Review paper

Organic acid induced release of nutrients from metal-stabilized soil organic matter — The unbutton model

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ARTICLE INFO

ABSTRACT

Processes of soil organic matter (SOM) stabilization and the reverse, destabilization of SOM resulting in subsequent release and mobilization of nutrients from SOM, remain largely unresolved. The perception of SOM as supramolecular aggregates built of low molecular mass biomolecules is currently emerging. Polyvalent metal cations contribute to SOM tertiary structure by bridging functional groups of such molecules (Simpson et al., 2002). The strong bond to metals protects high quality organic material from being immediately accessed and decomposed. Here we propose a three-step process by which low molecular mass organic acids (LMMOAs) and hydrolytic enzymes act in series to destabilize SOM supramolecules to release organic nitrogen (N) and phosphorus (P) for local hyphal and root uptake. Complexation of the stabilizing metals by fungal-released LMMOA gives fungal-root consortia direct access to organic substrates of good quality. Because of their small sizes and carboxyl group configuration, citric and oxalic acids are the most effective LMMOAs forming stable complexes with the main SOM bridging metals Ca and Al in SOM. Citrate, forming particularly strong complexes with the trivalent cations Al and Fe, is dominant in soil solutions of low-productive highly acidic boreal forest soils where mycorrhizal associations with roots are formed predominantly by fungi with hydrophobic hyphal surfaces. In these systems mycelia participate in the formation of N-containing SOM with a significant contribution from strong Al bridges. In less acidic soils of temperate forests, including calcareous influenced soils, SOM is stabilized predominantly by Ca bridges. In such systems mycorrhizal fungi with more hydrophilic surfaces dominate, and oxalic acid, forming strong bidentate complexes with Ca, is the most common LMMOA exuded. A plant-fungus driven biotic mechanism at the supramolecular aggregate level (10^3—10^5 Da) resolves micro-spatial priming of SOM, where the destabilization step is prerequisite for subsequent release of nutrients.

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1. Introduction

Nitrogen (N) mineralization in forest soil is a process that cannot be understood without plants present (Dijkstra et al., 2009; Frank and Groffman, 2009), since they play an active role in the process (Högberg and Read, 2006). Most N or phosphorus (P) taken up by plants is not recently fixed or weathered, rather released from soil organic matter (SOM) molecules mainly derived from microbial internal structures and cell walls, which constitute a considerable part of SOM (Guggenberger et al., 1999; Godbold et al., 2006; Miltner et al., 2012; Clemmensen et al., 2013). In fact, small organic molecules may dominate the N uptake (Näsholm et al., 1998). The importance of mycorrhizae for plant nutrient uptake has long been recognized (Smith and Read, 2008), but the exact supply mechanisms are not yet well understood (Meyer et al., 2010; Mayor et al., 2012). Nitrogen delivering SOM in forest soils with low N availability is largely built from hydrophobic fungal wall remains (Unestam and Sun, 1995; Jones et al., 2004; Clemmensen et al., 2013) originating from the hydrophobic mycelia and rhizomorphs of some of the most abundant mycorrhizal fungal species present (Hobbie and Agerer, 2010; Lilleskov et al., 2011). These fungi have been proposed to actively take up and transport Fe and Al cations (Clarholm and Skyllberg, 2013). During the decomposition of hyphae, wall-bound metals will be incorporated in the SOM macromolecules where they function as bridge-builders.

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The method traditionally used to measure N mineralization by laboratory incubation involves sieving of the soil, a process that destroys active fungal hyphae and leaves bacteria to perform mineralization. Such studies demonstrate that SOM in fertile forests is of a quality that allows bacteria to mineralize N (Verchot et al., 2001). In contrast, incubation of sieved SOM from poor forest sites results in N immobilization, or far lower rates of N mineralization as compared to rates of N uptake observed in the field (Popovic, 1980; Nadelhoffer et al., 1991). A possible interpretation of these results is that under field conditions there is an on-going, active plant-initiated release and uptake of N in poor soils, which is not accounted for in laboratory incubations. Although most important in nutrient poor fungal-dominated soils, the process is suggested to take place also under more fertile conditions (Phillips et al., 2013). Processes regulating N availability in soils are of great interest since it is the most common growth-limiting nutrient for plants worldwide (Vitousek and Horwarth, 1991; LeBauer and Treseder, 2008), still these processes are not yet well understood (McDowell, 2003; Smith and Read, 2008).

Mild soil extraction methods demonstrate that most of the N in SOM appears to be present as peptides and α-amino acids (Knicker et al., 1993; Leinweber and Schulten, 2000; Knicker, 2011), forms that are accessed by most organisms. Yet, easily decomposable N forms are always present in the "humus" fraction (Tisdall and Oades, 1982; Elliott, 1986; Sollins et al., 1996; Derrien et al., 2007). These two observations suggest that high quality N-containing organic compounds in SOM are somehow protected from immediate degradation.

The currently most accepted perception of the structural composition of SOM (Sutton and Sposito, 2005; Kelleher and Simpson, 2006; Schmidt et al., 2011) suggests it comprises a mixture of organic components released at various stages of litter decomposition, including polysaccharides, polypeptides, aliphatic chains and aromatic lignin fragments, and small biomolecules. Together they serve as building blocks in the secondarily built supramolecular aggregate structure of SOM (Wershaw, 1985; Piccolo et al., 1996; Engebretson and von Wandruska, 1997). The supramolecules are held together by non–covalent bonds like van der Waals forces, H-bonds (Piccolo et al., 1996; Piccolo, 2002), and bonds between organic functional groups with polyvalent metals acting as bridges (Simpson et al., 2002). Besides forming the tertiary structure, the polyvalent cations stabilize the molecule and have been suggested to protect the easily degradable substrate from immediate degradation (Simpson et al., 2002; Clarholm and Skyllberg, 2013). The abundant metals Ca, Al and Fe form such bridges with predominantly oxygen containing functional groups, and they are also present in soil in sufficient amounts to be of importance for protection of easily decomposable N containing material (Kögel-Knabner and Kleber, 2012). Wagai et al. (2013) suggested that accumulation and mineralization of organic N and C in soils may be more dependent on the dynamics of organic Fe and Al complexe formation rather than on the existence of N and C adsorbing and stabilizing mineral phases such as oxyhydroxides of Fe and Al, and poorly crystalline aluminosilicates, the forms which until today have been most in focus (Schneider et al., 2010).

It was recently demonstrated that Al is a much more frequent SOM stabilizing metal in the most acidic, nutrient poor forest soils with low Ca concentrations, as compared to less acidic more productive soils where Ca bridges are in high predominance (Clarholm and Skyllberg, 2013). These authors suggested an active transportation and incorporation of Al cations in SOM by fungi to stabilize pH in acidic organic horizons. If combined with the observed lower N mineralization rates in low fertility coniferous forest floors and higher N mineralization rates in more fertile soils, the relative abundance of Al and Ca (and differences in their stabilizing effect of SOM) is suggested to play a major role for the release of soil N and P. Aluminium ions form multiple bridges in SOM and these are stronger compared to those formed by Ca. This could contribute to the large recalcitrance of SOM in low productive forests. The hydrophobic nature of SOM in these soils also makes water-depending enzymatic reactions less efficient.

Low molecular mass organic acids (LMMOAs) are released by vascular plants (Tyler and Ström, 1995), free-living fungi (Gadd, 1999), fungi forming ectomycorrhiza with boreal forest trees (Wallander and Wickman, 1999; Ahonen Jonnarth et al., 2000; van Hees et al., 2005) as well as by bacteria (Jones, 1998). Monocarboxylic acids like formic and acetic acids are the most common, but a number of other aliphatic and aromatic, mainly carboxylic acids have been detected in the rhizosphere soil (Ryan et al., 2001). Amounts of LMMOAs determined in undisturbed soil have been reported to be small, comprising about 0.5–5% of the total dissolved C (van Hees et al., 2000; Strobel, 2001). This and the high turnover rates of LMMOAs make their occurrence and behaviour in soil hard to trace and measure (van Hees et al., 2003).

The suggested major functions of LMMOAs released by plants and microbes in soil are: 1) to detoxify Al ions in solution by strong complex formation (Ahonen Jonnarth et al., 2000; Ma et al., 2001), 2) to increase the bioavailability of P and K by increasing rates of mineral weathering by complexation of mainly mineral bound Ca^{2+} (in calcareous soils) and Al^{3+} (in acidic soils) (Dutton and Evans, 1996; Landeweert et al., 2001), and 3) to increase the bioavailability of trace metals such as Fe^{3+}, Zn^{2+} and Cu^{2+} through complex formation with LMMOAs and subsequent active uptake of the formed organic complexes into cells. The latter function is suggested to be fulfilled by the release of specific metal binding LMM organic molecules known as siderophores (Powell et al., 1980). In studies focussing on Al-toxicity and K or P availability, the LMMOAs oxalic, citric and malic acids have been suggested to be the most important molecules exuded by plants and mycorrhizae (Fox, 1995).

In this paper we suggest yet another, so far unrecognized, role of LMMOA exudation: to enable destabilization of SOM by facilitating the breakage of metal bridges. In particular oxalate and citrate have exceptional affinities for the dominant bridge-forming polyvalent metal cations in SOM, as well as a suitable size and sufficient lipohilicity (citrate) to penetrate hydrophobic SOM structures (Piccolo, 2002). The purpose of this paper is to discuss this new perspective on plant and fungal exudation of LMMOAs in soils, and outline a mechanistic model including a first unbutton step to destabilize SOM.

2. A three-step mechanism for active nutrient acquisition from SOM

We propose that active N and P acquisition from SOM is achieved by a three-step process as pictured in Fig. 1, and performed by plant-microbe consortia. In step 1 SOM is destabilized by LMMOAs exuded by root and fungi, which form particularly stable chemical complexes with the polyvalent SOM-bridging metals Ca, Al and Fe. In step 2 exuded hydrolytic enzymes degrade the destabilized and newly exposed organic compounds, and release N and P in bioavailable forms. In step 3 there is a local uptake of N and P by roots and fungi. Steps of this serial action have been recognized previously, but they have not been put into the context of the emerging new information about SOM composition and structure, in particular the role of Ca and Al in the stabilization of SOM and plant-fungi-soil feedback mechanisms. Here we consider all these aspects and propose a three-step mechanism by which recalcitrant SOM can sustain sufficient delivery of N and P to plants also in relatively infertile acidic soils.