

Report Number 10/62

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 European Journal of **Soil Science**

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Journal:	<i>European Journal of Soil Science</i>
Manuscript ID:	EJSS-251-10
Manuscript Type:	Original Manuscript
Date Submitted by the Author:	25-Oct-2010
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Keywords:	carboxylic acid, citric acid, freundlich isotherm, mathematical model, rhizosphere, hysteresis

Adsorption and desorption dynamics of citric acid anions in soil

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Summary

The functional role of organic acid anions (e.g. citrate, oxalate, malonate, etc) in soil has been intensively investigated with special focus either on (i) microbial respiration and soil carbon dynamics, (ii) nutrient solubilization, or (iii) metal detoxification. Considering the potential impact of sorption processes on the functional significance of these effects, comparatively little is known about the adsorption and desorption dynamics of organic acid anions in soils. The aim of this study therefore was to experimentally characterize the adsorption and desorption dynamics of organic acid anions in different soils using citrate as a model carboxylate. Results showed that both adsorption and desorption processes were fast, reaching a steady state equilibrium solution concentration within approximately 1 hour. However, for a given total soil citrate concentration (c_{tot}) the steady state value obtained was critically dependent on the starting conditions of the experiment (i.e. whether most of the citrate was initially present in solution (c_l) or held on the solid phase (c_s)). Specifically, desorption-led processes resulted in significantly lower equilibrium solution concentrations than adsorption-led processes indicating time-dependent sorption hysteresis. As it is not possible to experimentally distinguish between different sorption pools in soil (i.e. fast, slow, irreversible adsorption/desorption), a new dynamic hysteresis model was developed that relies only on measured soil solution concentrations. The model satisfactorily explained experimental data and was able to predict dynamic adsorption and desorption behaviour. To demonstrate its use we applied the model to two relevant scenarios (exudation and microbial degradation), where the dynamic sorption behaviour of citrate occurs. Overall, this study highlights the complex nature of citrate sorption in soil and concludes that existing models need to incorporate both a temporal and sorption hysteresis component to realistically describe the role and fate of organic acids in soil processes.

Keywords: Carboxylic acid, Citric acid, Freundlich isotherm, Mathematical model, Rhizosphere, Hysteresis

Introduction

Low molecular weight (LMW) organic acid anions play an important role in many soil biogeochemical processes as they positively influence the growth of plants and microorganisms by enhancing nutrient solubility (e.g. P, Fe, Zn) and by complexing and detoxifying metals present in high concentrations (e.g. Al, Cd, Zn; Neumann et al., 1999; Dakora and Phillips, 2002; Ryan et al., 2001). In addition, organic acid anions provide the soil microbial community with a relatively labile source of carbon (C) which promotes microbial activity and growth (Jones, 1998). Due to rapid removal processes from soil solution (i.e. sorption and biodegradation), organic acid anions typically only constitute a minor fraction of the dissolved organic carbon (DOC) in soil (<10% of total DOC; van Hees et al., 2002). Nevertheless, they have been found to make an important contribution to total soil respiration, with 20-75% of total soil respiration being potentially derived from organic acid breakdown (van Hees et al., 2008).

Whilst small amounts of carboxylic acids can enter soil from precipitation, organic wastes and as a by-product of soil organic matter (SOM) mineralization, it is assumed that active excretion and passive exudation by living plant roots and microorganisms represents their main route of entry into soil (Jones et al., 2004; van Hees et al., 2008). Furthermore, increased exudation rates are often observed as a metabolic response to environmental stress (Hoffland et al., 1989; Zhang et al., 1997; Ryan et al., 1995). Ultimately, this is expected to lead to localized hotspots of organic acid activity in soil and both spatially and temporally heterogeneous concentration patterns.

Due to their proposed role in pedogenic processes, the fate of organic acids has been intensively studied in plant-microbial-soil systems. To date, the main focus of investigations

has either been on (i) organic acid mineralization patterns and their role in soil C dynamics (van Hees et al., 2008; Oburger et al., 2009), (ii) the role of organic acids in nutrient solubilization (mainly P; e.g. Palomo et al., 2006), or (iii) organic acids as an Al^{3+} detoxification mechanism (e.g. Ma, 2005). In all these different aspects, the sorption (i.e. adsorption and desorption) behaviour of organic acid anions plays a key role, as it will ultimately determine their movement, residence time, availability and functional effect in soil (Jones et al., 1996a). While adsorption of organic acid anions has been intensively studied in a range of soils (Jones and Brassington, 1998; Ström et al., 2001; van Hees et al., 2003, Oburger et al., 2009), comparatively little information is available on their desorption dynamics. Traditionally, it has been assumed that sorption of organic acid anions, like that of other anions in soil (e.g. SO_4^{2-}) is fully reversible and therefore sorption can simply be described by a single soil-solution partition coefficient (Darrah, 1991). Whether organic acid adsorption is fully reversible, however, remains critical in regulating the effective zone of influence around exuding organisms. In a recent study, Strahm and Harrison (2008) observed that at low pH very little malonate could be desorbed from a variable charge soil in a sequential desorption approach and that decreased biodegradation rates correlated well with these reduced desorption patterns.

Due to the lack of available techniques to experimentally measure organic acid anion gradients in soil at sufficient spatial resolution (e.g. diffusion away from roots), mathematical models are often used to predict organic acid movement in soil (Jones et al., 1996b; Kirk et al., 1999). As some organic acid anions (e.g. oxalate, citrate) may strongly adsorb to the soil's solid phase (e.g. oxalate, citrate), it is critical to accurately describe sorption processes that represent a key control on the diffusional flux. Parametrisation of kinetic sorption models, however, is difficult, since the number of model parameters are generally high and initial conditions can sometimes not be obtained by experimental measurements (e.g. differentiation of the sorbed concentration in a slow and in a fast pool). There are several different modelling

approaches. The simplest approach is to use a time dependent explicit empirical equation (e.g. an extension to the Freundlich equation) that is fitted to kinetic sorption data (Barrow, 2008). Another approach uses multi-reaction models, which describe the reaction by ordinary differential equations using different pools with dissimilar reaction rates for the sorbed ion (e.g. a slow and a fast pool) (Selim and Zhu, 1997; Barrow et al., 2000). Finally, more complex models include diffusion into the matrix of the adsorbing material (Tsakiroglou and Ioannidis, 2008; Ptashnyk et al., 2010; Ptashnyk and Roose, 2010).

The aim of this study was to further elucidate the fate of organic acid anions in soil with special regard to sorption processes. We experimentally characterized the sorption behaviour of organic acids, by carrying out adsorption and desorption experiments under sterile conditions in 3 different agricultural soils using citrate as a model carboxylate. Experimental data was then used to develop a new kinetic sorption model that is able to predict the concentration of citrate in the soil solution over time.

Materials and Methods

Soils

Three agricultural soils were used in the study. Soils, sampling sites, and soil parameter determination procedure have been described in detail in Oburger et al. (2009). Briefly, a Eutric Cambisol topsoil (Ah horizon, 0-15 cm depth) and a Haplic Podzol topsoil (Ah horizon, 0-15 cm depth) and subsoil (Bs horizon, 20-40 cm depth) were collected at Abergwyngregyn, Gwynedd, UK (53°11'40"N, 41°01'00"W). All the soils were passed through a 4-mm sieve and stored field-moist at 4°C until analysis. Prior to experimentation the soil was sterilized by heating (30 min at 80°C) to prevent microbial degradation of the organic acids (Kuzyakov and Jones, 2006). The general properties of the soils are shown in Table 1. All treatments were carried out in duplicate unless otherwise stated.

Adsorption curves

To determine the sorption behaviour of citrate in the different experimental soils, concentration-dependent adsorption envelopes were measured at a 1:10 (w/v) soil-to-solution ratio. Briefly, heat sterilized soil (1 g dry weight) was shaken with 10 ml of 1, 5, 10, 25, 50 and 100 μM ^{14}C -citrate (0.3 kBq g^{-1}) for 1 hour at 20°C on a reciprocal shaker at 200 rev min^{-1} . The background electrolyte in the citrate solutions was 1 mM KCl. Subsequently, samples were centrifuged for 5 min at 18,000 g and the ^{14}C -citrate present in the supernatant solution determined by liquid scintillation counting using Ultima GoldTM XR scintillation fluid (PerkinElmer Corp., Shelton, USA) and a 1900CA TRI-CARB[®] Liquid Scintillation analyzer (Canberra Industries Inc., Meriden, CT).

Desorption curves

Desorption behaviour of citrate in the 3 experimental soils was determined by using a parallel batch extract approach. Soil (1 g) was spiked with 0.25 ml ^{14}C -labelled citrate (0.5 $\mu\text{mol g}^{-1}$; 0.3 kBq g^{-1}) and allowed to equilibrate for 30 min at 20°C. At this point, 99% of the added ^{14}C -citrate was adsorbed to the solid phase (data not presented). Subsequently, different volumes of KCl (1 mM) were added to the experimental soils resulting in final soil-to-solution ratios (w/v) of 1:1, 1:2.5, 1:5, 1:10, 1:25, 1:50, 1:75, and 1: 100. The background solution of 1 mM KCl was chosen as it does not significantly interact with citrate. Samples were then shaken for 1 hour at 200 rev min^{-1} , centrifuged (18,000 g, 5 min) and the supernatant recovered. The amount of ^{14}C -citrate desorbed into solution was determined by liquid scintillation counting as described above.

Adsorption kinetics

The adsorption kinetics of citrate to each soil were determined by measuring the change in concentration of ^{14}C -citrate in the soil solution over time, after the addition of 0.5 $\mu\text{mol g}^{-1}$

citrate soil. Briefly, 10 ml of ^{14}C -labelled citrate (0.3 kBq g^{-1} , $50 \mu\text{M}$) was added to 1 g of soil and the soil shaken as described above. At different times (1, 2, 5, 10, 30, 60, 120, 240 and 480 min) after ^{14}C -citrate addition, 100 μl of the soil suspension was removed, centrifuged and the ^{14}C remaining in solution determined as described above. These times were chosen to reflect expected residence times of organic acid anions in the rhizosphere (Ryan et al., 2001).

Desorption kinetics

For the desorption kinetics, soil (1 g) was incubated for 30 min with ^{14}C -citrate ($0.5 \mu\text{mol g}^{-1}$; 0.3 kBq) and then shaken with 10 ml of 1 mM KCl at 200 rev min^{-1} . At different times (1, 2, 5, 10, 30, 60, 120, 240 and 480 min) after KCl addition 100 μl of the soil suspension was removed, centrifuged and the ^{14}C remaining in solution determined as described above.

Results and discussion

Experimental results

The concentration and time-dependent citrate adsorption and desorption isotherms are presented in Figure 1. As expected, significant differences in sorption behaviour were observed in the three soils. In general, citrate adsorption increased with increasing amounts of anionic binding sites in the soils (Cambisol < Podzol Ah < Podzol Bs, Table 1) while citrate desorption did not follow the same trend (Podzol Ah > Cambisol > Podzol Bs). Citrate adsorption and desorption reactions were both fast, approaching steady state after approximately 1 hour (Fig. 1bc) within the experimental measurement period (see also kinetic data in Fig. 1a). This result implies that sorption processes of citrate are almost instantaneous, highly soil-type specific and dependent on carboxylate concentration. However, depending on the initial conditions (i.e. either all the citrate initially in solution as in the adsorption experiments or all on the solid phase as in the desorption experiments) the forward

(adsorption) and backward (desorption) reactions reached a different steady state during the experimental time period. This resulted in markedly different shapes for the adsorption and desorption curves in each soil, clearly indicating sorption hysteresis (Fig. 1a). Within a short time period (8 h), only a small proportion of the adsorbed citrate was readily desorbable (Fig. 1c). This desorption potential was also soil type dependent and represented $28 \pm 2\%$ of that initially held on the solid phase in the Cambisol, $44 \pm 3\%$ in the Podzol Ah and $23 \pm 1\%$ in the Podzol Bs. We therefore propose that the release of adsorbed citrate can be described by a two-pool model with a fast-release (labile) pool and a slow-release (fixed) pool of which the latter does not seem to influence the short-term sorption steady state. Our results, however, do not allow us to make any conclusions about whether this fixed pool represents truly irreversible sorption by the solid phase. Evidence presented in microbial biodegradation studies of organic acid anions in soils indicate that where mineralization is relatively rapid, irreversible sorption is unlikely (Ström et al., 2001; van Hees et al., 2003; Oburger et al., 2009ab).

Sorption hysteresis and the fate of citrate in soil

Sorption hysteresis is a frequently observed phenomenon that occurs when distinct discrepancies between adsorption and desorption curves are found (Zhang and Selim, 2005). True hysteresis in soils has been reported for inorganic and organic compounds, as a consequence of slow precipitation at the mineral surface and/or slow diffusion to sites within the soil matrix resulting in irreversible retention of the solute (Barrow, 1984; Huang et al., 1997; Zhang and Selim, 2005). Experimentally, solid-solute contact time is a crucial factor, as observed hysteresis can often be attributed to the failure of attaining true equilibrium during either or both sorption and desorption procedures (Lesan and Bhandari, 2003). Adsorption and desorption processes of highly reactive anions like phosphate or arsenate have been found to continue for weeks and even years (O'Reilley et al., 2001; Raven et al., 1998), but the same

196 authors also concluded that the majority of sorption reactions occurred within the first 2 to 24
197 h. In many longer-term sorption studies using non-sterile soil, however, microbial
198 immobilization of the added anions is also likely to occur. If these anions are subsequently
199 transformed and incorporated into the microbial community (e.g. PO_4^{3-} into microbial lipids),
200 based on known microbial biomass turnover times (ca. 1-3 months) they would appear to be
201 irreversibly fixed. In this study we used sterile soil to remove this potential artefact.

202 In contrast to inorganic nutrients or recalcitrant organic pollutants, where a better
203 knowledge of long-term sorption behaviour helps improving soil management practices, long-
204 time sorption experiments with low-molecular-weight carboxylates will only provide a partial
205 view of their fate due to the presence of other highly dynamic soil processes (e.g. organic acid
206 input via exudation and removal by rapid mineralization). The average half-life of C derived
207 from citrate in soil typically ranges from 2-20 d (Oburger et al., 2009b), however, primary
208 microbial removal of organic acids from the soil solution has an even shorter half life in the
209 region of 0.5-12 h (Oburger et al., 2009ab). Considering these highly dynamic processes,
210 short-term sorption reactions are particularly important since they will determine the
211 instantaneous solid-solution partitioning of organic anions. The question arises about how and
212 to what extent do sorption processes influence the bioavailability of these carboxylates, and
213 therefore their potential functional effect in soil (e.g. metal detoxification, nutrient
214 solubilization, soil respiration). Previous observations of reduced microbial degradation of
215 organic acid anions in strongly sorbing soils indicate that their bioavailability is controlled by
216 sorption processes (Ström et al., 2001; van Hees et al., 2003; Oburger et al., 2009a). The
217 distribution kinetics of organic acid anions between the soil solution, soil matrix, and
218 microbial biomass, however, still remain unknown.

Interpretation of experimental results with a new kinetic sorption model

The different shape of the adsorption and desorption curve indicates that in the experimental timescales used here there are two different equilibria for the forward and backward reaction. Here we aim at developing a model that represents this hysteresis effect and accurately describes sorption dynamics. The model describes all the experimental data by including the steady-states of both citrate adsorption and desorption. The simplest dynamic mathematical model that can describe the observed hysteresis effect is a kinetic model with three steady-states (two stable and one unstable), i.e., a model of the form

$$\frac{dc_l}{dt} = f_{ad}(c_l, ssr) \cdot f_{us}(c_l, ssr) \cdot f_{de}(c_l, ssr), \quad (1)$$

where, at equilibrium, f_{ad} becomes the steady-state that corresponds to the adsorption isotherm, f_{de} becomes the steady-state that corresponds to the desorption isotherm and because there has to be one unstable isotherm between two stable ones we include f_{us} as an unknown (not measured) unstable steady-state.

If Freundlich equations are used, the functions f_{ad} and f_{de} are given by

$$f_{ad} = \frac{r}{ssr} (c_t - ssr \cdot c_l) - k_{ad} \cdot c_l^{n_{ad}} \quad (2)$$

and

$$f_{de} = \frac{r}{ssr} (c_t - ssr \cdot c_l) - k_{de} \cdot c_l^{n_{de}}, \quad (3)$$

where r represents the reaction rate constant, ssr is the solution soil ratio (l g^{-1}), c_t is the total concentration in soil ($\mu\text{mol g}^{-1}$), c_l is the concentration of citrate in soil solution (μM), k and n are the Freundlich equation parameters, and the superscripts ad and de indicate the Freundlich parameters of the ad- and desorption isotherms, respectively. According to the experimental setup, c_s and c_l are dependent, i.e. $c_s = c_t - ssr \cdot c_l$. Therefore in Eqs. (2) and (3), the term $c_t - ssr \cdot c_l$ is used instead of c_s , where c_s is the concentration of adsorbed

citrate ($\mu\text{mol g}^{-1}$). The function $f_{us}(c_l, ssr)$ represents the unstable steady state which must lie between the two stable steady states. A simple functional form of f_{us} can be obtained interpolating between the f_{ad} and f_{de} :

$$f_{us} := \theta \cdot f_{ad} + (1 - \theta) \cdot f_{de}, \quad (4)$$

where θ is a value between 0 and 1.

In Figure 2 we illustrate this approach using a phase portrait, in which the three lines represent three steady states of the system. The arrows indicate the direction in which the model state (c_s, c_l) develops for both the ad- and desorption kinetic experiments. For adsorption scenarios, we start at the x -axis and, at equilibrium, the lower stable steady-state is reached. For desorption scenarios, we start at the y -axis and the upper stable steady-state is reached. In between the two stable steady-states, there is an unstable steady state. Depending on the starting point with respect to the unstable isotherm adsorption (Fig. 2, areas B and D) or desorption will occur (Fig. 2, areas A and C).

Fitting the model to the experimental data

The kinetic sorption model given by Eqns (8)-(11) has six parameters: two Freundlich parameters for adsorption (k_{ad} , n_{ad}), two Freundlich parameters for desorption (k_{de} , n_{de}), the rate r and the value θ . In a first step, the Freundlich parameters k_{ad} , k_{de} , n_{ad} and n_{de} are obtained by fitting two Freundlich isotherms to the ad- and desorption isotherm data. These parameters are used in the second step as initial parameters for fitting the full model.

When fitting the Freundlich parameters to experimental data, it must be considered that c_s and c_l are dependent so that a measurement error of c_l will result in an error of c_s . Therefore, the squared distance between an observed data point $(c_{s,i}, c_{l,i})$ and the Freundlich sorption curve is obtained by first evaluating $c_{l,i}$ from the implicit equation

$$c_t - ssr \cdot c_{l,i}^* = k_f \cdot c_{l,i}^{*n}, \quad (5)$$

The summed squared error sse is then given by

$$sse = \sum_{i=1}^N ssr^2 \cdot (c_{l,i}^* - c_{l,i})^2 + (c_{s,i}^* - c_{s,i})^2 \quad (6)$$

where N is the number of observations. Minimization of Eqn (6) yields the Freundlich parameters k and n . In the case of adsorption, ssr is constant and in the case of desorption, c_t is constant.

Parameter estimation of the full kinetic model is performed by minimizing the summed squared error

$$sse = \sum_{i=1}^N ssr^2 \cdot (c_{l,t_i}^* - c_{l,t_i})^2 + (c_{s,t_i}^* - c_{s,t_i})^2, \quad (7)$$

where c_{l,t_i} are the observed kinetic data at times t_i , and c_{l,t_i}^* are the model results which are obtained by numerically integrating the ordinary differential equations (Eqns. 1-4) using the Matlab function `ode15s`. The sorbed concentrations are calculated from the total concentration: $c_{s,t_i} = c_t - ssr \cdot c_{l,t_i}$ and $c_{s,t_i}^* = c_t - ssr \cdot c_{l,t_i}^*$. The total summed squared error is obtained by adding up the errors of the ad- and desorption data (Eqn. 6) and the kinetic ad- and desorption data (Eqn. 7).

Figure 1 shows the model results matched to the experimentally observed isotherm and kinetic data. In Figure 1a, we see the model fits for the ad- and desorption isotherms of each experimental soil. Since c_s and c_l are dependent, the error bars of the data points are not vertical but have a slope. In the case of adsorption, the slope is $-ssr$, see Eqn (2). In the case of desorption, the slopes of the error bars are different for each observation i and are given by $-ssr_i$, see Eqn (3). The kinetic data lie on the curve $c_s = c_t - ssr \cdot c_l$, which is represented by the dotted line (Fig. 1a). Figures 1b and 1c show the dynamic behaviour of the system and the observed kinetic data. In the adsorption experiment, initially all the citrate is present in soil

solution and none is present on the solid phase. In the desorption experiment, initially all the citrate is adsorbed to the solid phase and none is present in soil solution. The sorption parameters obtained from fitting the model are shown in Table 2.

This descriptive kinetic model represented the experimental data using parameters from the Freundlich isotherms. A big advantage of the approach presented here is its simplicity. In contrast to multi- pool approaches, the model depends only on one pool, the concentration in soil solution c_l , which can be measured. Therefore, the parameters of the model can be more easily fit while the model is still able to capture the hysteresis effect and the dynamic behaviour of the system. A drawback of the model is that mechanistic interpretation of underlying processes is not possible. However, the use of Freundlich isotherms makes it easy to interpret the parameters and to compare them to sorption parameters found in the literature (e.g. Ström et al., 2001).

In all soils, the adsorption isotherms had larger n values and smaller k values than in the desorption isotherm. This means that at low soil solution concentrations the soil-solution-to-solid phase partition coefficient (K_d) values are higher for the desorption isotherms than for the adsorption isotherm. However, with increasing soil solution concentration the K_d value of the desorption isotherm decreases stronger than in the case of adsorption. The parameter r describes the speed at which the states reach their equilibrium. Overall, the sorption rate was lower in the Cambisol in comparison to both Podzol horizons. The parameter θ determines the position of the unstable steady state (see Fig. 2 and Eqn. 4). In all soils θ was very small (Table 2), thus we deduce that the unstable steady state lies close to the desorption isotherm, and area C increases, while area B becomes vanishingly small (Fig. 2).

Modelling the sorption behaviour of citrate in soil – a theoretical case study

The model developed here was used to predict the solid-solution partitioning of citrate in one of the experimental soils (Podzol Bs) for two different but common scenarios in soil

(the pulse input of citrate by root exudation and the subsequent rapid microbial degradation of citrate after exudation ceases). The initial condition for both scenarios was an assumed root exudation event resulting in a citrate soil solution concentration of 40 μM (Jones et al., 1996b). In scenario 1 (Fig. 3) a consecutive exudation event occurred after 80 min, increasing the citrate solution concentration after the first exudation event (*steady state I* c_{I0}) by another 15 μM (c_{II}). The model reacts according to the changes in the system and predicts a new, adapted solid-solution partitioning of citrate (*steady state II* c_{II} , Fig. 3a). The time course of the changes in citrate soil solution concentration is shown in Figure 3b. In the second scenario (Fig. 4), rapid microbial degradation (no time dynamics of the mineralization process were considered) decreases the remaining soil solution concentration (*steady state I* c_{I0}) and therefore induces citrate desorption until a new steady state (*steady state II* c_{II}) is reached. Figure 4b shows the dynamic sorption behaviour of citrate before and after microbial degradation.

Conclusions and outlook

Adsorption processes are known to strongly affect the bioavailability of organic acid anions (e.g. citrate, malonate, oxalate, etc.) in soil, however, relatively little is known about the dynamics of this process or its reversibility (desorption). Our results show that under sterile conditions, both adsorption and desorption reactions reached a plateau after approximately 1 h in all soils, but the steady state solution concentrations of the forward and backward reactions differed significantly and sorption hysteresis of citrate was observed in all three soils within the period of time investigated here. A descriptive mathematical model was developed that was able to predict the change in citrate soil solution concentration in relation to dynamic sorption processes and captured the experimentally observed hysteresis effect. In contrast to multi-pool approaches, the model presented here depends only on measured citrate

concentrations in soil solution. A drawback of the model is that mechanistic interpretation of the underlying processes is not possible.

Our results highlight the impact that the dynamics of adsorption and desorption of organic acid anions will have on their bioavailability and functional role in soil. In non-sterile soils, it is impossible to experimentally distinguish between adsorption and microbial uptake, as only the change in soil solution concentration can be determined. We propose that the dynamic sorption model developed here could be combined with experimentally derived mineralization data to predict the fate of citrate-derived C over time in non-sterile soil. Ultimately, this will prove useful in the development of more robust mathematical models to describe organic acid fate in soil (e.g. in the rhizosphere, mycosphere, pedogenesis etc).

Acknowledgements

This work was supported by the Vienna Science and Technology Fund (WWTF, Grant No.: MA07-008), the Austrian Science Fund (FWF, Grant No.: P20069) and the UK Biotechnology and Biological Sciences Research Council. K.C. Zygalkakis was supported by Award No. KUKC1-013-04, made by King Abdullah University of Science and Technology (KAUST). Andrea Schnepf is a Hertha-Firnberg Research Fellow. Tiina Roose is a Royal Society University Research Fellow.

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Table 1

General properties of the three soils used in the organic acid sorption experiments.

		Cambisol Ah	Podzol Ah	Podzol Bs
pH (H ₂ O)		5.85 ± 0.12	4.95 ± 0.16	4.72 ± 0.04
Organic matter	(g kg ⁻¹)	12.9 ± 1.2	23.8 ± 3.0	10.3 ± 0.5
Crystalline oxides				
Fe	(g kg ⁻¹)	1.41 ± 0.05	1.88 ± 0.11	1.85 ± 0.02
Al	(g kg ⁻¹)	1.43 ± 0.06	2.32 ± 0.28	1.49 ± 0.29
Amorphous oxides				
Fe	(g kg ⁻¹)	5.0 ± 0.1	9.3 ± 0.0	11.8 ± 0.2
Al	(g kg ⁻¹)	1.6 ± 0.0	2.7 ± 0.0	3.6 ± 0.1
Total (aqua regia)				
Al	(g kg ⁻¹)	27.8 ± 0.6	25.7 ± 0.9	30.1 ± 0.8
Fe	(g kg ⁻¹)	45.8 ± 0.5	49.2 ± 0.5	57.9 ± 0.3
Ca	(g kg ⁻¹)	1.91 ± 0.06	0.29 ± 0.02	0.22 ± 0.01

Values represent means ± SEM (*n* = 3).

Table 2

Sorption constants obtained by fitting the Barrow-modified Freundlich model to the experimental adsorption and desorption data

Model parameters		Cambisol	Podzol Ah	Podzol Bs
Adsorption	<i>k_{ad}</i>	4.782×10^{-3}	5.489×10^{-3}	2.155×10^{-2}
	<i>n_{ad}</i>	0.899	0.93	0.737
	<i>sse</i>	1.146×10^{-3}	2.646×10^{-3}	3.483×10^{-3}
Desorption	<i>k_{de}</i>	0.208	0.127	0.298
	<i>n_{de}</i>	0.159	0.226	0.101
	<i>sse</i>	3.203×10^{-3}	2.514×10^{-3}	9.823×10^{-4}
Kinetic model	<i>r</i>	0.545	1.378	3.046
	<i>Θ</i>	3.866×10^{-4}	1.226×10^{-10}	1.352×10^{-13}
	<i>sse</i>	9.734×10^{-3}	1.267×10^{-2}	8.454×10^{-3}

Figure Legends

Figure 1

Adsorption and desorption isotherms with the corresponding kinetic data – experimental data and modelling results.

Figure 2

Phase portrait of the dynamic sorption model. Between the two stable steady states (ad- and desorption isotherm) lies an unstable steady states. Depending of the initial state (c_l , c_s) either adsorption (in area B and D) or desorption (in area A and C) occurs.

Figure 3

Predicted solid-solution partitioning of 40 μM citrate originated from a root exudation event in the Podzol Bs soil and the effect of consecutive exudation event (+ 15 μM) (a) and the time course of changes in soil solution concentration induced by citrate sorption and the second exudation event (b).

Figure 4

Predicted solid-solution partitioning of 40 μM citrate originated from a root exudation event in the Podzol Bs soil and the effect of microbial degradation (- 15 μM , no time dynamics of the mineralization process considered) (a) and the time course of changes in soil solution concentration induced by citrate sorption and microbial degradation (b).

Figure 1

Adsorption and desorption isotherms with the corresponding kinetic data – experimental data and modelling results.

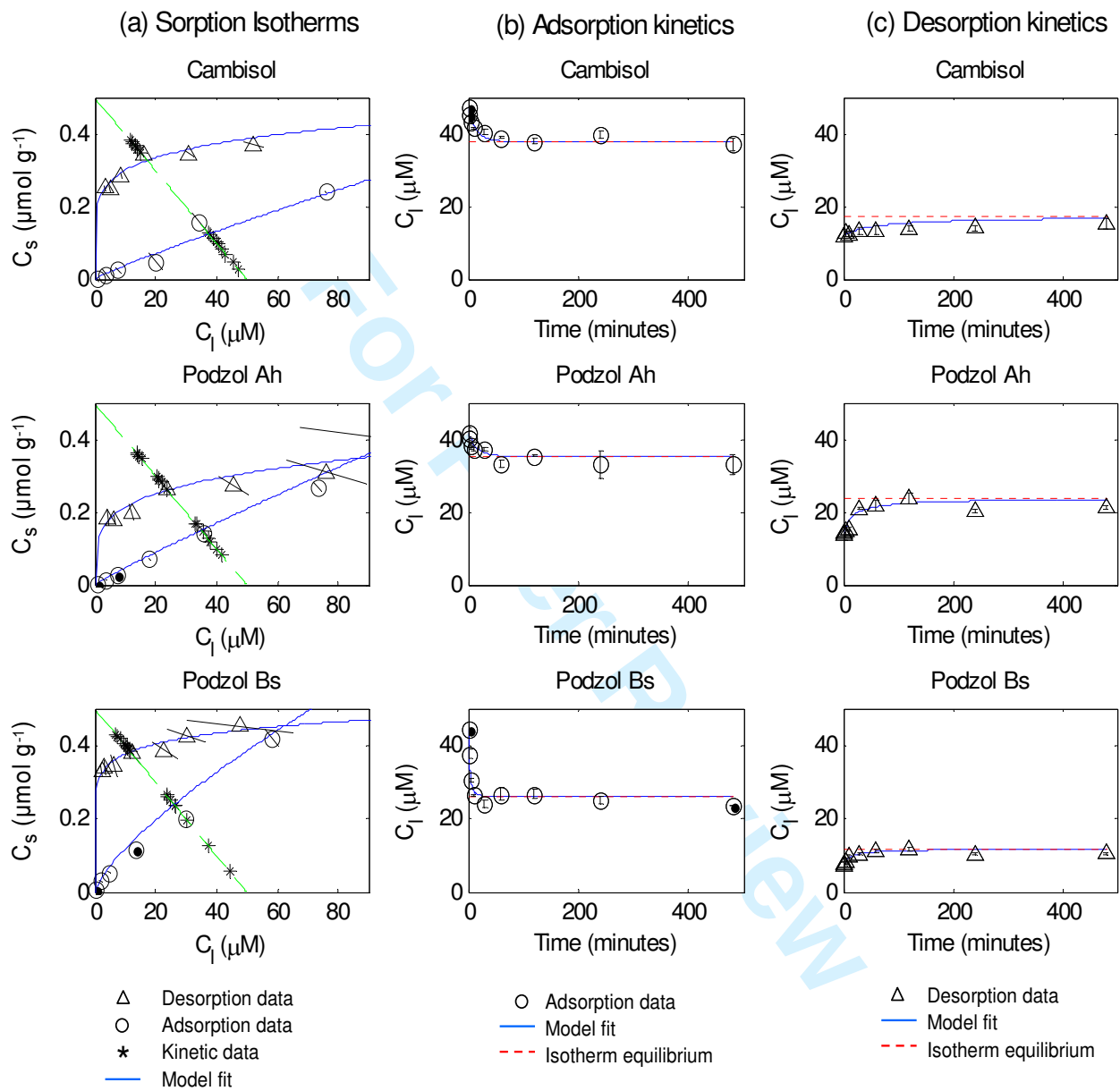


Figure 2

Phase portrait of the dynamic sorption model. Between the two stable steady states (ad- and desorption isotherm) lies an unstable steady state. Depending of the initial state (c_l , c_s) either adsorption (in area B and D) or desorption (in area A and C) occurs.

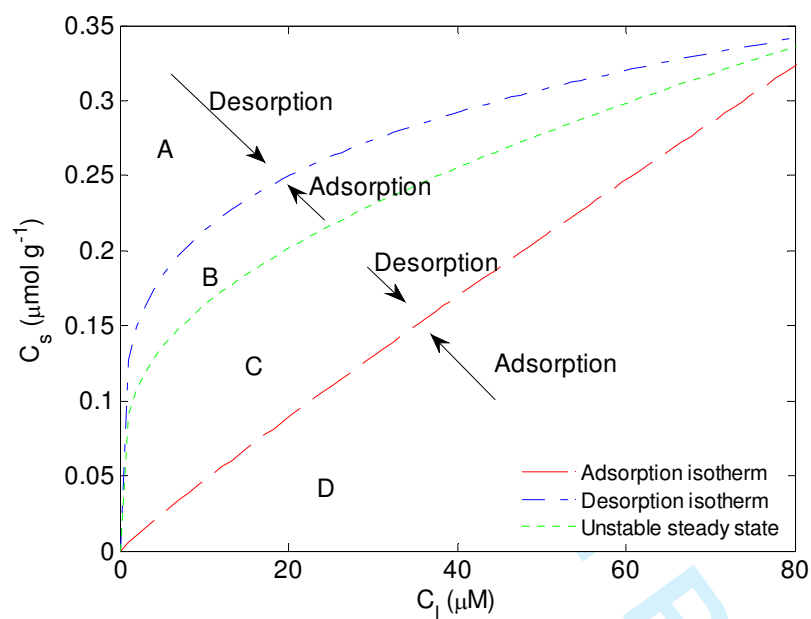


Figure 3

Predicted solid-solution partitioning of 40 μM citrate originated from a root exudation event in the Podzol Bs soil and the effect of consecutive exudation event (+ 15 μM) (a) and the time course of changes in soil solution concentration induced by citrate sorption and the second exudation event (b).

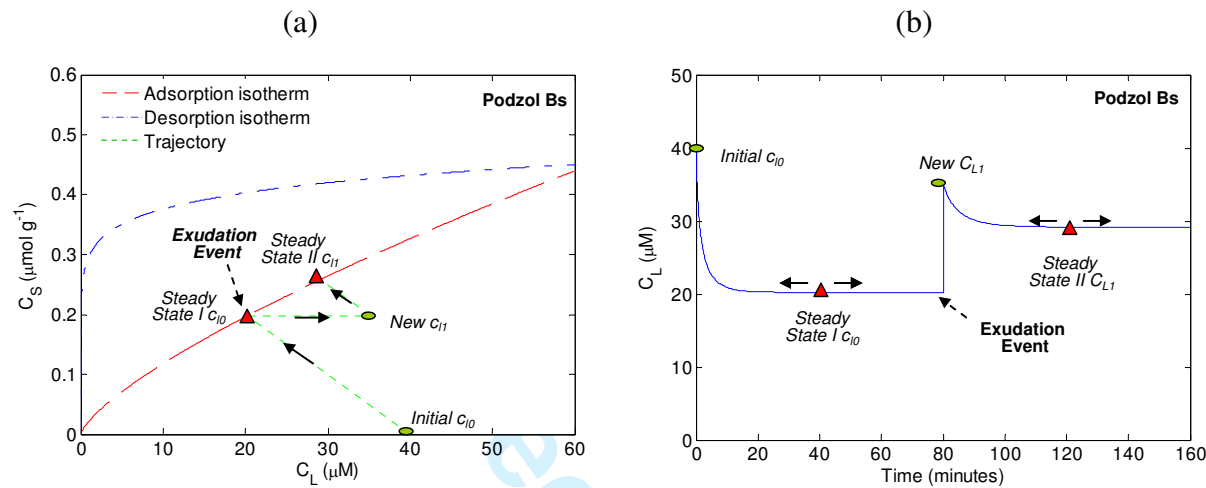
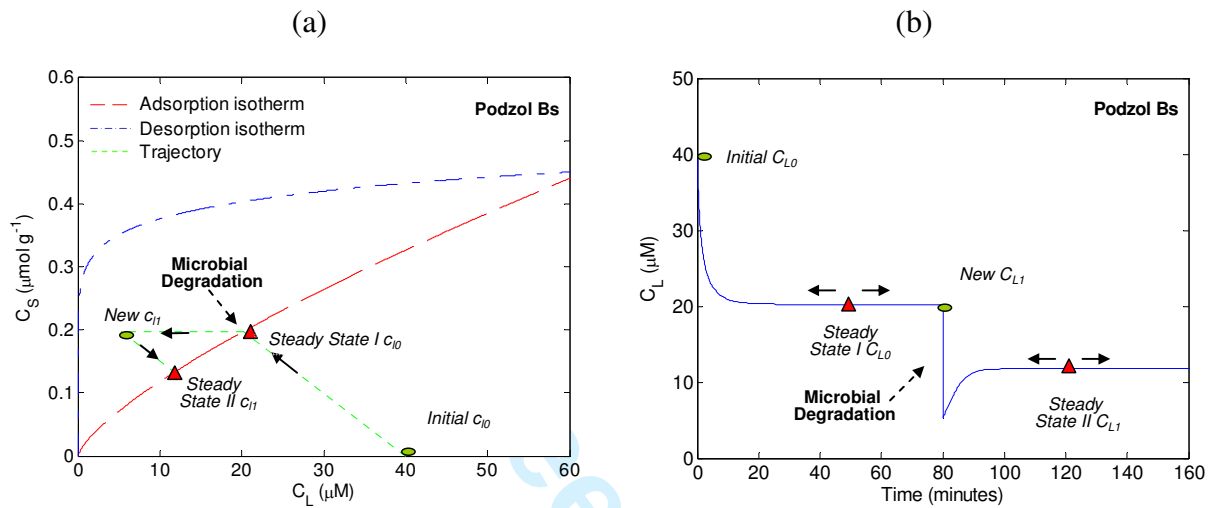


Figure 4

Predicted solid-solution partitioning of 40 μM citrate originated from a root exudation event in the Podzol Bs soil and the effect of microbial degradation ($\sim 15 \mu\text{M}$, no time dynamics of the mineralization process considered) (a) and the time course of changes in soil solution concentration induced by citrate sorption and microbial degradation (b).



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