Biogeosciences, 10, 1209–1218, 2013
www.biogeosciences.net/10/1209/2013/
doi:10.5194/bg-10-1209-2013

Biogeosciences
Open Access

Intra-aggregate CO_2 enrichment: a modelling approach for aerobic soils

D. Schlotter and H. Schack-Kirchner

Institute of Soil Science and Forest Nutrition, Albert-Ludwigs-Universität Freiburg, Bertoldstr. 17, 79085 Freiburg im Breisgau, Germany

Correspondence to: D. Schlotter (dominik.schlotter@bodenkunde.uni-freiburg.de)

Received: 31 July 2012 – Published in Biogeosciences Discuss.: 24 October 2012
Revised: 28 January 2013 – Accepted: 4 February 2013 – Published: 25 February 2013

Abstract. CO_2 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 CO_2 storage. But, up to now, there seems to be no feasible method for measuring CO_2 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 O_2 and CO_2 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 CO_2 partial pressure can never be higher than 0.9 kPa for siliceous, and 0.1 kPa for calcaric aggregates, independent of the level of water-saturation. This suggests that only for siliceous aggregates CO_2 produced by aerobic respiration might cause a high small-scale spatial variability in the soil solution chemistry. In calcaric aggregates, however, the contribution of carbonate species to the CO_2 transport should lead to secondary carbonates on the aggregate surfaces. As regards the total CO_2 storage in aerobic soils, both siliceous and calcaric, the effect of intra-aggregate CO_2 gradients seems to be negligible. To assess the effect of anaerobic respiration on the intra-aggregate CO_2 gradients, the development of a device for measuring CO_2 on a mm-scale in soils is indispensable.

1 Introduction

CO_2 dissolved in soil solution has a strong influence on soil solution chemistry, pH, and on dissolution dynamics of calcareous material (Lindsay, 1979). In soils CO_2 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 Kaupenjohann, 1994; Amelung and Zech, 1996). Therefore, depending on the respiration rate and diffusive conductivities, the CO_2 produced by respiration in the shell of aggregates should lead to CO_2 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 CO_2 gradients result in uncertainties in the estimation of the CO_2 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 calcaric soils, variations in the CO_2 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 (Rasmuson et al., 1990; Simunek and Suarez, 1993; 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, 1967; Revsbech and Ward, 1983; Stepniewski 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 Stepniewski, 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 ($\mathrm{mol\,m^{-2}\,s^{-1}}$) of a gas in soil can be described by Fick's law:

$$J = -D_{\mathrm{S}}^{\mathrm{Krogh},*} \cdot \frac{\partial P}{\partial z}, \tag{1}$$

where P (Pa) is the partial pressure of the gas, z (m) is the distance, and $D_{\mathrm{S}}^{\mathrm{Krogh},*}$ ($\mathrm{mol\,s^{-1}\,m^{-1}\,Pa^{-1}}$) is the Krogh diffusion coefficient for gas diffusion in water-saturated ($* = \mathrm{W}$) or aerated ($* = \mathrm{A}$) soil. $D_{\mathrm{S}}^{\mathrm{Krogh,\,W}}$ is the product of the gas diffusion coefficient for the water-saturated parts of the soil ($\mathrm{m^2\,s^{-1}}$) and the Henry's law constant K_{H} ($\mathrm{mol\,m^{-3}\,Pa^{-1}}$), while $D_{\mathrm{S}}^{\mathrm{Krogh,\,A}}$ is the product of the gas diffusion coefficient for the aerated soil parts ($\mathrm{m^2\,s^{-1}}$) and the term $(RT)^{-1}$, where R ($\mathrm{Pa\,m^{-3}\,mol^{-1}\,K^{-1}}$) is the ideal gas constant, and T (K) is the temperature. $D^{\mathrm{Krogh,\,W}}$ of CO_2 is approximately 25 times higher than $D^{\mathrm{Krogh,\,W}}$ of O_2 (Schack-Kirchner, 2012). Therefore, for equimolar fluxes in the aqueous phase, the gradient of the CO_2 partial pressure (pCO_2) must be 1/25th of the gradient of the O_2 partial pressure (pO_2). Considering that the maximum drop in pO_2 is from 21 kPa (atmospheric partial pressure) to 0 kPa, Greenwood (1970) concluded that pCO_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 pCO_2 gradient must be 1/0.8 times stronger than the gradient of pO_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 calcaric 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 ($\mathrm{pH} < \sim 4.5$), the carbonic acid (H_2CO_3) virtually does not dissociate. Therefore, the molar concentration of CO_2 dissolved in water, $[H_2CO_3^*]$, can simply be calculated with the Henry's law constant K_{H} ($\mathrm{mol\,m^{-3}\,Pa^{-1}}$):

$$[H_2CO_3^*] = K_{\mathrm{H}} \cdot pCO_2, \tag{2}$$

where pCO_2 (Pa) is the equilibrium CO_2 partial pressure, and $[H_2CO_3^*]$ is the sum of $[CO_{2,\mathrm{aq}}]$ and $[H_2CO_3]$, with $[CO_{2,\mathrm{aq}}]$ 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).

Gas	Parameter	Value	Unit	Comment	Reference
O_2	K_H	1.38×10^{-5}	$mol\,m^{-3}\,Pa^{-1}$		Lide (2002)
	D_0	1.90×10^{-5}	$m^2\,s^{-1}$	in air	Jaynes and Rogowski (1983)
	D^W	2.01×10^{-9}	$m^2\,s^{-1}$	in water	Lide (2002)
	D_S/D_0	34.24×10^{-3}	–	in soil (dm-m scale)	Schack-Kirchner et al. (2001)
CO_2	K_H	39.07×10^{-5}	$mol\,m^{-3}\,Pa^{-1}$		Carroll et al. (1991)
	K_d	4.44×10^{-7}	$mol\,L^{-1}$	$K_d = \frac{(HCO_3^-)(H^+)}{(H_2CO_3)}$	Stumm and Morgan (1996)
	D_0	1.59×10^{-5}	$m^2\,s^{-1}$	in air	Jaynes and Rogowski (1983)
	D^W	1.67×10^{-9}	$m^2\,s^{-1}$	in water	Lide (2002)
	D_S/D_0	34.24×10^{-3}	–	in soil (dm-m scale)	Schack-Kirchner et al. (2001)
HCO_3^-	D^W	1.04×10^{-9}	$m^2\,s^{-1}$	in water	Lide (2002)

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:

$$K_d = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}. \quad (3)$$

In a "CO_2–H_2O"-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 $[H_2CO_3^*]$ as $[H_2CO_3]$. The concentration of the dissolved CO_2 can then be calculated by adding $[H_2CO_3^*]$ 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 Calcaric soil, pH controlled by carbonic acid (system c)

For the "$CaCO_3$–CO_2–H_2O"-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, $[HCO_3^{-,\,resp}]$, was derived from the molar concentrations of the HCO_3^-, CO_3^{2-}, and Ca^{2+} ions by the following equation:

$$[HCO_3^{-,\,resp}] = [HCO_3^-] - ([Ca^{2+}] - [CO_3^{2-}]). \quad (4)$$

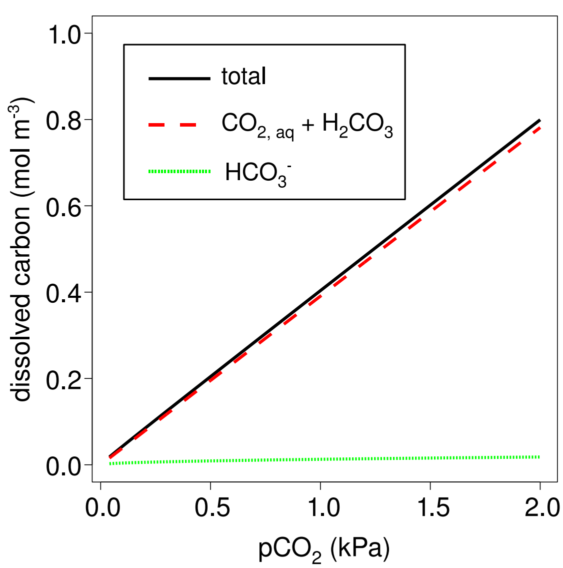

Fig. 1. Molar carbon concentrations of the different dissolved carbon species in a "H_2O-CO_2" -system (system b) as a function of the CO_2 partial pressure for $T = 293$ K. $CO_{2,\,aq}$ is the "physically" dissolved CO_2.

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 $HCO_3^{-,\,resp}$ 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):

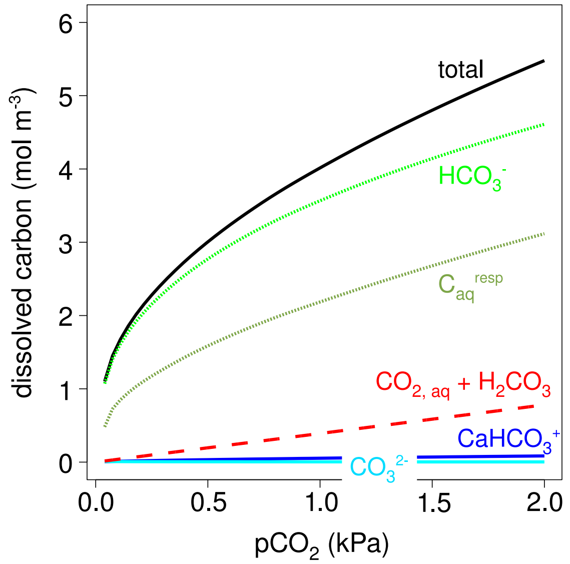

Fig. 2. Molar carbon concentrations of the different dissolved carbon species in a "H_2O-CO_2–$CaCO_3$"-system (system c) as a function of the CO_2 partial pressure for $T = 293$ K. C_{aq}^{resp} is the sum of all dissolved carbon species that originate from respiration.

$$[HCO_3^{-,\,resp}] = 9.70275 - 0.18389 \cdot pCO_2 + 1.97456 \cdot (pCO_2)^{0.5} - 0.03305 \cdot T, \tag{5}$$

where $0.04\,\text{kPa} < pCO_2 < 6\,\text{kPa}$, 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, (C_{aq}^{resp}), was obtained by adding $[H_2CO_3^*]$ to $[HCO_3^{-,\,resp}]$ (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 pCO_2 and $[HCO_3^{-,\,resp}]$, 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 pCO_2 values.

2.3 Model setup and solving procedure

To model the diffusion of O_2 and 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).

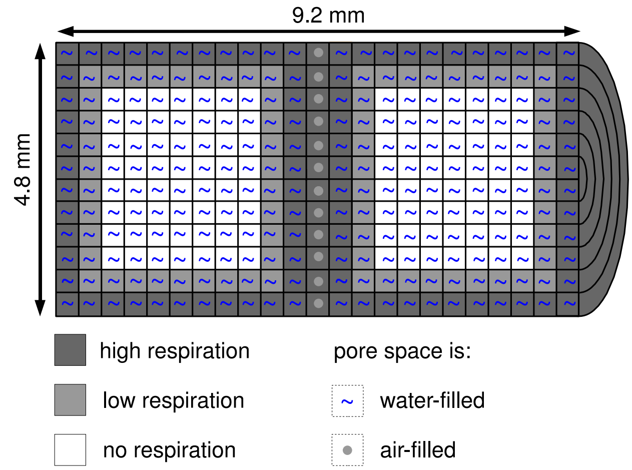

Fig. 3. The setup of the cylinder which represents a soil aggregate in our model. The porosity is uniformly distributed ($\phi = 0.3$). The pores in the middle slice are air-filled, the rest of the pore space is water-filled. Respiration takes place in the outer shell of the cylinder, in the aerated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

2.3.1 Gas diffusion in the inter-aggregate pore space

To calculate the O_2 and 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:

$$\epsilon \cdot \frac{\partial (C_S)}{\partial t} = \frac{\partial}{\partial z}\left(D_S \cdot \frac{\partial C_S}{\partial z}\right) + S(z), \tag{6}$$

where ϵ 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 the soil, 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 (ϵ), 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 N_2, O_2, and 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):

$$S(z) = S(z=0) \cdot \exp\left(-\frac{z}{L_S}\right), \tag{7}$$

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 0.015×10^{-3} mol m^{-3} 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 CO_2 flux of approximately $4 \times 10^{-6}\,\mathrm{mol\,m^{-2}\,s^{-1}}$ (e.g. Maier et al., 2010).

The CO_2 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 pO_2 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):

$$\gamma \cdot \phi \cdot \frac{\partial P}{\partial t} = \frac{\partial}{\partial z}\left(D_{\mathrm{A}}^{\mathrm{Krogh},*} \cdot \frac{\partial P}{\partial z}\right) + \frac{1}{r} \cdot D_{\mathrm{A}}^{\mathrm{Krogh},*} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial P}{\partial r}\right) + S(z,r), \tag{8}$$

where γ represents the Henry's law constant K_{H}, ($\mathrm{mol\,m^{-3}\,Pa^{-1}}$), if the diffusion takes place in water, and the factor $(R \cdot T)^{-1}$, if the diffusion takes place in air. R ($\mathrm{Pa\,m^{-3}\,mol^{-1}\,K^{-1}}$) 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 $D_{\mathrm{A}}^{\mathrm{Krogh},*}$ ($\mathrm{mol\,s^{-1}\,m^{-1}\,Pa^{-1}}$) the Krogh diffusion coefficient of the gas in the water-saturated ($* = \mathrm{W}$) or aerated ($* = \mathrm{A}$) parts of the aggregates. The relative diffusivity of the aggregates, in relation to the diffusion coefficients in free air or water (D_0 and D^{W}, Table 1), was set to 0.01, which is in accordance with experimental values obtained by Sexstone 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).

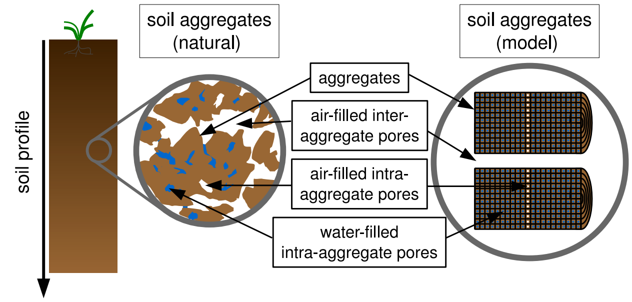

Fig. 4. Sketch of a soil profile with a cross-section of natural aggregates (left), and a representative of the cylindrical aggregates (right), used to model uptake/production and diffusion of O_2 and CO_2 inside the aggregates. The boundary condition of the cylindrical aggregates is defined by the pO_2 and pCO_2 values in the air-filled inter-aggregate pores, calculated with the one-dimensional diffusion model.

3 Results

In a siliceous aggregate at the soil surface, where the respiration is at its maximum and the pCO_2 at the aggregate boundaries is at its minimum, the intra-aggregate increase in pCO_2, calculated for system (b), is 0.875 kPa (Fig. 5). The slight decrease in pCO_2 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 HCO_3^- ions in system (b), which are not present in system (a) (Fig. 1). The pH values calculated from the modelled pCO_2 values for the unbuffered "CO_2–H_2O"-system decrease from 5.16 close to the aggregate surface to 4.91 near the centre of the water-saturated parts (Fig. 6).

The pCO_2 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 pCO_2 values at the aggregate boundaries the intra-aggregate pCO_2 increase is only 0.08 kPa (Fig. 7). This clear difference between calcaric and siliceous aggregates is caused by the higher solubility of CO_2 in the "$H_2O - CO_2 - CaCO_3$"-system compared to the "CO_2–H_2O"-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 pCO_2 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 pCO_2 in the aerated slice would still be less than 0.02 kPa.

The difference between the minimum pO_2 values inside the aggregates and the pO_2 values in the inter-aggregate air, i.e. the intra-aggregate pO_2 gradient, decreases with decreasing respiration and thus with increasing depth. This again

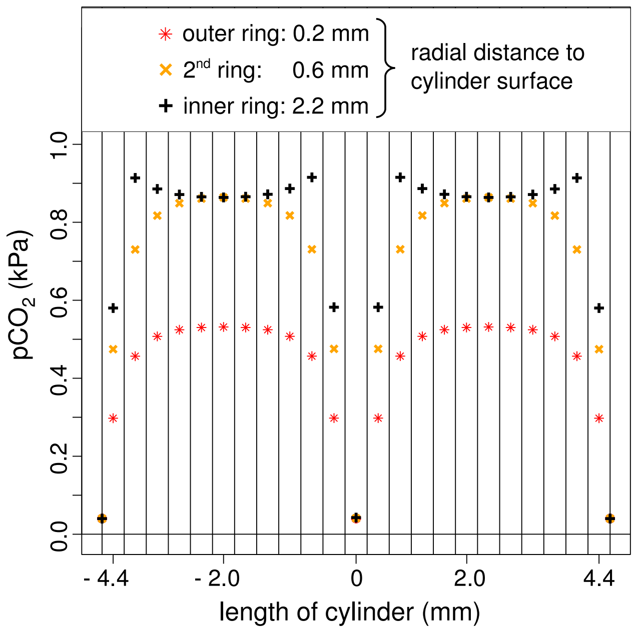

Fig. 5. Modelled CO_2 partial pressures in a siliceous, aerobic soil aggregate (system b) at the soil surface. The vertical lines mark the boundaries of the cylinder slices. The pore space of the middle slice is air-filled, the other slices are water-saturated (geometry and respiration as in Fig. 3). The pH values are controlled by the carbonic acid (Fig. 6).

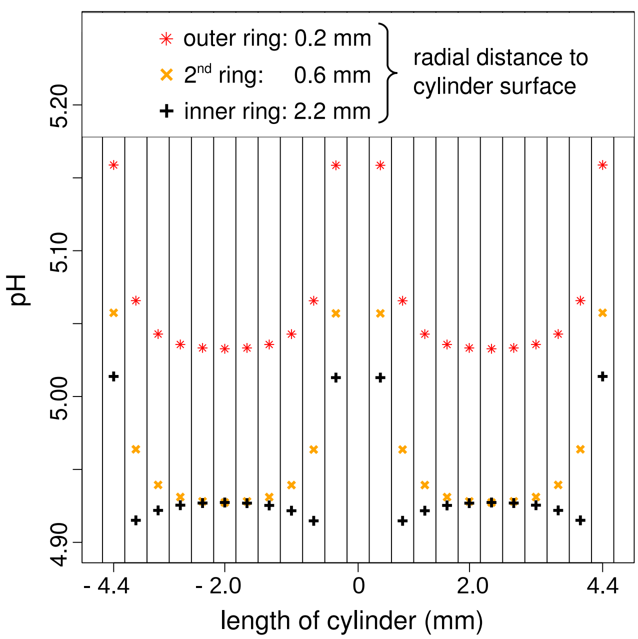

Fig. 6. pH values of the soil solution in the intra-aggregate pores, calculated for a "CO_2–H_2O"-system, using the CO_2 partial pressures shown in Fig. 5.

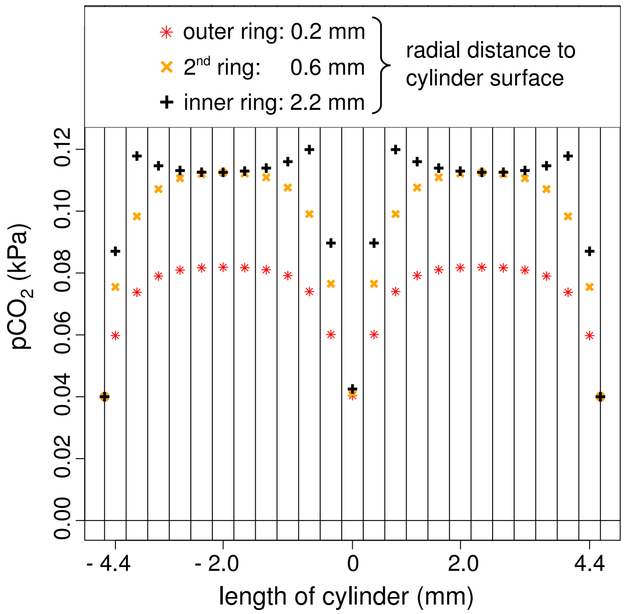

Fig. 7. Modelled CO_2 partial pressures in a calcaric, aerobic soil aggregate (system c) at the soil surface (geometry as in Fig. 3). The pH values are controlled by the carbonic acid.

results in decreasing intra-aggregate pCO_2 gradients (Fig. 8). As shown in Figs. 5 and 7 for topsoil aggregates, the intra-aggregate pCO_2 gradient is clearly higher in the siliceous aggregates than in the calcaric aggregates. Systems (a) and (b) differ only marginally. In case of a stronger increase in the inter-aggregate pCO_2 with depth, e.g. for $L_S = 0.3$ m in Eq. (7), the modelled maximum pCO_2 values inside the siliceous aggregates also increase with depth (in contrast to the decreasing values shown in Fig. 8). However, the intra-aggregate pCO_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 pCO_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 calcaric 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

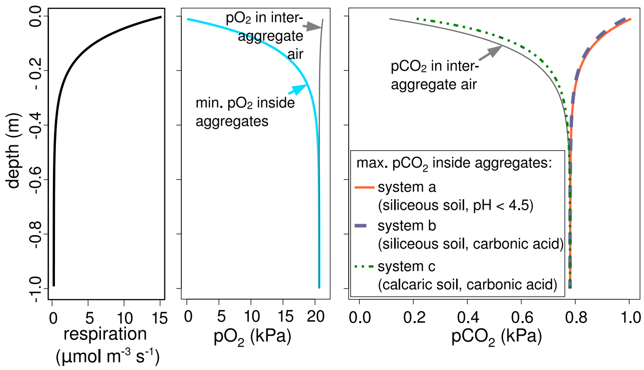

Fig. 8. Modelled O_2 (middle) and CO_2 (right) partial pressures (0–1 m soil depth) in the inter-aggregate air and the maximum values in the water phase inside the soil aggregates for siliceous and calcaric soil. Respiration (left) mainly takes place in the upper 30 cm of the soil.

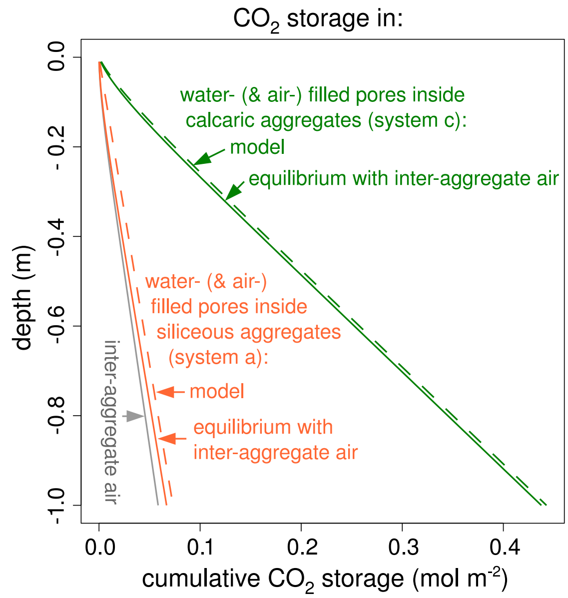

Fig. 9. Cumulative CO_2 storage in the inter-aggregate air and in the mainly water-filled pore space inside the siliceous and calcaric aggregates, based on the modelled CO_2 partial pressures (system a and c) (Fig. 8). Additionally, the CO_2 storage inside the aggregates is plotted for on an assumed equilibrium between the inter- and intra-aggregate pore space (no intra-aggregate CO_2 gradient).

strongly depend on the CO_2 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-calcaric, 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 (pH 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 CO_2 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 O_2 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 O_2 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 O_2 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 O_2 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 CO_2 gradients in the deeper soil. The maximum intra-aggregate pCO$_2$ gradients, however, always decrease with increasing depth.

For calcaric 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 $CaCO_3$. 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 pCO_2 gradient, or an increase in the solute concentration by evaporation or discrimination by roots (van Breemen and Buurman, 2002), intra-aggregate pCO_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 calcaric and siliceous soils. This can be explained by the relatively low maximum intra-aggregate pCO_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 pCO_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, pCO_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 pCO_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 pCO_2 in calcaric aggregates is always expected to be clearly lower than in siliceous aggregates, if the respiration rate in both aggregates is the same.

5 Conclusions

Despite the inclusion of air-filled intra-aggregate pores with low diffusive conductivities into our model, our results suggest that aerobic respiration can never cause intra-aggregate increases in pCO_2 of more than approximately 1 kPa, which is in accordance with Greenwood (1970). For calcaric soils our model even predicts much lower values. Therefore, in the case of aerobic respiration, only in non-calcaric soils intra-aggregate pCO_2 gradients might cause a high variability in the soil solution chemistry on a mm-scale. When estimating the total CO_2 storage in well aerated soils, our model suggests that the intra-aggregate increase in pCO_2 can be neglected for both siliceous and calcaric soils. Besides that, pCO_2 gradients in calcaric aggregates are a further explanatory approach for the formation of secondary carbonates on the walls of air-filled inter- and intra-aggregate pores.

If anaerobic respiration takes place, maximum intra-aggregate increases in pCO_2 cannot be predicted from maximum decreases in pO_2. Thus, for soils where anaerobic respiration controls the CO_2 production, the development of a method for measuring CO_2 inside natural aggregates on a sufficient spatial resolution might be the only option to assess the small-scale spatial variability of CO_2.

Acknowledgements. The article processing charge was funded by the German Research Foundation (DFG) and the Albert-Ludwigs University Freiburg in the funding programme Open Access Publishing.

Edited by: E. Veldkamp

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