintenance metabolism, the lower the availability of a substrate is. We hypothesize that various sorption mechanisms affect the stabilization of amino acid C on mineral surfaces not only by direct interaction of LMWOS-C with the mineral but also by changing C allocation: The stronger a substrate is sorbed, the more it's C is transformed to products, which are prone to be stabilized on the sorbents. In the case of polymeric microbial products (proteins, cell walls,...), this process could be identified by an equal incorporation of all three alanine C positions.

## 2. Materials and methods

### 2.1. Soil

Soil samples were taken from an Ap horizon of a loamy silt, haplic Luvisol (WRB 2006) from a long-term cultivated field in Bavaria near Hohenpözl (49.907 N, 11.152 E, 501 m asl, mean annual temperature 6.7 °C, mean annual precipitation 874 mm), where a continuous rotation of corn, barley, wheat and triticale was established. The soil had the following characteristics: pH<sub>KCl</sub> 4.9 and pH<sub>H2O</sub> 6.5, TOC and TN content were 1.77% and 0.19%, respectively, and potential CEC was 174 mmol<sub>c</sub> kg<sup>-1</sup>. The soil was stored field-moist at 5 °C for less than 1 month, sieved to 2 mm, and all roots were removed manually before adding to the minerals. 800 mg of field-moist soil were used per replicate.

### 2.2. Sorbents

Minerals were ordered from Kremer pigments (Aichstetten/Allgäu, Germany): smectite-dominated Bentonite (58900), kaolinite-dominated Kaolin (58250), haematite-dominated “Eisenoxid rot” (48600) and goethite-dominated “Eisenoxidocker” (40301). Activated charcoal was ordered from Sigma–Aldrich

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