Modelling low molecular weight organic acid dynamics in forest soils

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Abstract

Low molecular weight organic acids such as citrate and oxalate have been hypothesized to play a key role in rhizosphere ecology and pedogenesis. A mathematical site-specific model, DYNLOW, was constructed to describe the temporal and spatial dynamics of these organic acids in coniferous forest soils using the modelling software STELLA®. Experimentally derived values for biodegradation, adsorption, and daily values of soil temperature, moisture and hydrological flow were used to parameterize the model. The model describes the dynamics and downward movement of oxalate and citrate through the horizons (O, AE, E, Bhs, Bs) of three podzolic soil profiles in Sweden. After calibration, the model predicted average soil solution organic acid concentrations ranging from <1 to 90 μM, which was in agreement with experimental measurements (<1 to 116 μM). The model results indicated that microbial degradation of organic acids was in quantitative terms the biggest process regulating soil solution concentrations. Primary production rates of organic acid in the soil were predicted to be high (<1 to 1250 nmol g^{-1} soil d^{-1}) in comparison to the amount present at steady state in the soil solution pool (<0.1 to 240 nmol g^{-1} soil). The downward transfer of organic acids between soil horizons due to mass flow was predicted to be a small flux (<0.1 to 3% of the total loss) compared to that lost by microbial biodegradation. The model predicted that the amount of basal soil respiration that could be attributable to the microbial turnover of organic acids was on average $19\pm22\%$ of the basal CO_2 production across all sites and horizons for citrate and $7\pm7\%$ for oxalate. The model results are discussed in the context of pedogenesis, forest soil respiration and organic matter production.
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Keywords: Carbon flow; Dissolved organic carbon; Leaching; Podzolization; Respiration; Rhizosphere; Sorption

1. Introduction

Low molecular weight organic acids (LMWOA) have been hypothesized to play key roles in a number of soil processes which operate over a whole range of temporal and spatial scales from the rhizosphere up to the whole ecosystem level (Jones et al., 2003). LMWOAs typically contain 1–6 carbon atoms and 1–3 carboxyl groups, and generally constitute only a minor part of the dissolved organic carbon (DOC) in soil ($<3\%$ of the total; Strobel,

2001). Soil solutions typically contain a diverse range of organic acids with concentrations in aerobic soils typically ranging from 0.1 to 50 μM (Jones, 1998).

With respect to plant and microbial nutrition, LMWOAs have been hypothesized to play a crucial role in the solubilization and mobilization of poorly soluble soil nutrients such as Mn, Cu, Zn, Fe and P, and also in the detoxification of metals such as Zn and Al (Fox, 1995; Jones, 1998; Jones et al., 2003). In the case of pedogenesis, LMWOAs can significantly enhance the dissolution rate of primary minerals and are therefore likely to be of importance in processes such as podzolisation (Drever and Stillings, 1997; Lundström et al., 2000). Furthermore,

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LMWOAs are thought to be of significance in the hyphal weathering of soil minerals by ectomycorrhizal fungi (Landeweert et al., 2001). Most of the functions discussed above rely on the ability of the LMWOAs to complex metal cations and consequently it is the divalent and trivalent LMWOAs that have been directly implicated in these processes (e.g. malate, citrate and oxalate; Fox, 1995).

The behaviour of charged solutes like LMWOAs in soils is complex with removal from the solution phase occurring by the processes of sorption, fixation and chemical oxidation and biodegradation (Ryan et al., 2001). These relatively simple carbon substrates are rapidly mineralised by the soil microbial community with half-lives in soil ranging from 1 to 12 h (Jones and Darrah, 1994; Jones et al., 1996a,b; van Hees et al., 2002). Removal from the solution phase due to sorption is particularly important in soils containing high levels Al and Fe

oxyhydroxides (e.g. podzolic Bs horizons; Jones and Brassington, 1998; Karltun, 1998; van Hees et al., 2003a). Sorption to the soil's solid phase has also been shown to significantly slow down the microbial mineralisation of LMWOAs (Boudot, 1992; Jones and Edwards, 1998).

A number of potential sources of LMWOAs in soil have been identified including plant roots and soil micro-organisms where organic acid loss is due to both passive and active exudation and cell lysis (Ahonen-Jonnarth et al., 2000; Ryan et al., 2001). However, very little is known about the relative contribution of these plant and microbial sources of organic acids and the mechanisms that regulate them. The concentration of LMWOAs in soil solution is consequently dependent upon the balance between de novo production and degradation with the adsorbed pool acting as a buffer. The aim of this paper is to assess the importance of the major dynamic processes
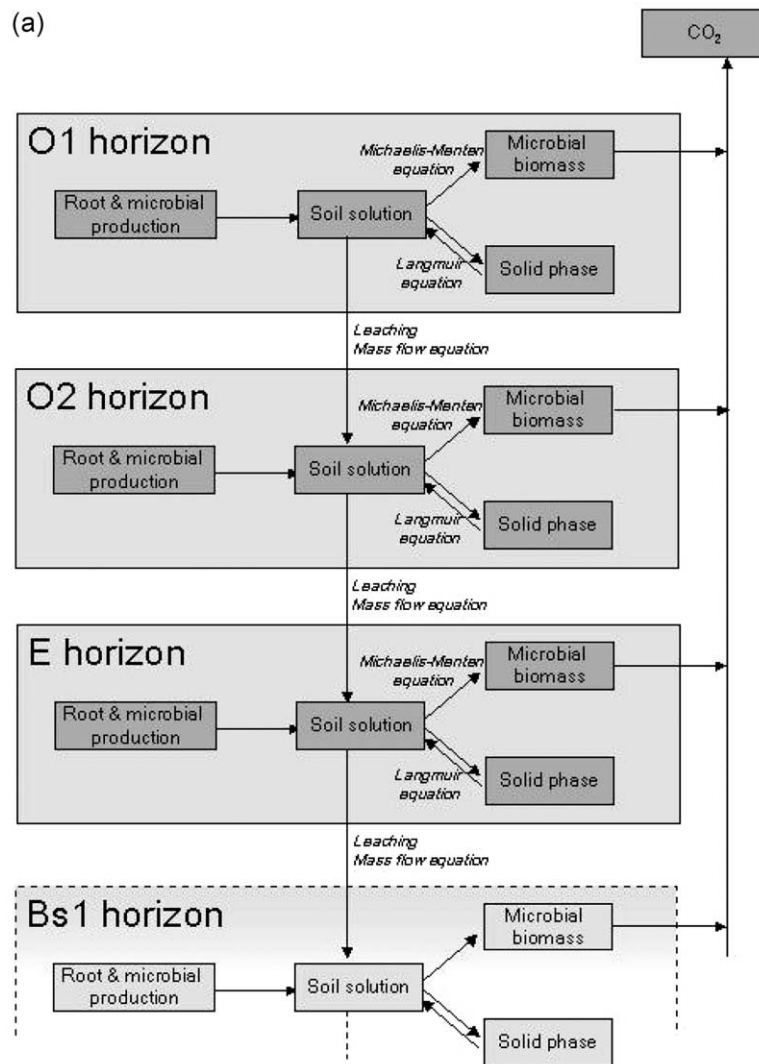

Fig. 1. (a) Generic model overview showing the major chemical and biological processes involved. (b) Detailed model overview using Forester symbols (Forester, 1961). Terms are explained in Table 1.