Intra-aggregate CO₂ enrichment: a modelling approach for aerobic soils

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Abstract. CO₂ concentration gradients inside soil aggregates, caused by the respiration of soil microorganisms and fungal hyphae, might lead to variations in the soil solution chemistry on a mm-scale, and to an underestimation of the CO₂ storage. But, up to now, there seems to be no feasible method for measuring CO₂ inside natural aggregates with sufficient spatial resolution. We combined a one-dimensional model for gas diffusion in the inter-aggregate pore space with a cylinder diffusion model, simulating the consumption/production and diffusion of O₂ and CO₂ inside soil aggregates with air- and water-filled pores. Our model predicts that for aerobic respiration (respiratory quotient = 1) the intra-aggregate increase in the CO₂ partial pressure can never be higher than 0.9 kPa for siliceous, and 0.1 kPa for calcareous aggregates, independent of the level of water-saturation. This suggests that only for siliceous aggregates CO₂ produced by aerobic respiration might cause a high small-scale spatial variability in the soil solution chemistry. In calcareous aggregates, however, the contribution of carbonate species to the CO₂ transport should lead to secondary carbonates on the aggregate surfaces. As regards the total CO₂ storage in aerobic soils, both siliceous and calcareous, the effect of intra-aggregate CO₂ gradients seems to be negligible. To assess the effect of anaerobic respiration on the intra-aggregate CO₂ gradients, the development of a device for measuring CO₂ on a mm-scale in soils is indispensable.

1 Introduction

CO₂ dissolved in soil solution has a strong influence on soil solution chemistry, pH, and on dissolution dynamics of calcareous material (Lindsay, 1979). In soils CO₂ usually originates from respiration of soil microorganisms and plant roots. Considering that aerobic soil microorganisms need access to water, nutrients (organic substance), and oxygen, it can be expected that aerobic respiration mainly takes place in the outer shell of the soil aggregates (Augustin, 1992). Steep oxygen gradients within 1 mm distance to the aggregate surface, which were observed in different studies (Sexstone et al., 1985; Zausig and Horn, 1992), as well as a higher microbial biomass close to the aggregate surface (Augustin, 1992), further support this assumption. Fungal hyphae in the soil matrix were also found to be mainly located within 50 µm to the next macropore (Schack-Kirchner et al., 2000). Lower concentrations of organic carbon in the surface fraction of aggregates were explained by a faster microbial decomposition compared to the aggregate cores (Wilcke and Kauppenjohann, 1994; Amelung and Zech, 1996). Therefore, depending on the respiration rate and diffusive conductivities, the CO₂ produced by respiration in the shell of aggregates should lead to CO₂ gradients from the water-filled intra-aggregate pores down to the air-filled intra- and inter-aggregate pores. These gradients might cause a high spatial variability in the chemical composition of the soil solution, and could possibly explain differences between soil solutions sampled with different extraction methods (Schlotter et al., 2012). Besides that, intra-aggregate CO₂ gradients result in uncertainties in the estimation of the CO₂ storage in soils, using the prevalent method of assuming a Henry’s law equilibrium between the air and the water phase (Flechard et al., 2007; Maier et al., 2010). Additionally, in calcareous soils, variations in the CO₂ partial pressure on the aggregate scale should lead to dissolution and precipitation of calcite.
(van Breemen and Buurman, 2002), and might thus be an explanation for secondary carbonates on the aggregate surfaces.

In the past few years efforts have been made to study the effects of structure and aggregation on soil processes (Totsche et al., 2010), using e.g. information on the internal pore topology from X-ray micro-tomography (Köhne et al., 2011). Koehler et al. (2010), for example, discussed the effect of soil structure on the performance of the soil-CO$_2$ profile method. However, models for CO$_2$ production and transport in soils usually assume a thermodynamic equilibrium between soil air and soil solution (Rasmussen et al., 1990; Simunek and Suarez, 1985; Fang and Moncrieff, 1999; Cannavo et al., 2006). There are several studies simulating intra-aggregate O$_2$ gradients with spherical diffusion models, assuming a uniform diffusive conductivity (Currie, 1961; Greenwood and Berry, 1962; Sierra et al., 1995; González et al., 2008), and O$_2$ profiles inside aggregates can also be measured with microelectrodes (Greenwood and Goodman, 1970; Revsbech and Ward, 1983; Stepniowski et al., 1991)

But, up to now, there seems to be no feasible method for measuring CO$_2$ inside natural aggregates with sufficient spatial resolution.

As long as CO$_2$ production and O$_2$ consumption have a known relation (i.e. a constant respiratory quotient – RQ) it is possible to calculate the CO$_2$ gradient corresponding to an O$_2$ gradient for given diffusive conductivities. Relatively stable RQs occur under aerobic conditions, with values close to 1 (Bridge and Rixon, 1976; Glinski and Stepniowski, 1985; Grant and Rochette, 1994). Assuming an RQ of 1, Greenwood (1970) calculated possible increases in the CO$_2$ partial pressure in water-saturated aggregates. However, Greenwood (1970) did neither consider a CO$_2$ enriched inter-aggregate air nor a partial aeration of the intra-aggregate pore space.

The objective of our study was to assess maximum intra-aggregate CO$_2$ gradients and their effects on soil solution chemistry and CO$_2$ storage. Therefore, we modelled the diffusion of O$_2$ and CO$_2$ in air-filled inter-aggregate pores and air- and water-filled intra-aggregate pores, with aerobic respiration in the water phase.

2 Modelling approach

2.1 Physical considerations

When modelling gas diffusion in soil, the solid phase is considered to be impermeable, and thus the diffusion coefficients for gas diffusion in pure air or water have to be reduced to take into account the porosity of the soil, and the connectivity and constrictivity of the pores. The diffusive molar flux $J$ (mol m$^{-2}$ s$^{-1}$) of a gas in soil can be described by Fick’s law:

$$ J = -D^{Krogh,*}_S \frac{\partial P}{\partial z}, \quad (1) $$

where $P$ (Pa) is the partial pressure of the gas, $z$ (m) is the distance, and $D^{Krogh,*}_S$ (mol s$^{-1}$ m$^{-1}$ Pa$^{-1}$) is the Krogh diffusion coefficient for gas diffusion in water-saturated (* = W) or aerated (* = A) soil. $D^{Krogh,W}_S$ is the product of the gas diffusion coefficient for the water-saturated parts of the soil (m$^2$ s$^{-1}$) and the Henry’s law constant $K_H$ (mol m$^{-3}$ Pa$^{-1}$), while $D^{Krogh,A}_S$ is the product of the gas diffusion coefficient for the aerated soil parts (m$^2$ s$^{-1}$) and the term $(RT)^{-1}$, where $R$ (Pa m$^{-3}$ mol$^{-1}$ K$^{-1}$) is the ideal gas constant, and $T$ (K) is the temperature. $D^{Krogh,W}_S$ of CO$_2$ is approximately 25 times higher than $D^{Krogh,W}_S$ of O$_2$ (Schack-Kirchner, 2012). Therefore, for equimolar fluxes in the aqueous phase, the gradient of the CO$_2$ partial pressure ($p$CO$_2$) must be 1/25th of the gradient of the O$_2$ partial pressure ($p$O$_2$).

Considering that the maximum drop in $p$O$_2$ is from 21 kPa (atmospheric partial pressure) to 0 kPa, Greenwood (1970) concluded that $p$CO$_2$ in the aqueous phase of aerobic soils can never be more than approximately 1 kPa higher than in the gas phase. In the gas phase, however, the Krogh diffusion coefficient of CO$_2$ is only approximately 0.8 times the coefficient of O$_2$ (Schack-Kirchner, 2012).

Therefore, for equimolar fluxes in the gas phase, the $p$CO$_2$ gradient must be 1/0.8 times stronger than the gradient of $p$O$_2$. To examine whether this effect is of importance for the CO$_2$ partial pressures in aerobic soil aggregates, we assigned an air-filled pore space to our aggregate model.

2.2 Chemical considerations

The model was run for 3 different systems: an acidic siliceous soil (system a), and a siliceous and calcareous soil where the pH is controlled by the carbonic acid (systems b and c). Depending on the chemical system, a different amount of CO$_2$ is dissolved in a solution in equilibrium with the CO$_2$ partial pressure, which affects the Krogh diffusion coefficient. The following considerations are based on Lindsay (1979). The chemical constants are specified in Table 1.

2.2.1 Acidic siliceous soil (system a)

If the pH is low ($p$H < ~ 4.5), the carbonic acid (H$_2$CO$_3$) virtually does not dissociate. Therefore, the molar concentration of CO$_2$ dissolved in water, [H$_2$CO$_3^-$], can simply be calculated with the Henry’s law constant $K_H$ (mol m$^{-3}$ Pa$^{-1}$):

$$ [H_2CO_3^+] = K_H \cdot pCO_2, \quad (2) $$

where $p$CO$_2$ (Pa) is the equilibrium CO$_2$ partial pressure, and [H$_2$CO$_3^-$] is the sum of [CO$_2$$_{aq}$] and [H$_2$CO$_3$], with [CO$_2$$_{aq}$] being the molar concentration of the “physically” dissolved CO$_2$. The Krogh diffusion coefficient of CO$_2$ in water was calculated in the common way, by multiplying the Fickian diffusion coefficient of CO$_2$ in water with the Henry’s law constant.
Table 1. Chemical constants and Fickian diffusion coefficients for O$_2$, CO$_2$, and HCO$_3^-$ for a temperature of 293 K. The temperature dependence of the diffusion coefficients was calculated according to Tucker and Nelken (1990).

<table>
<thead>
<tr>
<th>Gas</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>$K_H$</td>
<td>$1.38 \times 10^{-5}$</td>
<td>mol m$^{-3}$ Pa$^{-1}$</td>
<td></td>
<td>Lide (2002)</td>
</tr>
<tr>
<td></td>
<td>$D_0$</td>
<td>$1.90 \times 10^{-5}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>in air</td>
<td>Jaynes and Rogowski (1983)</td>
</tr>
<tr>
<td></td>
<td>$D_W$</td>
<td>$2.01 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>in water</td>
<td>Lide (2002)</td>
</tr>
<tr>
<td></td>
<td>$D_S/D_0$</td>
<td>$34.24 \times 10^{-3}$</td>
<td>–</td>
<td>in soil (dm-m scale)</td>
<td>Schack-Kirchner et al. (2001)</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$K_H$</td>
<td>$39.07 \times 10^{-5}$</td>
<td>mol m$^{-3}$ Pa$^{-1}$</td>
<td></td>
<td>Carroll et al. (1991)</td>
</tr>
<tr>
<td></td>
<td>$K_d$</td>
<td>$4.44 \times 10^{-7}$</td>
<td>mol L$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D_0$</td>
<td>$1.59 \times 10^{-5}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>in air</td>
<td>Jaynes and Rogowski (1983)</td>
</tr>
<tr>
<td></td>
<td>$D_W$</td>
<td>$1.67 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>in water</td>
<td>Lide (2002)</td>
</tr>
<tr>
<td></td>
<td>$D_S/D_0$</td>
<td>$34.24 \times 10^{-3}$</td>
<td>–</td>
<td>in soil (dm-m scale)</td>
<td>Schack-Kirchner et al. (2001)</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>$D_W$</td>
<td>$1.04 \times 10^{-9}$</td>
<td>m$^2$ s$^{-1}$</td>
<td>in water</td>
<td>Lide (2002)</td>
</tr>
</tbody>
</table>

2.2.2 Siliceous soil, pH controlled by carbonic acid (system b)

If the carbonic acid itself controls the solution pH, the dissociation of the carbonic acid into HCO$_3^-$ and H$^+$ is described by the dissociation constant $K_d$:

$$ K_d = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} . \quad (3) $$

In a “CO$_2$–H$_2$O”-system with pCO$_2$ values in the range of atmospheric values or higher, the dissociation of HCO$_3^-$ can be neglected. Hence [H$^+$] can be calculated for a given pCO$_2$ using Eqs. (2) and (3), and treating [H$_2$CO$_3^+$] as [H$_2$CO$_3$]. The concentration of the dissolved CO$_2$ can then be calculated by adding [H$_2$CO$_3^+$] to [HCO$_3^-$] (Fig. 1). For this system, the resulting Krogh diffusion coefficient of CO$_2$ in water was calculated by multiplying the Fickian diffusion coefficient of HCO$_3^-$ in water with the factor between pCO$_2$ and [HCO$_3^-$], and adding this value to the “common” Krogh diffusion coefficient, calculated as in system a.

2.2.3 Calcareic soil, pH controlled by carbonic acid (system c)

For the “CaCO$_3$–CO$_2$–H$_2$O”-system the buffering of the carbonic acid by the dissolution of CaCO$_3$ has to be taken into account. The set of all chemical reactions involved was solved with an iterative procedure. The concentrations of all ions were calculated for a range of pCO$_2$ values and temperatures, using the dissociation constants from Stumm and Morgan (1996) (Fig. 2). The molar concentration of HCO$_3^-$ ions originating from respiration, [HCO$_3^-$]$^{\text{resp}}$, was derived from the molar concentrations of the HCO$_3^-$, CO$_3^{2-}$, and Ca$^{2+}$ ions by the following equation:

$$ [\text{HCO}_3^-]^{\text{resp}} = [\text{HCO}_3^-] - ([\text{Ca}^{2+}] - [\text{CO}_3^{2-}]) . \quad (4) $$

This calculation is based on the idea that the molar concentration of HCO$_3^-$ ions originating from the dissolution of CaCO$_3$ (i.e. not to be considered for CO$_2$ diffusion) is equivalent to the term ([Ca$^{2+}$] – [CO$_3^{2-}$]), representing the molar concentration of free Ca$^{2+}$ ions that are not balanced by free CO$_3^{2-}$ ions. Based on these HCO$_3^-$$^{\text{resp}}$ concentrations for different pCO$_2$ values (kPa) and temperatures, T (K), a regression function was developed using the “lm” function in R 2.12.0 (R Development Core Team, 2012):
\[ [\text{HCO}_3^{\text{resp}}] = 9.70275 - 0.18389 \cdot p\text{CO}_2 \]
\[ + 1.97456 \cdot (p\text{CO}_2)^{0.5} - 0.03305 \cdot T, \]
where \( 0.04 \text{ kPa} < p\text{CO}_2 < 6 \text{ kPa} \) and \( 273 \text{ K} < T < 298 \text{ K} \). The adjusted \( R^2 \) is 0.98. The total concentration of C-species related to the CO\(_2\) transport in the solution, \( [\text{CaCO}_3^{\text{aq}}] \), was obtained by adding \( [\text{H}_2\text{CO}_3^+] \) to \( [\text{HCO}_3^{\text{resp}}] \) (Fig. 2). Similar to system b, the resulting Krogh diffusion coefficient of CO\(_2\) in water in this system was calculated by multiplying the Fickian diffusion coefficient of HCO\(_3^-\) in water with the factor between \( p\text{CO}_2 \) and \( [\text{HCO}_3^{\text{resp}}] \), and adding this value to the “common” Krogh diffusion coefficient, calculated as in system a.

For all the 3 systems, we calculated the amount of CO\(_2\) stored in the inter-aggregate air and in the intra-aggregate pore space, based on the modelled \( p\text{CO}_2 \) values.

### 2.3 Model setup and solving procedure

To model the diffusion of \( \text{O}_2 \) and \( \text{CO}_2 \) in air-filled inter-aggregate pores and air- and water-filled intra-aggregate pores, we set up and combined a one-dimensional diffusion model with a cylinder diffusion model (Fig. 4). We assumed that 20% of the soil volume consist of air-filled pores, which are mainly the macropores (inter-aggregate pores). Thus almost 80% of the soil volume consist of aggregates. The porosity of the aggregates was set to 30%. Only 1/23rd of the intra-aggregate pores are air-filled, the rest is water-filled (Fig. 3).

![Fig. 2. Molar carbon concentrations of the different dissolved carbon species in a “\( \text{H}_2\text{O-}\text{CO}_2-\text{CaCO}_3^- \)”-system (system c) as a function of the \( \text{CO}_2 \) partial pressure for \( T = 293 \text{ K} \). \( \text{CaCO}_3^{\text{aq}} \) is the sum of all dissolved carbon species that originate from respiration.](image)

![Fig. 3. The setup of the cylinder which represents a soil aggregate in our model. The porosity is uniformly distributed (\( \phi = 0.3 \)). The pores in the middle slice are air-filled, the rest of the pore space is water-filled. Respiration takes place in the outer shell of the cylinder, in the aerated slice, and close to the aerated slice.](image)

#### 2.3.1 Gas diffusion in the inter-aggregate pore space

To calculate the \( \text{O}_2 \) and \( \text{CO}_2 \) concentration profiles in the air-filled inter-aggregate pore space, we set up a one-dimensional finite-difference diffusion model for 0–1 m depth. The model is based on Fick’s second law:

\[ \epsilon \frac{\partial (C_S)}{\partial t} = \frac{\partial}{\partial z} \left( D_S \frac{\partial C_S}{\partial z} \right) + S(z), \]

where \( \epsilon \) is the air-filled volume fraction of the soil, \( C_S \) (mol m\(^{-3}\)) the concentration of the studied gas in the soil air, \( t \) (s) the time, \( z \) (m) the depth, \( D_S \) (m\(^2\) s\(^{-1}\)) the diffusion coefficient of the gas in free air and \( S \) (mol m\(^{-3}\) s\(^{-1}\)) the source or sink (respiration rate). \( D_S \) was derived from the Fickian diffusion coefficient of the gas in free air (\( D_0 \)) and the air-filled volume fraction of the soil (\( \epsilon \)), using the regression function from Schack-Kirchner et al. (2001) (Table 1). The air-filled volume fraction of the soil, which mainly consists of the inter-aggregate pores, was set to 0.2. The Fickian diffusion coefficient in free air (three-component system of \( \text{N}_2, \text{O}_2, \) and \( \text{CO}_2 \)) was calculated according to Jaynes and Rogowski (1983), using binary diffusion coefficients from Fuller et al. (1966). The vertical distribution of the soil respiration per soil volume (\( S(z) \)) was described with an exponential model (Novak, 2007):

\[ S(z) = S(z = 0) \cdot \exp(-\frac{z}{L_S}), \]

where \( z \) is the soil depth, and \( L_S \) is the shape factor that describes the rate of decrease with depth. \( S(z = 0) \) was set to \( 0.015 \times 10^{-3} \text{ mol m}^{-3} \text{ s}^{-1} \) (Schack-Kirchner and Hildebrand, 1998), and the shape factor \( L_S \) to 0.1 m. This resulted
in a typical value for the total CO₂ flux of approximately $4 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ (e.g. Maier et al., 2010).

The CO₂ concentrations in the air-filled inter-aggregate pores were obtained by solving the fully implicit differencing scheme of Eq. (6) for stationary conditions, using the “Solve.tridiag” function in R 2.12.0 (R Development Core Team, 2012). The upper boundary condition was set to a constant atmospheric partial pressure (0.04 kPa), the lower boundary at 1 m depth was defined by a no-flow barrier.

### 2.3.2 Gas diffusion in the intra-aggregate pore space

In our model the soil aggregates are represented by cylinders, which consist of 0.4 mm thick slices and rings, each of which can have a different set of parameters. The pore space in the middle slice is air-filled, the rest of the pores are water-filled. Based on the observation that the outer shell of the aggregates represents the “hot spot” of aerobic soil respiration (e.g. Augustin, 1992), we assigned the respiration rate $S(z,r)$, defined by Eq. (7), to the parts of the cylinder which are close to the surface and the aerated slice (Fig. 3). The boundary conditions of the cylinders were defined by the concentration profiles in the inter-aggregate pore space, obtained from Eq. (6) (Fig. 4). The size of the cylinder was adjusted such that the minimum $pO₂$ values were as low as possible, but no anaerobic zones occur at any depth.

For the cylinder geometry Fick’s second law for diffusion is (e.g. Marsal, 1976):

$$\gamma \cdot \Phi \cdot \frac{\partial P}{\partial t} = \frac{\partial}{\partial z} \left( D_{A}^{Kroh, \ast} \cdot \frac{\partial P}{\partial z} \right) + \frac{1}{r} \cdot D_{A}^{Kroh, \ast} \cdot \frac{\partial}{\partial r} \left( r \cdot \frac{\partial P}{\partial r} \right) + S(z,r),$$

where $\gamma$ represents the Henry’s law constant $K_H$ (mol m$^{-3}$ Pa$^{-1}$), if the diffusion takes place in water, and the factor $(RT)^{-1}$, if the diffusion takes place in air. $R$ (Pa m$^{-3}$ mol$^{-1}$ K$^{-1}$) is the universal gas constant, $T$ (K) is the temperature, $\Phi = 0.3$ is the intra-aggregate pore volume fraction, $P$ (Pa) the partial pressure of the studied gas, $z$ and $r$ (m) the distances in longitudinal and radial direction, and $D_{A}^{Kroh, \ast}$ (mol s$^{-1}$ m$^{-1}$ Pa$^{-1}$) the Krogh diffusion coefficient of the gas in the water-saturated ($* = W$) or aerated ($* = A$) parts of the aggregates. The relative diffusivity of the aggregates, in relation to the diffusion coefficients in free air or water ($D_A$ and $D_W$, Table 1), was set to 0.01, which is in accordance with experimental values obtained by Sexton et al. (1985) and Sierra et al. (1995).

We implemented the cylinder diffusion model as an embedded “C”-function in “R”. The differential equations were solved numerically using the alternating-direction implicit method (ADI) (Press et al., 1988).

In a siliceous aggregate at the soil surface, where the respiration is at its maximum and the $pCO₂$ at the aggregate boundaries is at its minimum, the intra-aggregate increase in $pCO₂$ calculated for system (b), is 0.875 kPa (Fig. 5). The slight decrease in $pCO₂$ along the cylinder axis towards the centre of the water-saturated parts is caused by the cylinder geometry. For an acidic siliceous soil (system a) the intra-aggregate increase is 0.023 kPa higher. This slight difference is caused by the additional diffusive transport of the small amount of HCO₃⁻ ions in system (b), which are not present in system (a) (Fig. 1). The pH values calculated from the modelled $pCO₂$ values for the unbuffered “CO₂-H₂O”-system decrease from 5.16 close to the aggregate surface to 4.91 near the centre of the water-saturated parts (Fig. 6).

The $pCO₂$ gradients modelled for the calcaric soil aggregates (system c) are much lower than the ones for the siliceous aggregates. For maximum aerobic respiration and minimum $pCO₂$ values at the aggregate boundaries the intra-aggregate $pCO₂$ increase is only 0.08 kPa (Fig. 7). This clear difference between calcaric and siliceous aggregates is caused by the higher solubility of CO₂ in the “H₂O – CO₂ – CaCO₃”-system compared to the “CO₂–H₂O”-system, leading to higher diffusive conductivities (Krogh diffusion coefficients).

These results were obtained for a common relative diffusivity of the aggregates of 0.01 (see section 2.3.2). The increase in $pCO₂$ in the aerated slice is less than 0.003 kPa in all cases. But even if the relative diffusivity would be reduced to 0.001, the maximum increase in $pCO₂$ in the aerated slice would still be less than 0.02 kPa.

The difference between the minimum $pO₂$ values inside the aggregates and the $pO₂$ values in the inter-aggregate air, i.e. the intra-aggregate $pO₂$ gradient, decreases with decreasing respiration and thus with increasing depth. This again
Fig. 5. Modelled CO$_2$ partial pressures in a siliceous, aerobic soil aggregate (system b) at the soil surface. The vertical lines mark the boundaries of the cylinder slices. The pore space of the middle slice is air-filled, the other slices are water-saturated (geometry and respiration as in Fig. 3). The pH values are controlled by the carbonic acid (Fig. 6).

As shown in Figs. 5 and 7 for topsoil aggregates, the intra-aggregate $p$CO$_2$ gradient is clearly higher in the siliceous aggregates than in the calcareous aggregates. Systems (a) and (b) differ only marginally. In case of a stronger increase in the inter-aggregate $p$CO$_2$ with depth, e.g. for $L_5 = 0.3$ m in Eq. (7), the modelled maximum $p$CO$_2$ values inside the siliceous aggregates also increase with depth (in contrast to the decreasing values shown in Fig. 8). However, the intra-aggregate $p$CO$_2$ gradient still decreases with depth.

The results presented here were all obtained for a temperature of 293 K. Changing the temperature, however, only affects the steepness of the modelled partial pressure gradients, but (virtually) not the total intra-aggregate increase/decrease.

Despite the clear intra-aggregate CO$_2$ enrichment in the topsoil, the cumulative CO$_2$ storage based on the modelled intra-aggregate $p$CO$_2$ values between 0 and 1 m depth (Fig. 9, dashed lines) is only slightly higher than the cumulative storage calculated for an assumed Henry’s law equilibrium between the intra-aggregate pores and the inter-aggregate air (Fig. 9, solid lines) for both siliceous and calcareous soils. This statement also holds true for a slower decrease in respiration with depth.

4 Discussion

Kohler and Hildebrand (2003) found that cation release rates, especially of Ca$^{2+}$, measured in a long lasting percolation experiment with samples from a siliceous C horizon, did
strongly depend on the CO₂ partial pressure in soil air. For a $pCO_2$ of 1 kPa, silicate weathering rates were significantly higher compared to a $pCO_2$ of 0.1 kPa. Hence, for non-calcareous, aggregated soils with high aerobic respiration in the shell of the aggregates (topsoil), the modelled maximum intra-aggregate increase in $pCO_2$ of 0.9 kPa suggests a high variability of the soil solution chemistry ($p$H values) on a mm-scale. This supports the assumption that $pCO_2$ gradients between the mobile and the quasi-stationary parts of the soil solution, originating from inter- and intra-aggregate pores, respectively, can lead to higher calcium concentrations in desorption solutions compared to, for example, suction cup solutions (Schlotter et al., 2012). However, it is important to note that the modelled decrease of pH values inside the siliceous aggregates is based on the assumption that the carbonic acid controls the solution chemistry. If the soil is exposed to stronger acids, e.g. from anthropogenic acid input, these acids can cause an acidification of the aggregate surfaces (Hantschel et al., 1986; Hildebrand, 1994), which again might lead to higher pH values of the intra-aggregate soil solution compared to the solution percolating through the macropores (Kaupenjohann, 2000). Thus, for acidic forest soils, higher ion concentrations in solutions obtained by applying high pressures on soil samples than in solutions obtained with low suctions (Nissinen et al., 2000; Geibe et al., 2006) can most likely not be explained by intra-aggregate CO₂ gradients. Additionally, when assuming a common decrease in aerobic respiration with depth and a constant diffusive conductivity within the aggregates, the effect of the intra-aggregate $pCO_2$ gradients on the soil solution chemistry should be of importance only in the topsoil. In our model scenarios the minimum O₂ partial pressure inside the aggregates does not drop to values close to zero, except for the aggregates close to the soil surface. Thus the intra-aggregate increase in $pCO_2$ is not influenced by the O₂ partial pressure at the aggregate surface. If we would assume a strong decrease in the diffusive conductivity of the bulk soil with increasing depth, the O₂ partial pressure at the aggregate surfaces might become too low to allow for aerobic respiration with the given respiration rate. Thus the respiration rate would need to be reduced, leading again to lower $pCO_2$ gradients inside the aggregates. Assuming a constant diffusive conductivity of the aggregates for the whole soil profile seems reasonable (e.g. Sierra and Renault, 1998). But even for decreasing aggregate diffusive conductivities with depth, the decreasing O₂ partial pressure in the inter-aggregate pore space would lead to decreasing maximum intra-aggregate $pCO_2$ gradients. As long as there is enough oxygen available, small-scale variations in the respiration rate and/or in the diffusive conductivity of soil aggregates can lead to spot-like increasing intra-aggregate CO₂ gradients in the deeper soil. The maximum intra-aggregate $pCO_2$ gradients, however, always decrease with increasing depth. For calcareous soils our model predicts that aerobic respiration has no major effect on the small-scale spatial variability of the solution chemistry. The $pCO_2$ gradients inside the aggregates are always low, even for high respiration, and the carbonic acid is buffered by the dissolution of CaCO₃. However, even low $pCO_2$ gradients would lead to corresponding gradients in the concentrations of calcium and carbonate ions in the water-filled intra-aggregate pores, resulting in a diffusional transport of these ions towards the aggregate surface and the air-filled intra-aggregate pores. Thus, besides the
percolation of soil solution along a decreasing $p$CO$_2$ gradient, or an increase in the solute concentration by evaporation or discrimination by roots (van Breemen and Buurman, 2002), intra-aggregate $p$CO$_2$ gradients are a further possible explanation for secondary carbonates on the walls of macropores and air-filled intra-aggregate pores, as observed, for example, in a typical chernozem (Bronger, 2003).

There is a high interest in accurately quantifying soil respiration with a high temporal resolution, in order to investigate the role of ecosystem respiration in terms of global change. This requires detailed information about changes in the CO$_2$ storage in soils (Flechard et al., 2007; Maier et al., 2011). The prevalent method of estimating the CO$_2$ storage, by assuming a Henry’s law equilibrium between the air and the water phase, neglects the enrichment of CO$_2$ inside aggregates, and therefore underestimates the CO$_2$ storage in soils (Maier et al., 2010). However, our model suggests that for aerobic respiration the underestimation of the total CO$_2$ storage by the prevalent method is low and can be neglected for both calcareous and siliceous soils. This can be explained by the relatively low maximum intra-aggregate $p$CO$_2$ gradients, which decrease with increasing depth, and by the commonly observed decrease in respiration, leading to a convergence of the CO$_2$ concentrations in the inter- and intra-aggregate pore space.

When CO$_2$ is produced under anaerobic conditions, the RQ rises to infinity (Glinski and Stepniewski, 1985). Therefore, our modelling approach cannot be used to predict maximum intra-aggregate increases in $p$CO$_2$ if anaerobic respiration dominates the CO$_2$ production. A change from aerobic to anaerobic conditions usually leads to a decrease in the microbial activity in soils (Linn and Doran, 1984; Skopp et al., 1990; Grant and Rochette, 1994). Thus, $p$CO$_2$ gradients inside anaerobic aggregates might often be in a similar range as in aerobic ones. But this assumption cannot be tested with our modelling approach. Total $p$CO$_2$ values in soils with limited aeration, however, can reach up to 50 kPa and more (Greenway et al., 2006). Independent of the amount of anaerobic respiration, the intra-aggregate increase in $p$CO$_2$ in calcareous aggregates is always expected to be clearly lower than in siliceous aggregates, if the respiration rate in both aggregates is the same.

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