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 0.08 kPa for calcaric 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 calcaric 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 calcaric, 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...
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In the last years efforts have been made to study the effects of structure and aggregation on soil processes (Totsche et al., 2010), using, for example, information on the internal pore topology from X-ray micro-tomography (Köhne et al., 2011). However, models for CO₂ 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 O₂ 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 O₂ 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 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:

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

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 aggregates.
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\section{Introduction}
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\item \textit{(w = W)} or aerated (\textit{* = A}) soil. \(D_{S}^{Krogh, W}\) 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 \(D_{S}^{Krogh, A}\) 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 (Schack-Kirchner, 2012). \(D_{S}^{Krogh, W}\) of CO$_2$ is approximately 25 times higher than \(D_{S}^{Krogh, W}\) of O$_2$. 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 one of O$_2$. 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.

\subsection{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.

\begin{discussion}
\end{discussion}
2.2.1 Acidic siliceous soil (system a)

If the pH is low (pH < ~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$^{-1}$):

$$[\text{H}_2\text{CO}_3^*]=K_H \cdot p\text{CO}_2 \tag{2}$$

where $p\text{CO}_2$ (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.

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 $K_d$:

$$K_d = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} \tag{3}$$

In a “CO$_2$-$\text{H}_2\text{O}$”-system with $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ 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\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O”-system the buffering of the carbonic acid by the dissolution of CaCO\textsubscript{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 \(p\text{CO}_2\) values and temperatures, using the dissociation constants from Stumm and Morgan (1996) (Fig. 2). The molar concentration of HCO\textsubscript{3}\textsuperscript{−} ions originating from respiration, \([\text{HCO}_3^{-}\text{, resp}]\), was derived from the molar concentrations of the HCO\textsubscript{3}\textsuperscript{−}, CO\textsubscript{3}\textsuperscript{2−}, and Ca\textsuperscript{2+} ions by the following equation:

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

This calculation is based on the idea that the molar concentration of HCO\textsubscript{3}\textsuperscript{−} ions originating from the dissolution of CaCO\textsubscript{3} (i.e. not to be considered for CO\textsubscript{2} diffusion) is equivalent to the term \(([\text{Ca}^{2+}] - [\text{CO}_3^{2-}])\), representing the molar concentration of free Ca\textsuperscript{2+} ions that are not balanced by free CO\textsubscript{3}\textsuperscript{2−} ions. Based on these HCO\textsubscript{3}\textsuperscript{−}\text{, resp} concentrations for different \(p\text{CO}_2\) 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):

\[
[\text{HCO}_3^{-}\text{, resp}] = 9.70275 - 0.18389 \cdot p\text{CO}_2 + 1.97456 \cdot (p\text{CO}_2)^{0.5} - 0.03305 \cdot T
\] (5)

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\textsubscript{2} transport in the solution, \(C_{aq}^{\text{resp}}\), 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\textsubscript{2} in water in this system was calculated by multiplying the Fickian diffusion coefficient of HCO\textsubscript{3}\textsuperscript{−} 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\textsubscript{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 O$_2$ and CO$_2$ in air-filled inter-aggregate pores and air- and water-filled intra-aggregate pores, we 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, which contain mostly water-filled meso- and micropores (intra-aggregate pores). The porosity of the aggregates was set to 30 %. This results in a total porosity of the soil of almost 50 %.

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:

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

(6)

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 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 ($\epsilon$), 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 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):

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

(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 \( \times 10^{-3} \) 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 \( \times 10^{-6} \) 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 is 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:

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

(8)
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 $(R \cdot T)^{-1}$, 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 $D^{Krogh, *}_A$ (mols$^{-1}$ m$^{-1}$ Pa$^{-1}$) the Krogh diffusion coefficient of the gas in the water-saturated ($\ast = W$) or aerated ($\ast = A$) 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).

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

### 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 increase in $pCO_2$ in the aerated slice is less than 0.003 kPa in both cases. The pH values calculated from the modelled $pCO_2$ values for the unbuffered “CO$_2$-H$_2$O”-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$_2$O – CO$_2$ – CaCO$_3$”-system compared to the “CO$_2$-H$_2$O”-system, leading to higher diffusive conductivities (Krogh diffusion coefficients).

The difference between the maximum $pCO_2$ values inside the aggregates and the $pCO_2$ values in the inter-aggregate air, i.e. the intra-aggregate $pCO_2$ increase, decreases with decreasing respiration and thus with increasing depth (Fig. 8). As shown in Figs. 5 and 7 for topsoil aggregates, the intra-aggregate $pCO_2$ increase is clearly higher in the siliceous aggregates than in the calcaric aggregates, as long as respiration occurs. Systems (a) and (b) differ only marginally. In spite of increasing $pCO_2$ values in the inter-aggregate air, the model predicts a decrease in the maximum $pCO_2$ values inside the siliceous aggregates with depth. However, if a slower decrease in respiration with depth is assumed, e.g. with $L_s = 0.3$ m in Eq. (7), the stronger increase in $pCO_2$ values in the inter-aggregate air causes similarly increasing $pCO_2$ values inside the siliceous aggregates.

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 strongly depend on the CO\(_2\) partial pressure in soil air. For a \(p\text{CO}_2\) of 1 kPa, silicate weathering rates were significantly higher compared to a \(p\text{CO}_2\) 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 \(p\text{CO}_2\) of 0.9 kPa suggests a high variability of the soil solution chemistry (pH values) on a mm-scale. This supports the assumption that \(p\text{CO}_2\) 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, e.g. 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, the effect of the intra-aggregate \(p\text{CO}_2\) gradients on the soil solution chemistry should be of importance only in the topsoil and possibly at some “respiration hotspots” in the subsoil. Strong CO\(_2\) enrichment in the intra-aggregate pores at deeper depths, as supposed by Koehler et al. (2010), seems only possible if the respiration inside aggregates is high at these depths, or if the diffusive conductivity of the intra-aggregate pore space is extremely low.
For calcaric soils our model predicts that aerobic respiration has no major effect on the small-scale spatial variability of the solution chemistry. The $p\text{CO}_2$ 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 $p\text{CO}_2$ 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 $p\text{CO}_2$ gradient, or an increase in the solute concentration by evaporation or discrimination by roots (Breemen and Buurman, 2002), intra-aggregate $p\text{CO}_2$ gradients are a further possible explanation for secondary carbonates on the walls of macropores and air-filled intra-aggregate pores, as observed, e.g. 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 commonly observed decrease in respiration with depth, 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). Thus our modelling approach can not be used to predict maximum intra-aggregate increases in $p\text{CO}_2$ if anaerobic respiration dominates the CO$_2$ production. But 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), and therefore $p\text{CO}_2$ gradients inside anaerobic aggregates are
probably not higher than in aerobic ones. 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, only in the highly respiring parts (topsoil) of 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 $pCO_2$ can not 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 $CO_2$.

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References


14809
Lindsay, W. L.: Chemical Equilibria in Soils, John Wiley and sons, New York, Chichester, Brisbane, Toronto, 1979. 14796, 14799
Schack-Kirchner, H. and Hildebrand, E. E.: Changes in soil structure and aeration due to liming and acid irrigation, Plant Soil, 199, 167–176, 1998. 14803


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Table 1. Chemical constants and Fickian diffusion coefficients for O\textsubscript{2}, CO\textsubscript{2}, and HCO\textsubscript{3}\textsuperscript{-} 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\textsubscript{2}</td>
<td>(K_H)</td>
<td>1.38 \times 10^{-5}</td>
<td>mol m\textsuperscript{-3} Pa\textsuperscript{-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\textsuperscript{2}s\textsuperscript{-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\textsuperscript{2}s\textsuperscript{-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></td>
<td>(K_H)</td>
<td>39.07 \times 10^{-5}</td>
<td>mol m\textsuperscript{-3} Pa\textsuperscript{-1}</td>
<td></td>
<td>Carroll et al. (1991)</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>(K_d)</td>
<td>4.44 \times 10^{-7}</td>
<td>mol l\textsuperscript{-1}</td>
<td></td>
<td>Stumm and Morgan (1996)</td>
</tr>
<tr>
<td></td>
<td>(D_0)</td>
<td>1.59 \times 10^{-5}</td>
<td>m\textsuperscript{2}s\textsuperscript{-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\textsuperscript{2}s\textsuperscript{-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\textsubscript{3}\textsuperscript{-}</td>
<td>(D_W)</td>
<td>1.04 \times 10^{-9}</td>
<td>m\textsuperscript{2}s\textsuperscript{-1}</td>
<td>in water</td>
<td>Lide (2002)</td>
</tr>
</tbody>
</table>
Fig. 1. Molar carbon concentrations of the different dissolved carbon species in a “H₂O-CO₂”-system (system b) as a function of the CO₂ partial pressure for T = 293 K. CO₂,aq is the “physically” dissolved CO₂.
Fig. 2. Molar carbon concentrations of the different dissolved carbon species in a “H$_2$O-CO$_2$-CaCO$_3$”-system (system c) as a function of the CO$_2$ partial pressure for $T = 293$ K. $C^\text{resp}_{aq}$ is the sum of all dissolved carbon species that originate from respiration.
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.
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.
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 “CO₂-H₂O”-system, using the CO₂ 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.
Fig. 8. Modelled CO\textsubscript{2} 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 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).