
Biogeochemistry **55:** 145–177, 2001.

A mechanistic model on methane oxidation in a rice rhizosphere

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Key words: diffusion, heterotrophic respiration, iron oxidation, methanogenesis, methanotrophy, reduction, root oxygen release

Abstract. A mechanistic model is presented on the processes leading to methane oxidation in rice rhizosphere. The model is driven by oxygen release from a rice root into anaerobic rice soil. Oxygen is consumed by heterotrophic and methanotrophic respiration, described by double Monod kinetics, and by iron oxidation, described by a second order reaction. Substrates for these reactions – ferrous iron, acetate and methane – are produced by an exponential time dependent organic matter mineralisation in combination with modified Michaelis Menten kinetics for competition for acetate and hydrogen. Compounds diffuse between rhizosphere, root and atmosphere. A diffusion resistance between the rice root and shoot is included. Active transport across the root surface occurs for root exudation and plant nutrient uptake. Iron adsorption is described dependent on pH. The model predicts well root oxygen release, compound gradients and compound concentrations in a rice rhizosphere. Methane oxidation estimates are comparable to experimental estimates. A sensitivity analysis showed however that methane oxidation is highly dependent on model initialisation and parameterisation, which is highly dependent on the history of the rhizosphere and root growth dynamics. Equilibrium is not obtained within the period that a single root influences a soil microsite and results in a large change in methane storage. Equilibrium is moreover dependent upon the diffusion resistance across the root surface. These factors make methane oxidation dynamics highly variable in space and time and dependent on root dynamics. The increased understanding of methane oxidation does not directly lead to increased predictive abilities, given this high variability and the uncertainties involved in rhizosphere dynamics.

Introduction

Rice paddies are suspected to contribute substantially to the increasing atmospheric methane concentration. Methane emission reflects the balance between methane production and oxidation. Methane oxidation in rice paddies occurs at the soil-water interface and in the rhizosphere, where both oxygen and methane are available. Methane oxidation rates in the rhizosphere

are highly variable and plant mediated transport is the dominant methane emission pathway (Schütz et al. 1989). A better mechanistic understanding of rice rhizospheric methane oxidation is thus important for a good prediction of global methane emissions.

Various processes determine rhizospheric methane oxidation (schematically represented in Figure 1). Methane is produced at anaerobic sites in a rice paddy by methanogens, which compete for carbon substrates with microorganisms that use alternative electron acceptors of which iron oxides are the most important (Van Bodegom & Stams 1999; Inubushi et al. 1984). Carbon substrates become available via soil organic matter mineralisation, root decomposition and root exudation (Van Bodegom et al. 2001). Root exudates diffuse towards the anaerobic sites. Methane diffuses towards the root surface and is released into the atmosphere through aerenchyma channels present in rice roots and shoots (Nouchi & Mariko 1993). Oxygen diffuses through the same aerenchyma channels into the soil – root oxygen release – while part of the oxygen is already consumed in the roots by root respiration (Ando et al. 1983). Methane oxidation can occur at sites where methane and oxygen concentration profiles overlap. Methanotrophs have to compete for the available oxygen with other processes, of which heterotrophic respiration and iron oxidation are most important (see below). Iron oxidation again depends on adsorbed iron and pH (Kirk et al. 1990) and thus on CO_2 production and plant nutrient uptake.

Various models have been developed for some of the processes mentioned above. Some process-based methane emission models describe organic substrate production and methane production (e.g. Cao et al. 1995), but do not consider competition with alternative electron acceptors (Arah & Stephen 1998; Cao et al. 1995; Walter et al. 1996). Cao et al. (1995) treats methane oxidation as a fraction of methane production and Walter et al. (1996) assumes no oxygen limitation on methane oxidation. A kinetic model describing methane oxidation in rice paddies (Cai & Yan 1999) neither assumes oxygen limitation of methane oxidation nor includes methane production. Grant (1999) and Ridgwell et al. (1999) present methane oxidation models that can only be used in aerobic soils without plants and are therefore not suitable for rice paddies. Armstrong & Beckett (1987) present a mechanistic model on oxygen dynamics within an aerenchymous root, but include no rhizospheric oxygen dynamics. Available rhizosphere models describe iron dynamics (Jones et al. 1996; Kirk 1993) or dynamics of heterotrophic respiration (Darrah 1991a, b; Newman & Watson 1977), but no methane oxidation. The most comprehensive rhizosphere model that can be used to estimate methane oxidation is described by Segers and Leffelaar (2001) for wetland plants. Parameterisation of wetland dynamics is very

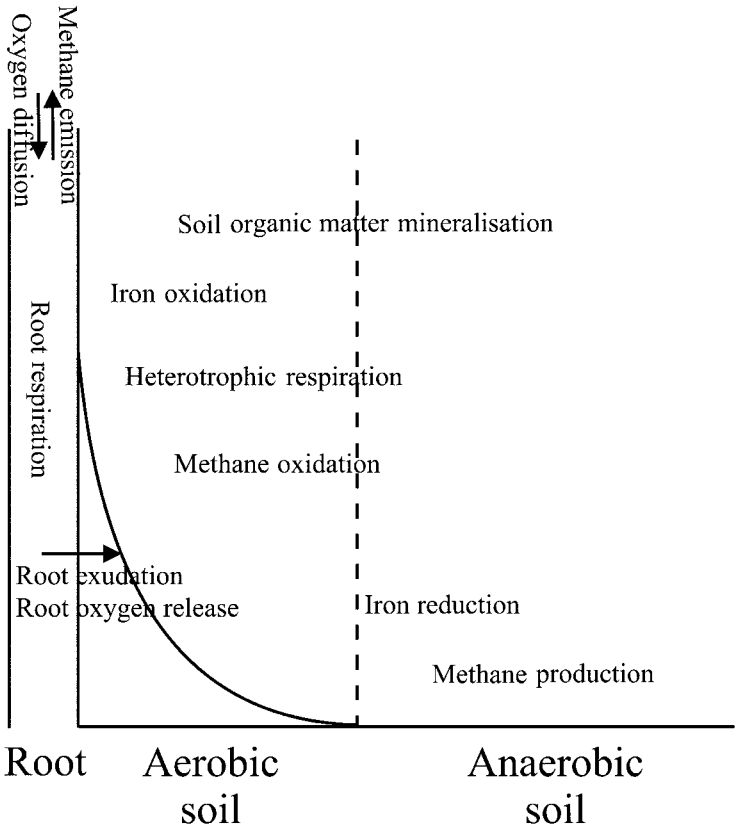


Figure 1. Schematic representation of a rhizosphere and its processes.

complicated and Segers and Leffelaar (2001) therefore simplifies electron acceptor dynamics, soil organic matter mineralisation, heterotrophic respiration and root gas transport. This makes the model of Segers and Leffelaar (2001) less suitable for a mechanistic understanding of methane oxidation dynamics.

The objective of this paper is the presentation of a model to increase the understanding of the mechanisms, interactions and the dynamics determining methane oxidation in rice rhizosphere, as none of the described models are directly suitable for this objective. Available information on all underlying processes shown in Figure 1 is combined for a full account of the mechanisms and interactions involved. Model performance is compared to other models and to in-situ measurements to test its validity. A model sensitivity analysis is presented to determine the variability in modelled methane oxidation as a function of the underlying processes and as a function of model initialisation.

By this combination, the variability in methane oxidation dynamics can be understood.

Model description

The mechanistic model describes the kinetics of aerobic oxidation of the most important electron donors and the diffusion of those electron donors from a rice root surface and their production within a rice rhizosphere. Transport within the rhizosphere and the release of gaseous compounds via the root to the atmosphere is described. Methane oxidation in a rice rhizosphere system can be simulated mechanistically by this combination of kinetics and transport.

Aerobic oxidation

Methane oxidation in rice rhizosphere is oxygen limited (Bosse & Frenzel 1997). It is therefore of prime importance to estimate the dynamics of oxygen consumption processes properly. Although denitrifiers can outcompete rice plants for nitrate (Reddy & Patrick 1986), denitrification is a minor soil sink of reducing equivalents because nitrate concentrations are low and denitrification is negligible in unfertilised rice paddies (Arth et al. 1998). Nitrifying bacteria are outcompeted by plant roots and heterotrophs at limiting amounts of ammonia (Reddy et al. 1989; Verhagen et al. 1995). Sulphur oxidisers have been found in rice rhizosphere (Stubner et al. 1998) and sulphate concentrations are significantly higher in rice rhizosphere in comparison with the bulk soil (Dannenberg & Conrad 1999; Wind et al. 1995), but incubation measurements of oxidation rates and Most Probable Number determinations indicated that sulphur oxidation rates are lower than other oxidation rates (Van Bodegom et al. unpublished results). The most important oxygen sinks in a rice rhizosphere are therefore iron oxidation (Equation 1), microbial methane oxidation (Equation 3) and microbial heterotrophic respiration (Equation 4).

$$4Fe^{2+} + O_2 + 10H_2O -> 4Fe(OH)_3 + 8H^+ \quad (1)$$

Iron oxidation rate, R_{Feox} (mol m^{-3} water s^{-1}), is given by (Ahmad & Nye 1990):

$$R_{Feox} = k \cdot [Fe_s^{2+}] \cdot [O_2] \quad (2)$$

in which k is the iron oxidation constant ($0.344.10^{-3}$ m^3 mol^{-1} s^{-1}, according to Ahmad & Nye (1990)), subscript s reflects that iron is adsorbed to clay

particles. Compound concentrations are in the water phase (mol m^{-3}) and corrected for the solubility in the gas phase, if applicable. Similarly to Kirk et al. (1990), only fast iron oxidation is considered in this study. 0.25 moles of O_2 are consumed during the oxidation of one mol of ferrous iron.

Heterotrophic respiration is simplified to oxidation of acetate, because acetate is the most important organic acid in rice soils (e.g. Chin & Conrad 1995; Sigren et al. 1997) and around decaying rice roots (Conrad & Klose 1999).

$$CH_4 + (2-\alpha_m)O_2 -> (1-\alpha_m)CO_2 + (2-\alpha_m)H_2O + \alpha_m < CH_2O >_m \quad (3)$$

$$CH_3COO^- + H^+ + 2(1-\alpha_h)O_2 -> 2(1-\alpha_h) CO_2 + 2(1-\alpha_h)H_2O + 2_h < CH_2O >_h \quad (4)$$

in which $<CH_2O>$ represents a simplified description of microbial biomass. α is a reaction coefficient which is numerically equal to the microbial yield Y (in mol microbial carbon per mol carbon consumed). Subscript $_m$ indicates methanotrophs and subscript $_h$ indicates heterotrophs. α_m and α_h equal 0.264 (Harwood and Pirt 1972) and 0.34 (Tros et al. 1996), respectively. Microbial growth is taken proportional to biomass and the specific growth rate μ (s^{-1}) is expressed by Double Monod kinetics as:

$$\mu_i = \mu_{max,i} \frac{[O_2]}{K_{sO2_i} + [O_2]} \cdot \frac{[C_i]}{K_{sCi} + [C_i]} \quad (5)$$

in which μ_{max} is the maximum specific growth rate (s^{-1}) and equals 3.2 10^{-5} (Harwood and Pirt 1972) and 8.2 10^{-5} (Tros et al. 1996) for methanotrophs and heterotrophs, respectively. K_s is the affinity constant for a compound (mol m^{-3}) and C_i stands for methane or acetate for methanotrophs or heterotrophs, respectively. Values for KsC_h, KsC_m, KsO_{2h} and KsO_{2m} were 1.56 (Tros et al. 1996), 0.037 (Sipkema et al. 1998), 10.7 10^{-3} (Krooneman et al. 1996) and 4.7 10^{-3} (Gerritse & Gottschall 1993), respectively. Total microbial oxygen consumption is not only influenced by growth, but also by maintenance and growth independent microbial decay. These processes are usually neglected in experiments in which kinetic parameters are measured and are thus implicitly incorporated into these parameters. This allows a definition of microbial oxygen consumption rate, $R_{O2,i}$ (mol O_2 m^{-3} water s^{-1}):

$$R_{O2_i} = \mu \cdot B_i \cdot \frac{v_i - \alpha_i}{\alpha_i} \quad (6)$$

in which B is the microbial biomass (mol C m^{-3}) and v is a stoichiometry coefficient, which is 2 and 1 for methanotrophs and heterotrophs, respectively. Microbial carbon substrate consumption, $R_{C,i}$ (mol C m^{-3} water s^{-1}), is calculated analogously as:

$$R_{C_i} = \frac{\mu_i \cdot B_i}{\eta_i \cdot \alpha_i} \tag{7}$$

in which η is a stoichiometry coefficient for the number of moles C in the substrate (1 and 2 for methanotrophs and heterotrophs, respectively). The fraction of consumed carbon substrate that is not incorporated into biomass is oxidised to CO_2.

Production of electron donors

Within a rice rhizosphere, production and consumption of carbon substrates and ferrous iron can occur simultaneously. The production of acetate and CO_2/H_2 is driven by soil organic matter mineralisation, P_{min} (in mol C m^{-3} s^{-1}), neglecting root decay and the decomposition of organic fertilisers, and is described by Yang (1996):

$$P_{min} = C_{org} \cdot (1 - S_{min}) \cdot K_{d_{min}} \cdot e^{-K_{d_{min}} \cdot time\_season} \tag{8}$$

in which C_{org} is the soil organic carbon pool (mol C m^{-3}) and:

$$K_{d_{\min}} = R_{\min} \cdot time\_season^{-S_{\min}} \tag{9}$$

R_{min} and S_{min} were determined experimentally (Van Bodegom et al. 2001). R_{min} (1.25 10^{-4} s^{Smin-1}) is the relative decomposition rate at *time_season* = 1 and S_{min} (0.585) represents the rate of change of $K_{d,min}$ · *time_season* is the time after flooding the soil (s) and is taken 40 days after transplanting in the default settings, because at that point a reasonable rice root system has been developed.

Methane is produced from acetate and from CO_2/H_2. Methanogens have to compete for these substrates with heterotrophs and ferric iron reducing bacteria that also use acetate and CO_2/H_2:

$$CH_3COO^- + H^+ -> CO_2 + CH_4 \tag{10}$$

$$CO_2 + 4H_2 -> 2H_2O + CH_4 \tag{11}$$

$$8Fe(OH)_3 + CH_3COO^- + 17H^+ -> 8Fe^{2+} + 2CO_2 + 22H_2O \tag{12}$$

$$2Fe(OH)_3 + H_2 + 4H^+ -> 2Fe^{2+} + 6H_2O \tag{13}$$

Both methane production, $R_{CH4,j}$, and ferric iron reduction, $R_{Fered,j}$, are inhibited in the presence of oxygen. Moreover, in incubation studies methane production seems to be inhibited directly in the presence of reducible ferric iron (Van Bodegom & Scholten 2001). Microbial biomass dynamics seems not important for methane production (subscript $_p$) and ferric iron reduction (subscript $_f$) (Van Bodegom & Stams 1999; Segers & Kengen 1998). Both rates can thus be described by a modified Michaelis Menten kinetics:

$$R_{CH4j} = V_{\max_{j_p}} \cdot \frac{[e^- donor_j]}{K_{M,j_p} + [e^- donor_j]} \cdot \frac{1}{1 + K_{i,O2_p} \cdot [O_2]} \cdot \frac{1}{1 + K_{i,Fe} \cdot [Fe_s^{3+}]} \tag{14}$$

$$R_{Fered_j} = V_{\max_{j_f}} \cdot \frac{[e^- donor_j}{K_{M,j_f} + [e^- donor_j]} \cdot \frac{[Fe_s^{3+}]}{K_{M,Fe+[Fe_s^{3+}]}} \cdot \frac{1}{1 + K_{i,O2_f} \cdot [O_2]} \tag{15}$$

in which the e^- $donor_j$ is either H_2 or acetate and the maximum conversion rate $Vmax_{H2,p}$ equals 7.6 10^{-6} mol $m^{-3}s^{-1}$, $Vmax_{Ac,p}$ equals 3.8 10^{-6} mol $m^{-3}s^{-1}$, $Vmax_{H2,f}$ and $Vmax_{Ac,f}$ equal 1.2 10^{-4} mol $m^{-3}s^{-1}$ as was estimated from incubation studies (Van Bodegom & Scholten 2001). The affinity constant $km_{H2,p}$ is 13.3 10^{-3} mol m^{-3}, $km_{Ac,p}$ is 2.56 mol m^{-3}, $km_{H2,f}$ is 0.22 10^{-3} mol m^{-3}, $km_{Ac,f}$ is 0.23 mol m^{-3} and km_{Fe} is 61 mol m^{-3} (Van Bodegom & Scholten 2001). The inhibition constant $K_{i,O2}$ (defined similarly in Arah & Stephen (1998)) for methane production is estimated at 47 m^3mol^{-1} (using activity data presented by Fetzer & Conrad 1993; Nedwell & Watson 1995). $K_{i,O2}$ for ferric iron reduction will be smaller and is chosen at 2/3 of the value for methane production. $K_{i,Fe}$ is estimated from incubation studies at 8.3 m^3 mol^{-1} total reducible iron (Van Bodegom & Scholten 2001). The ferric iron concentration has a subscript $_s$ to indicate that $Fe^{3+}$is precipitated as $Fe(OH)_3$ and dissolved and reduced by microbes, leading to a release of ferrous iron into the soil solution.

Root compound conversions

The important process within a root that influences methane oxidation is root respiration, R_{resp} (mol O_2 cm^{-3} root s^{-1}), which is described according to Luxmoore (1970a), neglecting the influence of assimilates on root respiration:

$$R_{resp} = resp_{max} \cdot \frac{[O_2]_{root}}{K_{resp} + [O_2]_{root}} \tag{16}$$

in which $[O_2]_{root}$ is the concentration in a root (mol m^{-3} gas), $resp_{max}$ is the maximum rate of root respiration ($3.23.10^{-9}$ mol cm^{-3} root s^{-1} for rice (Luxmoore 1970b)) and K_{resp} (6.42 mol m^{-3} gas for rice roots (Luxmoore 1970b)) is the oxygen concentration at which respiration is half $resp_{max}$. Root respiration is assumed to occur across the whole root length, which is assumed to be 0.22 m (Armstrong et al. 1991; Kludze & Delaune 1995). CO_2 is produced by root respiration.

All biological reactions are presumed to proceed with a temperature dependence that can be described by a Q_{10} value, which is the relative increase in reaction rates at a temperature increase of 10 °C, of 2 (Atlas & Barta 1987).

Iron adsorption

Iron transport in rice rhizosphere is complex and highly dependent on pH dependent solubility. All ferric iron is immobile, indicated as $[Fe_s^{3+}]$, precipitated as $Fe(OH)_3$ neglecting other iron precipitates and is produced by iron oxidation and decreased by iron reduction. Ferrous iron is present in two forms: $[Fe^{2+}]$, mobile in the soil solution and produced by iron reduction, and $[Fe_s^{2+}]$ which is immobile, adsorbed to clay particles and consumed by iron oxidation. The equilibrium between $[Fe^{2+}]$ and $[Fe_s^{2+}]$, which is assumed to occur almost instantaneously, is given by (Kirk et al. 1990):

$$[Fe^{2+}] = \left(\frac{\{Fe_s^{2+}\} + \{Fe_s^{3+}\}}{a}\right)^{1/m} \cdot \left(\frac{\{Fe^{2+}\}}{\{Fe_s^{2+}\} + \{Fe_s^{3+}\}}\right)^{1/n} \tag{17}$$

in which $\{.\}$ represents a concentration expressed in mol kg^{-1} soil, a and m are Freundlich isotherm parameters (0.032 kg^{-1} mol^{1-m} m^{3m} and 0.57, respectively (calculated from Ahmad & Nye (1990)). n describes the pH dependence of Fe^{2+} adsorption on partially oxidised soil (Kirk et al. 1990):

$$n = n_A \cdot e^{-n_B \cdot pH} \tag{18}$$

in which n_A is 30 and n_B is 0.9 pH^{-1} (Kirk et al. 1990). The pH is determined by the soil acidity, *[HS]* (mol m^{-3} water) and the soil buffer capacity b_{HS} (39.6 mol m^{-3} water pH^{-1}, calculated from Kirk et al. (1990)) (Nye 1972):

$$\frac{dpH}{dt} = -\frac{1}{b_{HS}} \cdot \frac{d[HS]}{dt} \tag{19}$$

Temporal change in [HS] is determined by the production of acidity (in this study iron oxidation), consumption of acidity (in this study iron reduction)

and transport of the most dominant base pairs in a soil layer *l*, H^+-H_2O and H_2CO_3-HCO_3^-:

$$\frac{dHS}{dt}_l = (Flow_{H^+_{l-1}} - Flow_{H^+_l}) - (Flow_{HCO3^-_{l-1}} - Flow_{HCO3^-_l}) + \lambda \cdot R_{FeOx} \cdot V_{w_l} - \lambda \cdot R_{Fered} \cdot V_{w_l} \quad (20)$$

in which λ is a stoichiometry constant depicting the number of H^+ transferred per iron (2) and $V_{w,l}$ is the water volume (m^3) in soil layer *l*. Transport is driven by diffusive flows from layer *l* to layer *l* + *1* (Eq. 21) and layer 1 is located closest to the root.

Concentrations and flows of H^+ are calculated by combining Eq. 19, 20, 21 and an active root release of H^+ to balance nitrogen uptake (next section). Concentrations and flows of HCO_3^-, $Flow_{HCO3-}$, are calculated from concentrations and flows of total CO_2 available in a soil layer (which is CO_2(l) + CO_2(g)+ H_2CO_3(l)+ HCO_3^-(l), neglecting CO_3^{2-} because pH < 8). Total CO_2 is transported through the system via diffusion through water and gas phase. Total CO_2 is produced by soil mineralisation, methane production, iron reduction, root respiration and respiration coupled to methane and acetate oxidation (all treated above). Total CO_2 is distributed among water and gas phase as a function of pH in each soil layer *l* according to chemical equilibria for dissolution of CO_2 (pK_1 = 1.406), hydration of CO_2 to H_2CO_3 (pK_2 = 2.616) and the acid-base reaction of H_2CO_3 to HCO_3^- (pK_a = 3.76) (Garrels & Christ 1965; Kerns 1960).

Transport

All reactions described above can occur at different distances, *r*, from the root. In the model, a cylindrical geometry of 20 layers around a root has been incorporated. The layer thickness increases linearly with distance from the root, as the steepest gradients will occur closest to the root. The first soil layer has the same thickness as the root radius, r_{root} (m), which was estimated at 0.37 10^{-3} m from primary root data (Drenth et al. 1991).

Under influence of all reactions, gradients develop between compartments and diffusive flows occur. In the model, convective flows are neglected, because these flows contribute little to total water and solute transport in rice systems (Denier van der Gon & van Breemen 1993; de Willigen & van Noordwijk 1994). It is also assumed that the contribution of gas bubbles to transport is negligible at the short distances considered in the model. Adsorption of organic acids on iron oxides is also neglected, contrary to the model of Jones et al. (1996). The diffusive flow (mol s^{-1}) out of soil layer *l* to layer *l* +

1 for all mobile compounds, *M* (O_2, CH_4, acetate, H_2, CO_2, HCO_3^-, H_2CO_3, Fe^{2+} and H^+), can thus be described by:

$$Flow_{Ml} = D_{eff_M} \cdot A_l \cdot \frac{d[M]}{dr} \tag{21}$$

in which $D_{eff,M}$ is the effective diffusion coefficient (m^3 water m^{-1} soil s^{-1}) and A_l is the cross section area (m^2 soil) between soil layer l and layer $l + 1$. $D_{eff,M}$ is given by:

$$D_{eff_M} = \frac{D_{A_M} \cdot \tau_B \cdot \varepsilon^{\tau_A}}{\alpha_M} + D_{W_M} \cdot \tau_B \cdot \theta^{\tau_A} \tag{22}$$

in which ε is the gas filled porosity (m^3 gas m^{-3} soil), θ is the water filled porosity (m^3 water m^{-3} soil), α_M is the Ostwald coefficient (m^3 gas m^{-3} water) and is taken from Wilhelm et al. (1977) for all M that can occur in the gas phase. τ_B and τ_A determine soil tortuosity – path length extension – and have values of 0.9 and 2.3, respectively (Campbell 1985). $D_{A,M}$ is the diffusion coefficient of compound M in air (m^2 gas s^{-1}) and is calculated against N_2 as a function of temperature according to theory by Hirschfelder et al. (1964). $D_{W,M}$ is the diffusion coefficient of a compound M in water (m^2 water s^{-1}) (CH_4: 2.22 10^{-9} m^2s^{-1} (Jähne et al. 1987), O_2: 2.99 10^{-9} m^2s^{-1} (Langø et al. 1996), H_2: 5.34 10^{-9} m^2s^{-1} (Langø et al. 1996), HCO_3^- and H_2CO_3: 1.40 10^{-9} m^2s^{-1} (Nye 1972), CO_2: 2.22 10^{-9} m^2s^{-1} (Langø et al. 1996), Fe^{2+}: 0.707 10^{-9} m^2s^{-1} (O'Connor et al. 1971), H^+: 8.4 10^{-9} m^2s^{-1} (Nye 1972), acetate: 0.672 10^{-9} m^2s^{-1} (Darrah 1991a) all at 30 °C). Temperature dependence of $D_{W,M}$ is described by a Q_{10} value of 1.31 (Segers & Leffelaar 2001).

Besides various soil layers, a root compartment and an atmospheric compartment are distinguished. The root and atmospheric compartments are dominated by the gas phase and exchange between these compartments is given by:

$$Flow_{M'_{air-root}} = \omega_{r,t} \cdot A_t \cdot \#_r \cdot ((M'_{air}) - (M'_{root})) \tag{23}$$

in which (M′) is the concentration of a volatile compound M′ (O_2, CH_4, CO_2, H_2) in the gas phase (mol m^{-3} gas), $\omega_{r,t}$ is the conductance at the rice root-shoot interface (estimated at 2.04 10^{-6} m^3 gas m^{-2} tiller s^{-1} using diffusion experiments with tracer gases through this interface (Groot et al. unpublished results)), A_t is the cross section area of a tiller (estimated to be $3.2.10^{-5}$ m^2) and $\#_r$ is the number of roots per tiller (estimated to be 22 (Colmer et al. 1998; Harada & Yamazaki 1993)). (M'_{root}) is corrected for root porosity. $\omega_{r,t}$ is by far the most important limiting factor for gas transport in a rice plant

(Butterbach-Bahl et al. 1997). All other mechanisms of transport through the rice plant can therefore be neglected and do not have to be dealt with explicitly. This also implies that (M'_{root}) can be assumed to be homogeneous and that root respiration does not have to be solved spatially explicitly (contrary to Armstrong and Beckett (1987)), because exchange between roots and atmosphere is about 45 times slower than mixing within a root. This also allows the assumption that exchange sites between root and soil (mainly at root tips and root hairs (Flessa & Fischer 1992)) are homogeneously spread across the root surface. In addition, it is assumed that compound exchange between soil and root is not limited by root access. The root surface itself does not introduce an additional resistance, analogous to the situation at a leaf surface, where the limited area of the stomata does not introduce an extra resistance for transport (Monteith & Unsworth 1990). This leads to:

$$Flow_{M'\ root-soil} = \frac{1}{\frac{r_{root}\cdot\alpha_C}{D_{A_{M'}}\cdot A_{root}\cdot\varepsilon_{root}} + \frac{r_{root}}{D_{A_{M'}}\cdot A_{root}\cdot(1-\varepsilon_{root})} + \frac{0.5\cdot r_1}{D_{eff_{M'}}\cdot A_{0.5}}} \cdot([M']_1 - \alpha_C \cdot (M'_{root})) \quad (24)$$

in which A_{root} is the root surface available for gas exchange (m^2) assuming an active root length available for exchange of 0.075 m (Armstrong 1971b), ε_{root} is the root porosity to convert $D_{A,M}$ to a root surface (0.3 m^3 gas m^{-3} root (Butterbach-Bahl et al. 1997)), $A_{0.5}$ is the soil cross section area halfway the first soil layer (m^2) and r_1 is the thickness of the first soil layer (m).

Root oxygen release can also be calculated with Eq. 24, because biochemically and photo-synthetically produced oxygen are not of importance in rice (Ando et al. 1983). If oxygen gradients within the root are important, then the model will underestimate root oxygen release, because oxygen concentrations at the root cortex is above the average root oxygen concentration (Armstrong & Beckett 1987).

Root exudation, assumed to be either acetate – shown to be a major constituent of root exudates (Dannenberg & Conrad 1999) – or converted instantaneously into acetate (Dannenberg & Conrad 1999), cannot be described by diffusion equations, because exudation is partly an active process, e.g. to allow phosphate uptake:

$$Flow_{C\ h,root-soil} = E \cdot A_{root} \quad (25)$$

in which E is the root exudation rate (estimated at $9.6.10^{-10}$ mol m^{-2} root s^{-1} (Hoffland et al. 1989; Delhaize et al. 1993), which is similar to data presented by Lu et al. (1999) for default root radius and root length.

For H^+ diffusion across the root surface, an eq. similar to Eq. 24 is used, using an apoplast pH of 6.5 (Mattsson et al. 1998):

$$Flow_{H+_{root-soil}} = \frac{1}{\frac{r_{root}}{(1-\varepsilon_{root})\cdot A_{root}\cdot D_{W_{H+}}} + \frac{0.5\cdot r_1}{D_{W_{H+}}\cdot \tau_B \cdot \theta^{\tau_A}\cdot A_{0.5}}} \cdot([H^+]_1 - [H^+_{root}]) \quad (26)$$

In addition, an active root release of H^+ to balance plant uptake of ammonia is included. As default, a nitrogen uptake of 5 kg N ha^{-1} day^{-1} is assumed.

Boundary and initial conditions

The atmosphere represents one system boundary (for which the exchange is dealt with above). The 2nd boundary occurs at the interface between rhizosphere and bulk soil. It is assumed that net exchange at this boundary is zero. Zero exchange occurs if there is an equilibrium between bulk soil and outer soil layer or if the outer soil layer meets the outer layer of a proximate root.

The amount of a compound M in a compartment is calculated from the production and consumption rates (corrected for compartment volume) and flows into and out of the compartment. The concentration of compound M is calculated from the amount M and compartment volume. The model simulation starts with an anaerobic soil, which is one of the equilibria produced by the model. At time zero, the system is perturbed by the arrival of an oxygen releasing root. Dissolved methane is assumed to be 0.35 mol m^{-3} water (Rothfuss & Conrad 1993; 1998) and initial acetate concentration is estimated at 0.05 mol m^{-3} for anaerobic soil in equilibrium (Chin & Conrad 1995; Rothfuss & Conrad 1993). All iron is assumed to be reduced and is estimated from the total reducible iron content, on average 180 μmol g d.w.$^{-1}$ (Yao & Conrad 1999). Total dissolved CO_2 is estimated to be 6 mol m^{-3} (Conrad et al. 1986). Soil pH is chosen to be initially 6.7 (Ponnamperuma 1972). Initial microbial biomass of heterotrophs and methanotrophs is estimated from biomass data presented for anaerobic bulk soil in rice paddies (Gilbert & Frenzel 1998; Kumaraswamy et al. 1997). Gaseous concentrations in the root are assumed to be in equilibrium with the atmosphere. The model was run to simulate 48 hours. This is about the maximum united period that a microsite is under influence of oxygen release from a single rice root (Flessa & Fischer 1992). Compound balances were included in the model and never showed relative deviations $> 10^{-6}$. The model was written in FST (Rappoldt & van Kraalingen, 1996) and is available upon request.

Results

Model performance

The driving force of the model is diffusive transport of oxygen from the atmosphere into the anaerobic soil. Part of the oxygen did not reach the soil, but was consumed in the roots, 4.11 μmol cm^{-2} root surface day^{-1}. Root oxygen release (ROL) was one of the diffusive flows calculated by the model and decreased in time (under influence of increasing soil oxygen concentrations) from 2.7 μmol cm^{-2} root day^{-1} to 1.8 μmol cm^{-2} root day^{-1}. The combination of root respiration, ROL and oxygen exchange with the atmosphere led within two hours to stable root oxygen concentrations of 2.37 mol m^{-3} gas (5.7% v/v).

Under influence of ROL, oxygen was introduced into an initially anaerobic rhizosphere and an oxygen gradient was established within few minutes. Most of the oxygen was consumed directly (total oxygen consumption, which is treated below, was more than 99% of the ROL), but rhizospheric oxygen consumption never fully equalled ROL. This led to slightly increasing oxygen concentrations in time without obtaining stable gradients (Figure 2). No oxygen was present beyond 3 mm from the root surface.

The introduction of oxygen into the rhizosphere triggered many oxidative processes. Ferric iron concentration increased (Figure 3(a)) and ferrous iron concentration decreased (Figure 3(b)) instantaneously near the root surface, but the maximum ferric iron concentration moved away from the root surface in time. Around one 1 mm from the root surface, the ferric iron accumulated to concentrations that were higher than the initial total iron concentration due to the combined effect of the presence of a precipitate sink and ferrous iron diffusion towards the root. The pH decreased 2 units near the root surface under influence of iron oxidation (Figure 3(c)). Iron reduction had a minor counteracting influence on the pH decrease, because iron reduction rates were on average 25 times lower than iron oxidation rates. Maximum iron reduction rates occurred around 2 mm from the root surface, while the maximum iron oxidation rates occurred at 0.5 mm from the root surface (Figure 4(c)). Neither active (via nutrient uptake) nor passive (via carbon dioxide diffusion) flows of H^+ across the root surface had a big influence on the soil pH: Neglect of both flows caused an additional pH decrease in the soil layer closest to the root of 0.17 unit.

Iron oxidation was the most important oxidative process in the rice rhizosphere and accounted initially for 97% of the consumed oxygen. Iron oxidation rates decreased in time under influence of a decrease in available reduced iron (Figure 3(b), ferrous iron concentration in the soil solution was negligibly small) and accounted for 80% of the oxygen consumption

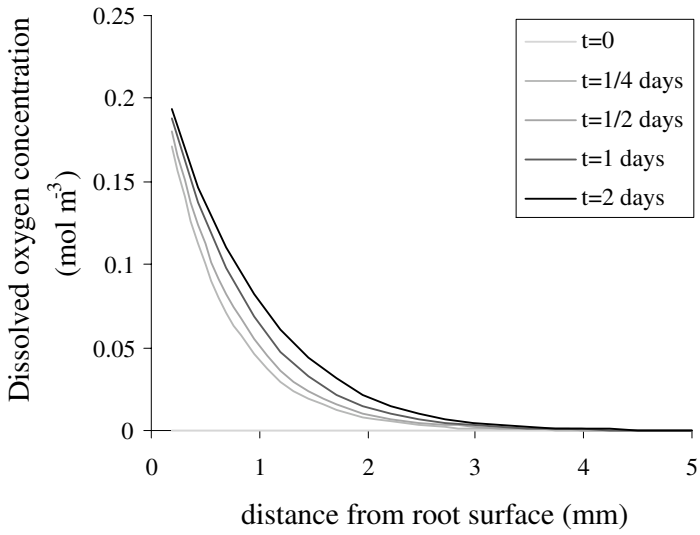


Figure 2. Development of oxygen gradients in a rice rhizosphere after introduction of a rice root at an anaerobic microsite at t = 0.

after two days of root influence. Methanotrophic and heterotrophic respiration increased in time, both relatively and absolutely. Heterotrophs were the stronger competitors for oxygen – accounting for 15% of the consumed oxygen after two days – and had their oxygen consumption maximum at the root surface (Figure 4(b)). Methanotrophs had their oxygen consumption maximum at lower oxygen concentrations around 1.5 mm from the root surface (Figure 4(a)). This is in agreement with results on microbial competition in batch cultures (Van Bodegom et al. unpublished results), results that could be well described by the kinetic description of the model (results not shown).

Microbial competition for oxygen also influenced the carbon profiles in the rhizosphere. Acetate concentrations increased in time (Figure 5(a)); root exudation rates and soil mineralisation rates exceeded acetate consumption, due to oxygen limitations and limited potential anaerobic conversion rates. Even though acetate was released from the root, the highest acetate concentrations occurred near the outer border of the rhizosphere, because aerobic acetate conversions were more effective than anaerobic conversions. Methane

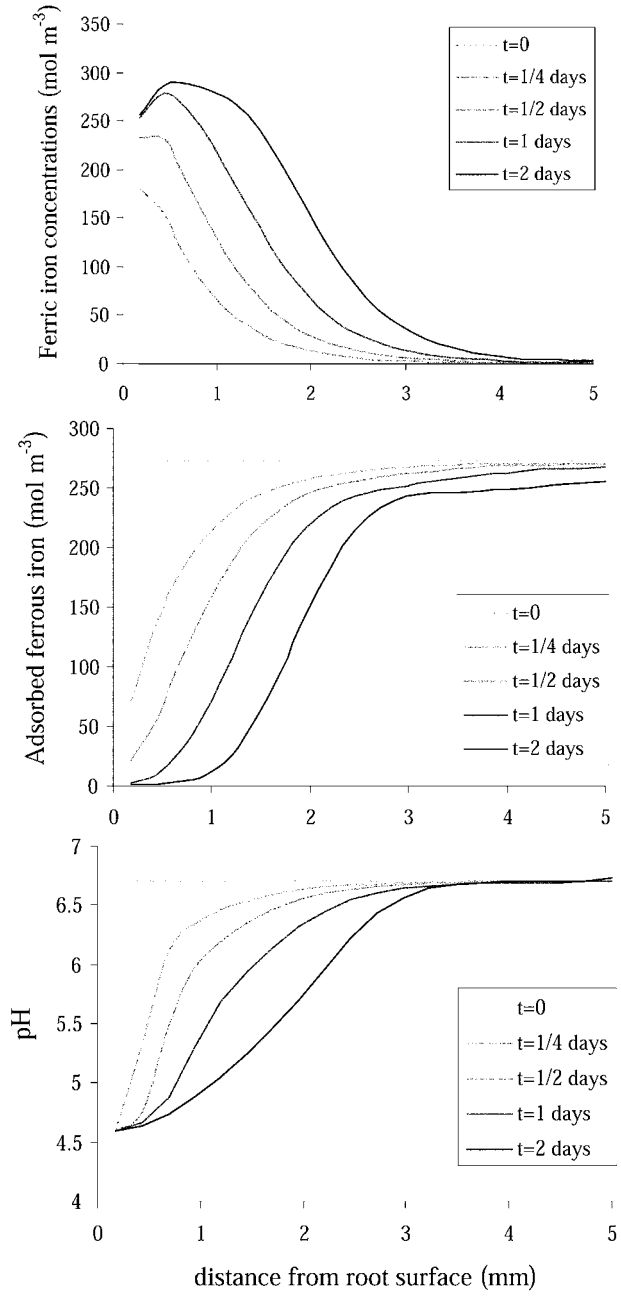


Figure 3. Development of gradients for (a) total ferric iron, (b) adsorbed ferrous iron and (c) pH in a rice rhizosphere after introduction of a rice root at an anaerobic microsite at t = 0.

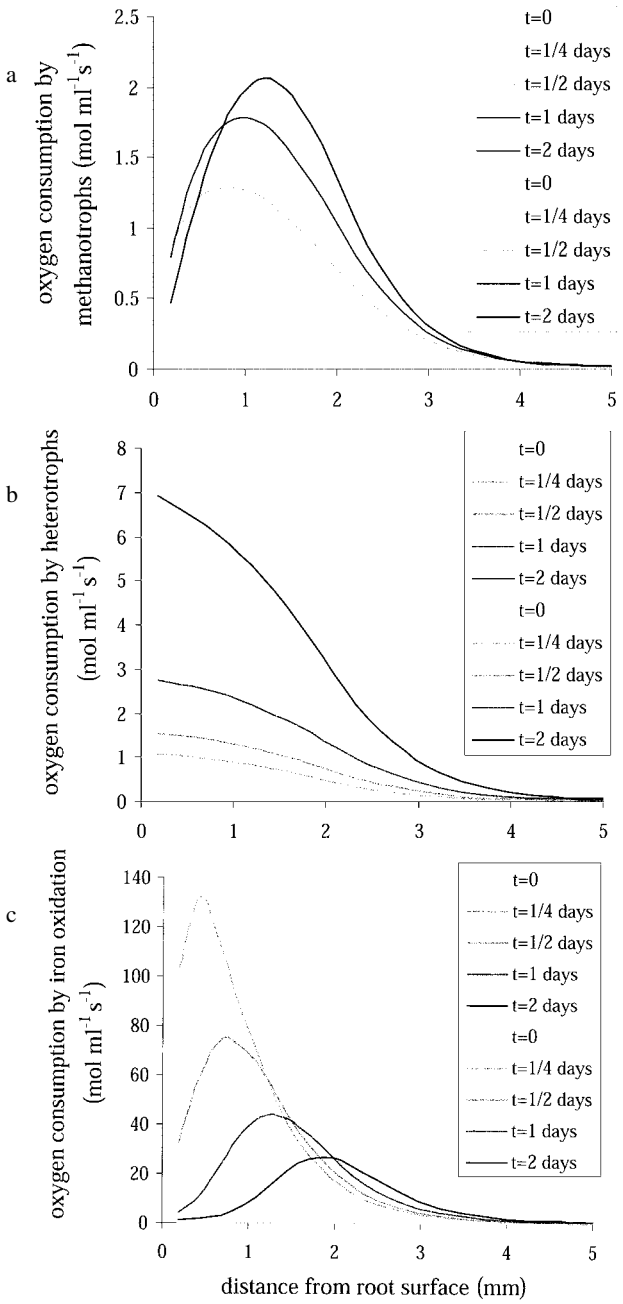


Figure 4. Competition for oxygen: Oxygen consumption rates by (a) methanotrophs, (b) heterotrophs and (c) iron oxidation in a rice rhizosphere after introduction of a rice root at an anaerobic microsite at t = 0.

concentrations decreased after introduction of the root (Figure 5(b)). This was only partly due to oxygen inhibition on methane production – which occurred only in the first 2 mm from the root surface. The main reason for the decrease in methane concentrations was the presence of an escape pathway by the root; methane emissions (Figure 5(c)). Methane oxidation was only a minor sink for methane, accounting for 8.5% of the total methane loss (= oxidation + emission) after two days. A much larger value for methane oxidation – 33% – was calculated if methane oxidation was expressed as a fraction of the actual methane production in the rhizosphere during two days. These two estimates would have been the same if there had been no change in methane storage, because in that case production equals oxidation + emission (giving the same denominator). However, the non-equilibrium conditions in the rhizosphere result in a large change in methane storage during the period that a soil microsite is in contact with a rice root. Due to the change in methane storage, the methane oxidation fraction becomes denominator – either methane production or total methane loss – dependent.

Model sensitivity

Based on the large number of interactions and non-linear relationships of the processes, it can be expected that methane oxidation will be dependent on model parameter estimates (which were calculated as averages from published data) and on model initialisation (taken from average anaerobic conditions). A sensitivity analysis, changing each parameter independently – which is correct because each parameter is independent – was carried out to determine the dependence of the methane oxidation fraction as a fraction of methane lost (Figure 6).

Methane oxidation was mainly limited by oxygen. The sensitivity of methane oxidation on methane production (influenced by C_{org} and $Vmax_{Ac,P}$) and on initial methane concentrations was less than the sensitivity on parameters influencing competition for oxygen. The highest sensitivity was obtained for parameters influencing the competition for oxygen between methanotrophs and iron oxidation. Methanotrophs had a better competitive ability at a higher initial biomass (B_m), higher maximum relative growth rate ($\mu_{max,m}$) and a higher affinity for oxygen (lower $Ks_{O2,m}$) and if iron oxidation proceeded slower, i.e. at a lower k and at lower total iron concentrations ([Fe^{2+}+ Fe^{3+}]). Heterotrophs had much less effect on methane oxidation as shown by the very small sensitivity for B_h and [CH_3COOH]. The sensitivity for root exudation and kinetic parameters of the heterotrophs was even less (results not shown). This can be explained from the smaller competitive ability of heterotrophs compared to iron oxidation. Soil oxygen concentrations were mainly determined by the oxygen consumption processes in the

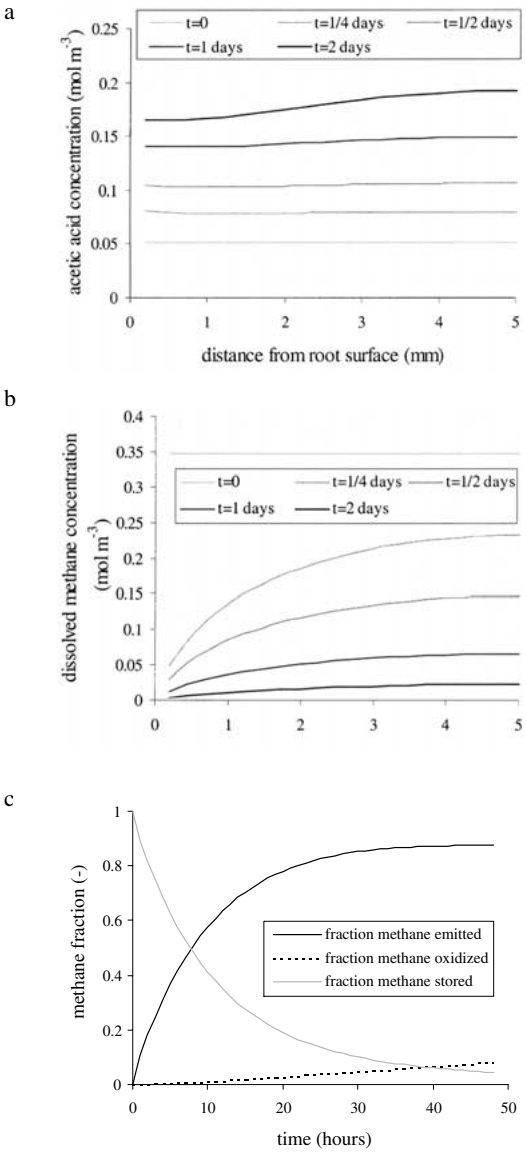


Figure 5. Development of (a) acetate gradients, (b) methane gradients and (c) methane dynamics in the rice rhizosphere after introduction of a rice root at an anaerobic microsite at t = 0.

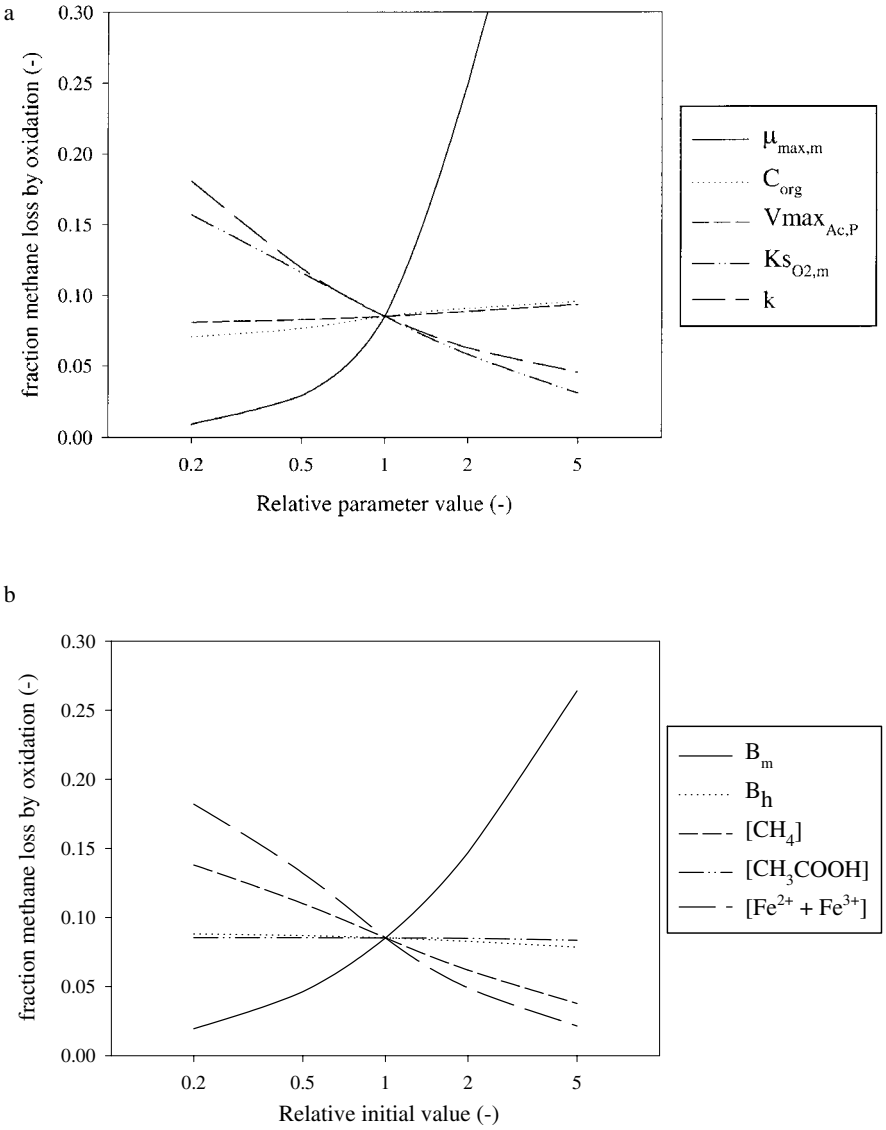


Figure 6. Sensitivity of the model expressed as the fraction of lost methane via methane oxidation affected by (a) model parameter values; maximum methanotrophic specific growth rate $\mu_{max,m}$, soil organic carbon C_{org}, maximum methane production rate on acetate $V_{maxAc,P}$, methanotrophic affinity constant for oxygen $K_{sO2,m}$ and relative iron oxidation rate k and (b) model initialisation; initial methanotrophic biomass B_m, heterotrophic biomass B_h, methane concentration $[CH_4]$, acetic acid concentration$[CH_3COOH]$ and total iron concentration $[Fe^{2+} + Fe^{3+}]$. All values are expressed relative to those of the default settings.

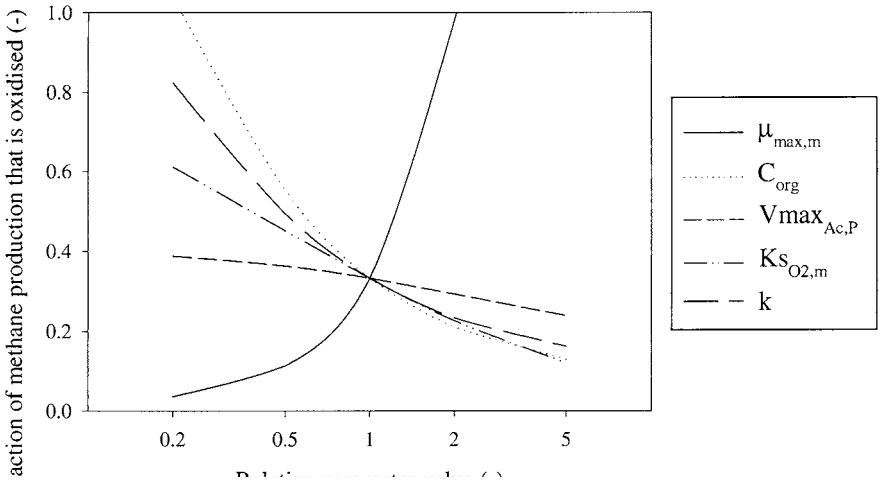
soil. The conductivity of the root-shoot barrier ($\varepsilon_{r,t}$) and root respiration hardly influenced ROL (due to efficient exchange with the atmosphere) and thus hardly influenced methane oxidation (results not shown).

Methane oxidation is usually estimated from a difference in methane emissions with and without addition of specific inhibitors on methane oxidation, and is thus directly related to the methane oxidation fraction presented in Figure 6. However, these estimates are usually related to methane production. This procedure neglects the large changes – also in comparison to methane production rates – in soil methane storage in proximity of a rice root. Because this may have major implications for the interpretation of methane oxidation rates, a sensitivity analysis on methane oxidation as a fraction of methane production was performed (Figure 7).

In general, the sensitivities in Figure 7 were similar to those in Figure 6, with a few exceptions. The sensitivity for C_{org} was much higher; a high C_{org} resulted in high methane production compared to total soil stored methane and led to a seemingly lower efficiency of methane oxidation. A similar reasoning can be followed for $Vmax_{Ac,P}$, which showed a negative relationship with methane oxidation fraction, whereas it had a slightly positive relation in Figure 6. The positive relationship in Figure 6 was caused by the inhibition of a higher $Vmax_{Ac,P}$ on iron recycling, thus increasing the competitive ability of methanotrophs. Also the initial [CH_4] shows a reverse relationship with methane oxidation in Figure 7 compared to Figure 6. A high initial [CH_4] leads to a higher contribution of methane oxidation coming from stored methane. In that case, methane oxidation expressed as a fraction of methane production, neglecting the contribution from changes in stored methane, shows an apparently more efficient conversion of methane production to methane oxidation. In some conditions the methane oxidation fraction increased even above one. Care has to be taken when relating methane oxidation to methane production.

The sensitivity analysis showed that the methane oxidation fraction is highly sensitive and non-linearly influenced by model parameterisation and initialisation, which makes methane oxidation hard to predict. Not only methane oxidation, but also the steady state for oxygen is influenced by the model parameterisation. At default conditions, oxygen amounts in the rice rhizosphere tended to increase in time. Decreasing the transport conductivity across the root-soil interface led however to decreasing oxygen in the rice rhizosphere (Figure 8, initialised with oxygen concentrations above zero to allow comparison). Decreasing oxygen concentrations in the rice rhizosphere have been predicted by Kirk (1993) and might well have been caused by his choice on transport conductivity across the root-soil interface (which value was unfortunately not documented).

a



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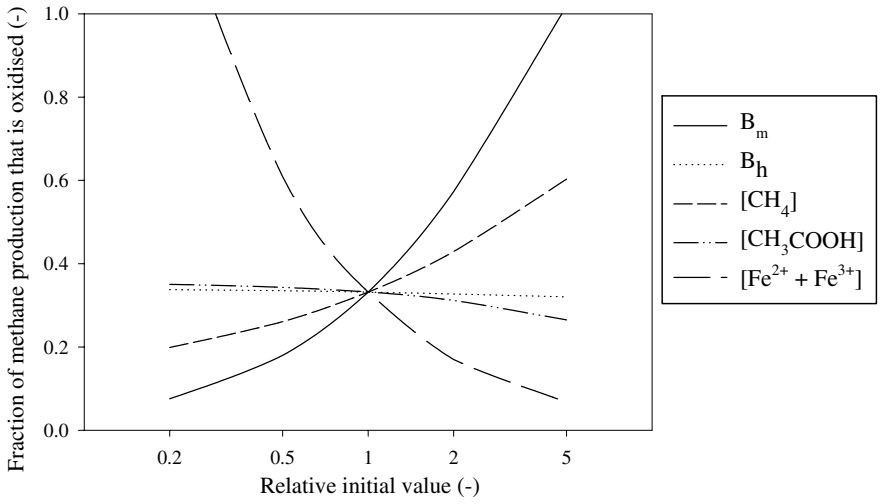

Figure 7. Sensitivity of the model expressed as the fraction of methane production that is oxidised under influence of (a) model parameter values and (b) model initialisation. Parameters are as in Figure 6.

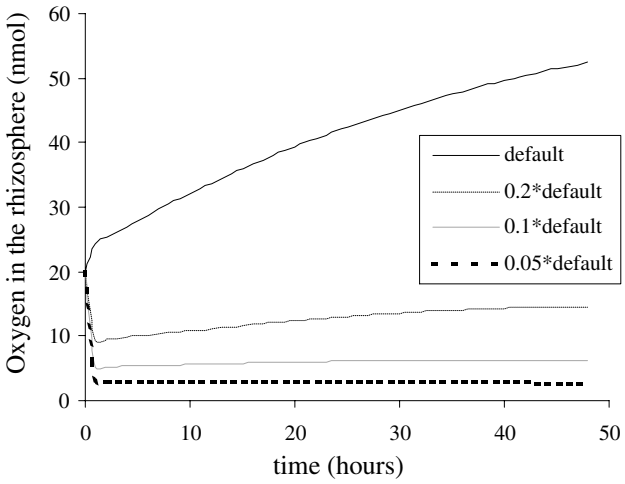

Figure 8. Average oxygen concentrations in the first 3 mm of the rice rhizosphere in time as a function of conductivity over the soil-root interface, relative to its default description.

Discussion

Model limitations

Like all models, the model presented in this paper has several limitations. It is important to understand these limitations to interpret model performance. Microbial aerobic dynamics were limited to one methanotrophic species and one heterotrophic species, whereas many organisms interact in a rice rhizosphere. Arguments for excluding nitrification and sulphur oxidation are given in section 2, but one can still argue that one representative of a microbial group cannot mimic a complete microbial assemblage. The affinity constants were, however, averages taken from published values and were similar to affinity constants found for dominant microorganisms isolated from a rice paddy (Van Bodegom et al. unpublished results). The maximum relative growth rates were also average published values and might thus represent average conditions. Bodelier et al. (2000) showed, however, that methanotrophic activity in rice paddies might be increased significantly by nitrogen fertilisation. Such interactions are not explicitly accounted for by the model and need more research as the sensitivity analysis showed that $\mu_{max,m}$ had a large influence on the fraction of methane oxidised. Many of the para-

meter values for other processes, like iron oxidation, methane production and soil mineralisation, are variable or uncertain. For these parameter values a sensitivity analysis has been carried out and the influence could be quantified, although the variability in parameter values limits the application of the model for prediction purposes.

In addition, methanotrophs (Bosse & Frenzel 1997; Gilbert & Frenzel 1998) and heterotrophs (Watanabe et al. 1979) have also been found at the rice root surface. These are not explicitly accounted for by the model, but the first soil layer is so thin (1/4* root diameter) that it can be assumed that this soil layer represents the root surface as these would be hard to distinguish experimentally. Methanotrophs have also been found inside the rice root (Bosse & Frenzel 1997; Gilbert et al. 1998). The activity of the microorganisms inside the root is not known, however, and the possible contribution of these organisms to total methane oxidation could not be quantified. Their influence will probably be small, given the short residence time of methane within the root.

A more important limitation of the model derives from the use of a homogeneous cylindrical geometry around the active part of a primary root. An alternative spherical geometry around each root tip (of the primary and the laterals roots) would not represent reality either, because such geometry would need the assumption of a full sphere around a tip, while in reality each tip is in exchange with the other parts of the root. Application of a spherical geometry did not lead to different results for the methane oxidation fraction (results not shown), although the gradients within the soil were steeper, because of the faster volume change with distance from the root surface. The reason for the comparable results for different geometries is that the exchange across the root surface and within the root are not the limiting factors for methane oxidation.

A final limitation of the model is that root growth dynamics were not accounted for explicitly. None of the models mentioned in the introduction of the paper include root growth dynamics. This dynamics may be important because of the absence of a steady state within the period over which a root is influencing a certain microsite. The implications of this limitation are therefore explored later on.

Model performance

There are no mechanistic models on methane oxidation in a rhizosphere, except for the model of Segers and Leffelaar (2001), and there are no *in situ* measurements on methane oxidation in the rhizosphere, but model outcomes can be compared with various measurements and model estimates for different parts of the model.

The model was driven by root oxygen loss (ROL) into a rice rhizosphere. Unfortunately, many measurements of ROL expressed ROL per plant or per gram root, which would require additional conversion with additional uncertainty. Those data were therefore excluded from comparison. Armstrong (1969, 1971a) and Colmer et al. (1998) measured in rice 4.2–6.8, 1.9–3.6 and 0.8–1.5 μmol cm^{-2} root day^{-1} , respectively. These measurements are all in the same range as the ROL calculated by the model. Our calculated root respiration of 4.1 μmol cm^{-2} root day^{-1} is similar to 3.0–4.2 measured by Armstrong (1971a) and 2.1–2.5 μmol cm^{-2} root day^{-1} (Armstrong 1971b). The ratio of root respiration and ROL can also be compared with measurements. Ueckert et al. (1990) showed that ROL was increased by a factor 2.6 when root respiration was inhibited, which means that root respiration is 1.6* ROL. In our model we obtain an estimate of 1.52–2.28*ROL. Root respiration had little influence on ROL as was shown in our sensitivity analysis, although root respiration was higher than ROL. This is in accordance with Colmer et al. (1998) who state root respiration rates are not a major factor determining the pattern of ROL along roots. Root oxygen concentrations are the resultant of root respiration, gas exchange with the atmosphere and ROL. Our modelled oxygen concentration of 5.7% v/v is comparable with 2–14% v/v (Raalte 1940) and 0.4–10.4% v/v (Revsbech et al. 1999). Modelled root cortex oxygen concentrations (Armstrong & Beckett 1987) vary between 0–20% v/v depending on root length and diffusion characteristics.

Oxygen release into the anaerobic soil led to oxygen gradients, that extended no further than 3 mm from the root surface. Armstrong (1970) modelled an extent of 2.3–2.9 mm for rice roots and Kirk (1993) modelled a 3 mm extent. Modelled oxygen concentrations varied from 0–190μM with an average of 60μM. These concentrations are comparable to those experimentally found by Frenzel et al. (1992) 10–115 μM, Gilbert and Frenzel (1998) 10–152 μM and Revsbech et al. (1999) 0–96 μM.

The introduction of oxygen triggered iron oxidation, leading to ferrous iron depletion and an accumulation of immobile ferric iron near the root surface, which has also been found by Kirk (1993). Ferric iron accumulated to concentrations higher than the initial values. This is in accordance with measurements of Conlin and Crowder (1989) and Wang and Peverly (1999). Such metal accumulation might either intensify toxicity or might be beneficial for micronutrient uptake. A steep pH gradient of 2 units established near the root surface under influence of acidity produced by iron oxidation, which was not balanced by acid consumption by iron reduction, similar to what was modelled by Kirk (1993). Measurements indicate variable gradients of 1–2.5 units (Begg et al. 1994), 0.6 units (Gilbert & Frenzel 1998) and 0.2 units (Revsbech et al. 1999).

Methanotrophs and heterotrophs have to compete for oxygen with iron oxidation, the process dominating oxygen consumption. Reddy et al. (1980) also found that at first oxygen consumption is dominated by iron oxidation and that only thereafter other oxidation reactions occur. Howeler and Bouldin (1971) found a somewhat lower contribution of iron oxidation, 50%, to total oxygen consumption in swamp soils. Swamp soils are however in general much richer in organic carbon than are rice paddy soils. A higher contribution of heterotrophic respiration can therefore by expected for swamp soils. Watson et al. (1997) neglected iron oxidation and calculated that 89–94.2% of the oxygen was consumed via heterotrophic respiration in peat soils. If we also neglect iron oxidation, we find that 75% of the oxygen is consumed by heterotrophic respiration in rice paddies.

Oxygen consumption by methanotrophs in combination with methane release to the atmosphere and methane production led to changes in methane gradients. Methane production was only inhibited in the first 1.5 mm from the root surface in the rice rhizosphere. In the remaining aerobic rhizosphere, the oxygen concentration was below $1/Ki,O_{2p}$ and methane production was almost equal to methane production under anaerobic conditions. This is again similar to experimentally determined methane production rates (Van Bodegom & Scholten 2001). The methane gradient in the rhizosphere was mainly determined by methane release to the atmosphere and was highly similar to the gradients measured by Gilbert and Frenzel (1998). In the rice root, methane concentrations were, with 140 ppm, much higher than background atmospheric concentrations. The authors are not aware of rhizospheric acetate data to compare the model estimates with. This is a pity, because other models on rhizospheric organic carbon predict similar (Jones et al. 1996), slightly higher (Newman & Watson 1977) or much higher (Darrah 1991a, b) carbon concentrations and all show decreasing organic carbon concentrations with distance from the root. This different trend from our model (Figure 5(a)) is explained by the fact that all other models were developed for aerobic systems, which do not have a large change in consumption efficiency with distance from the root surface.

Given the proper model performance on the individual processes, the model can be used to calculate methane oxidation rates and compare those values with measured values of methane oxidation. However, such a comparison may be difficult, because of the many different methods used to measure methane oxidation. Even methane oxidation estimates with specific inhibitors, which yield the most accurate estimates of methane oxidation, vary from 4% (Denier van der Gon & Neue 1996) to 52% (Epp & Chanton 1993). Bodelier et al. (2000) recently showed that methane oxidation is highly dependent on nitrogen fertilisation. The sensitivity analysis of the model

showed that high variabilities are probably not experimental artefacts, but reality. Methanotrophic biomass estimates in the rice rhizosphere can differ more than an order of magnitude, deviations in various published estimates of the maximum specific growth rates of the methanotrophs ($\mu_{max,m}$) and the methanotrophic constant for oxygen ($Ks_{O2,m}$) are more than 50% and methane concentrations in rice paddies have a spatial variability of more than 300% (Rothfuss & Conrad 1998). In addition, reducible iron concentrations vary considerably between different soils. Such differences in environmental conditions change modelled methane oxidation fractions by more than 250% as shown by the sensitivity analysis, even though only one parameter was changed at a time. A sensitivity analysis carried out by Segers (2000) also showed that methane oxidation fractions could vary between 0–100%.

On average, the model predicts a methane oxidation of 8.5% of the total loss of methane and 33% if expressed as a fraction of methane production. This is much smaller than the model estimates of Watson et al. (1997). A direct comparison with measured values is difficult, because the calculated methane oxidation fraction depends on the definition, i.e. whether methane oxidation is expressed per methane loss or as a fraction of methane production (compare Figures 6 and 7). The difference between these two definitions is usually not distinguished. This is not correct given the large change in methane storage due to methane released to the atmosphere. The asynchronisation of methane production and methane oxidation causes the definitions to represent highly different situations. Without correction for changes in methane storage, the calculated methane oxidation fraction marks an upper boundary (33% in the default simulation), representing a situation in which the losses of methane in the rhizosphere are quickly refilled by methane produced in the surrounding anaerobic soil. Such situations may occur in soils with low root length densities. In such situations, a diffusive flow instead of an equilibrium should be considered across the outer boundary of the rhizosphere. Such a diffusive flow did not change the value of the simulated methane oxidation fraction (results not shown). On the other hand, methane oxidation as a fraction of total methane loss (8.5%) represents a lower boundary for methane oxidation and is only representative for a rice plant if changes in methane storage are important and the distance between primary roots is equal or closer than 10 mm everywhere in the soil. Depending on the root length density the overall average for rhizospheric methane oxidation calculated by the model is thus 8.5–33%. That is similar to the range obtained by the use of specific inhibitors.

The model showed two important things: (i) The fraction of methane that is oxidised is highly dependent on model initialisation and other variable parameters. (ii) There is no steady state within the period that a single root influences a soil microsite, because the growing root passes too quickly. As soon as a root tip reaches an anaerobic microsite, oxygen concentrations increase according to the default simulation, because the consumption of oxygen by iron oxidation and microbial respiration is always smaller than ROL. However, after two days the system is not even close to the equilibrium of a fully aerobic rhizosphere (Figure 8). Moreover, this is not the only equilibrium that can be obtained. Results with decreased conductivity across the root-soil interface show that also a completely anaerobic rhizosphere is possible as an equilibrium (Figure 8).

It takes weeks to obtain either equilibrium (results not shown). Under influence of root growth, the positions of exudate and oxygen release change however continuously in time. After an oxygen releasing period, the microsite becomes anaerobic within a few hours (results not shown), because root growth rates are with 1–2 cm day^{-1} much higher than the few mm diffusion per day in water. Aerobic conditions develop again when a new root arrives at the microsite. The length of the period in between depends on the root length density and upon the spatial root distribution. Unfortunately, quantitative information on root dynamics is scarce, hampering predictive spatial modelling of oxygen consumption and methane oxidation. The qualitative data show at least that a steady state is not obtained during the oxygen releasing period. The rice rhizosphere is a dynamic, transient environment.

Methane oxidation is, among others, highly influenced by the initial microbial biomass, and especially by methanotrophic biomass. According to the model, methanotrophic biomass can increase from background numbers belonging to anaerobic conditions to maximally 8 times its initial value within two days if optimal conditions are present (heterotrophic biomass increased maximally by 400% at optimal conditions). Also experimentally, methanotrophic numbers in the rhizosphere have been found to be up to 100 times higher than in the bulk soil (Gilbert & Frenzel 1998; Kumaraswamy et al. 1997). Given this rapid growth and the temporal dynamics in a rice rhizosphere, it seems that the methanotrophic biomass is mainly determined by the extent to which methanotrophs are able to survive anaerobic periods and to which methanotrophs are affected by grazing. There is not much information available on this subject, although it seems that methanotrophs can survive anaerobic conditions for long periods (Roslev & King 1994, 1995). Methanotrophic biomass and methane oxidation is thus highly dynamic and will depend on the history of the microsite. A better prediction of methane

oxidation will be possible if more quantitative information on grazing, adaptation and survival capacities of methanotrophs and heterotrophs becomes available.

In time, not only microbial biomass may change, but also the concentrations of acetate, methane and ferrous iron will change. The turnover time for root exudates is less than 1/4 day (Jones & Darrah 1994). Consumption is larger than the production of carbon substrates and ferrous iron. Depending on root growth dynamics and root length densities, the carbon substrates or ferrous iron may thus become limiting, influencing the methane oxidation fraction (as shown in Figures 6(b) and 7(b)). Moreover, the effects described above will depend on whether a root tip or lateral roots are considered. Methane oxidation will thus be highly variable, both spatially and temporarily and will depend on the history of the microsite.

Conclusions

This paper presents a complex integrative mechanistic model on the processes leading to methane oxidation in rice rhizosphere. Modelled predictions on processes, among others root oxygen release, and modelled compound distributions were similar to distributions found experimentally. The introduction of a growing root into a reduced soil microsite leads to a fast increase in oxygen concentrations near the root, accumulation of ferrous iron, pH decrease and depletion of acetate and methane near the root surface. Estimates of methane oxidation depend on the definition used. Methane oxidation as a fraction of methane production (33%) neglects changes in methane storage and should only be applied in soil with low root densities. Methane oxidation as a fraction of total methane loss, which is a more appropriate measure in soils with high root length densities, gave a much lower estimate (8.5%). This range in estimates was similar to experimental estimates. Methane oxidation moreover depends on model initialisation and parameterisation and is especially sensitive to parameters influencing the competition between methanotrophs and iron oxidation. Other processes, e.g. methane production or heterotrophic respiration, have much less influence. This, and the absence of a steady state, makes methane oxidation dependent on the history of the soil microsite and on root growth dynamics. The resulting spatial and temporal variability and the uncertainties in rhizosphere dynamics hamper the application of the increased understanding obtained by the model for predictive purposes.

Acknowledgements

We thank Fons Stams for useful comments. The research was supported financially by the Dutch National Research Program on Global Air Pollution and Climate Change.

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