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Non-microbial methane formation in oxic soils

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BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Methane plays an important role as a radiatively and chemically active gas in our atmosphere. Until recently, sources of atmospheric methane in the biosphere have been attributed to strictly anaerobic microbial processes during degradation of organic matter. However, a large fraction of methane produced in the anoxic soil layers does not reach the atmosphere due to methanotrophic consumption in the overlying oxic soil. Although methane fluxes from aerobic soils have been observed an alternative source other than methanogenesis has not been identified thus far.

Here we provide evidence for non-microbial methane formation in soils under oxic conditions. We found that soils release methane upon heating and other environmental factors like ultraviolet irradiation, and drying-rewetting cycles. We suggest that chemical formation of methane during degradation of soil organic matter may represent the missing soil source that is needed to fully understand the complete methane cycle within the pedosphere. Although the emission fluxes are relatively low when compared to those from wetlands, they may be important in warm and wet regions subjected to ultraviolet radiation. We suggest that this methane source is highly sensitive to global change.

1 Introduction

Traditionally, biogenic methane (CH_4) was thought to be formed only by methanogens under strictly anaerobic conditions in wetland soils and rice paddies, intestinal tracts of termites and ruminants, human and agricultural waste. However, Keppler et al. (2006) demonstrated that plants produce CH_4 under aerobic conditions. Subsequently, this possibility has been critically debated (Dueck et al., 2007; Ferretti et al., 2007; Kirschbaum et al., 2007; Keppler and Röckmann, 2007; Vigano et al., 2008; Wang et al., 2008; Nisbet et al., 2009; Keppler et al., 2009; Beerling et al., 2008) and some researchers have suggested alternative explanations for the observed release of CH_4

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



from plants. Nevertheless, (Nisbet et al., 2009; Kirschbaum and Walcroft, 2008; Terazawa et al., 2007). recent observations have provided unambiguous evidence for several pathways by which CH₄ is generated under aerobic conditions, independent of microbial activity (Wang et al., 2008; Keppler et al., 2008; McLeod et al., 2008; Cao et al., 2008; Bruhn et al., 2009; Messenger et al., 2009; Brüggemann et al., 2009; Qaderi and Reid, 2009; Althoff et al., 2010). Although details of the mechanism(s) are still unknown, methoxy groups of plant pectin have been identified in several studies as a precursor compound of aerobic CH₄ emission from detached plant (Vigano et al., 2008; Keppler et al., 2008; McLeod et al., 2008; Bruhn et al., 2009). Furthermore, temperature and UV-light have been confirmed as environmental factors that control CH₄ emission from dried plant matter (Vigano et al., 2008; Keppler et al., 2008).

1.1 Previous observations of methane formation in aerobic soils

Whilst aerobic soils are considered to be net CH₄ sinks due to methanotrophic oxidation of CH₄ it has been shown that oxic upland forest soils produce CH₄. Although observations of CH₄ production in oxic soil are numerous (Megonigal and Guenther, 2008; Hao et al., 1988; Andersen et al., 1998; von Fischer and Hedin, 2007), all have been attributed to methanogenesis. Methane production by oxic eubacteria (Rimbault et al., 1988) and anaerobic microsites, a refuge for methanogens (Peters and Conrad, 1995), were offered as possible explanations even though CH₄ production from eubacteria could only be detected in trace quantities. In experiments by Kammann et al. (2009) soil cores emitted up to 6 µg CH₄ per core even after homogenization, which may be expected to lead to the destruction of anoxic microsites. Von Fisher and Hedin (2007) using stable carbon isotope studies showed that our understanding of CH₄ formation in oxic soils is incomplete and discussed that methanogens as the sole source for CH₄ in oxic soils should be critically reviewed.

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1.2 Possibility of non-microbial methane formation in soil

In this study we tested the previously postulated hypothesis that non-microbial CH₄ formation occurs in soils (Jugold and Keppler, 2009; Hurkuck et al., 2012). Following preliminary observations, we undertook a series of experiments measuring CH₄ formation from soils (see Table 1 and methods section) as a function of temperature, water content and UV-B irradiation. We used five different soils, including one highly organic soil (referred to as peat, Table 1), which had been lyophilised and homogenized prior to the experiments. Humic acid and lignin were used as alternatives for soil organic matter. Additionally, sub-samples of peat and lignin, sterilised using gamma radiation or autoclaving, were also used in our investigations.

2 Materials and methods

2.1 Origin of samples and preparation

Four soils and one peat type were used. If present, stones and larger wood particles were removed from the samples before they were lyophilised and then milled using an electronic coffee grinder (Elta UM105).

Soil SL was sampled at the Lerchenberg forest south of Mainz, Germany (49° 57' 47" N, 8° 11' 01" E). The sampling site is a deciduous forest dominated by beech trees (*Fagus sylvatica*), featuring few oaks and nearly no undergrowth. The sample was collected from the surface after brushing away the layer of leaf litter.

For soil SG the upper 10 cm of a pine forest soil was sampled at Mainz-Gonsenheim, Germany (50° 0' 24.4" N, 8° 11' 50.3" E). The soil in this area is rich in medium to coarse sand and powdery clay particles. It also contains rotting wood debris, pine twigs and is densely rooted.

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Soil SHA was topsoil of a *terra fusca* sampled at the “Nationalpark Hainich”, Germany (51° 04' 46" N, 10° 27' 08" E). The sampling site is a deciduous forest dominated by beech trees.

Soil SW was collected from the organic rich O-horizon of a deciduous forest soil. The vegetation is dominated by beech trees. The sampling site is situated south of Minden, Germany (52° 15' 17.4" N, 8° 52' 29.5" E).

Peat PH was sampled at the peat bog “Großes Torfmoor” near Hille, Germany (52° 19' 23.7" N, 8° 42' 34.7" E). The top 10 cm of *sphagnum* peat was collected as a bulk sample. A subsample was sterilised using gamma irradiation.

2.2 Reaction vials

Samples were incubated in glass vials (360 ml); made in-house by modification of a 300 ml Erlenmeyer-flask (Duran group) fitted with the neck of a 40 ml screw top vial (Supelco) sealed with a hole type screw cap (Supelco) containing a PTFE/silicone septum (Supelco). The UV reaction chambers were also custom built; 200 ml glass chambers with a quartz glass lid and a septa sealed side port for headspace sampling. The irradiated surface was 19.63 cm².

2.3 Determination of organic carbon

Organic carbon content of the samples was determined with a SC Analyser (SC-144 DR, LECO) by combustion of 0.1–0.5 g of sample material at 1300 °C. The carbon content was calculated by comparison to a calcium carbonate standard. For soil SW the organic carbon content was determined by loss on ignition. Therefore the weight loss after two hours at 600 °C was determined. Half of the loss was assigned to carbon combustion.

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.4 Methane measurements

Headspace above samples in the sealed vials were sampled (5 ml) with a Hamilton gas syringe and analysed using a gas chromatograph (Shimadzu GC-14B) with flame ionization detector (GC-FID). Two reference CH₄ standards (containing 8.905 ppm and 1.736 ppm) were used.

2.5 Statistical methods

The statistical comparison of different samples was examined with the open-source software “The R Project for Statistical Computing”, version 2.11.1 (The R Foundation for Statistical Computing).

2.6 Experimental setups

2.6.1 Temperature dependence

Sets of non-sterile and sterile peat samples (PH, 5 g per 360 ml screw cap vial, $n = 5$) as well as non-sterile sets of each soil sample were incubated for 24 h at temperatures ranging from 30 to 90 °C at 10 °C intervals. At the end of the incubation period a sample of the vial headspace was analysed for CH₄ content.

2.6.2 Drying-rewetting cycles

Peat PH (5 g in 360 ml screw cap vials, $n = 5$) was incubated for 24 h at either 30, 40 or 50 °C. Another set of samples was incubated under the same conditions but supplemented with 5 ml doubly distilled water. After incubation a sample of the headspace was analysed for CH₄ content. The samples were frozen and lyophilised again directly after measurements. After being rewetted and incubated again, headspace samples were analysed again for CH₄. This cycle was repeated five times.

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In a further experiment dependence of CH₄ release on the water-sample-ratio was investigated. For this samples of peat PH (5 g in 360 ml screw cap vials, n=5) were supplemented with 1, 5 and 10 ml doubly distilled water.

2.6.3 Experiments with H₂O₂

5 Samples PH or SHA (5 g in 360 ml vials, $n = 3$) and 10 ml aqueous solution with varying concentrations of H₂O₂ (0–25 mM) were added and vials immediately sealed. The samples were incubated for 24 h at 30 °C, after which a sample of the vial headspace was analysed for CH₄ content. The experiment was also repeated for lignin and humic acid with 25 mM H₂O₂.

10 2.6.4 UV irradiation experiments

An Osram Ultra-Vitalux lamp (300 W) served as UV source. The radiation of this lamp shows an UV-A/UV-B content comparable to solar radiation when the source is located at the appropriate distance. The total unweighted UV-B radiation was determined with a UV radiometer (UVlog, sglux, Berlin, Germany) precalibrated for the used lamp type.

15 For more details of the lamp characteristics we refer to Vigano et al. (2008). The UV lamp was placed above the leak tight UV reaction chambers. The height was adjusted so as to set the UV-B intensities to the desired value between 1 and 4 W m⁻². To exclude undesired UV-C radiation the quartz glass lids were covered with a 95 nm film of cellulose diacetate. Two fans were employed in order to keep the temperatures in the chambers at 30 °C (±2 °C). Temperature was monitored with a thermocouple. All
20 experiments were conducted with 2–5 g of sample material but the data is presented based on irradiated area rather than sample weight. Methane concentrations in the headspace were measured after 0, 24 and 48 h. The difference between 0 and 24 h was used to calculate emission rates.

25 The emissions induced solely by UV-B were calculated by subtracting the CH₄ concentration measured for the control samples from that measured for the UV irradiated

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



samples so as to eliminate the temperature effect. The temperature monitored in the vials during UV experiments ranged from 28 to 32 °C. The control samples, which were also placed under the UV lamp, but covered with UV-opaque glass, showed emissions (transferred to $\text{ng g}^{-1} (\text{dw}) \text{h}^{-1}$) comparable to those observed for the temperature experiments which were incubated in the dark at similar temperatures.

2.6.5 Isotopic data

$\delta^{13}\text{C}$ sample analysis was carried out using gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) which consisted of a cryogenic pre-concentration unit directly coupled to an HP 6890N gas chromatograph (Agilent, Santa Clara, USA), which was connected to a Delta^{PLUS}XL isotope ratio mass spectrometer (ThermoQuest Finnigan, Bremen, Germany) via an oxidation reactor [ceramic tube (Al_2O_3), length 320 mm, 0.5 mm i.d., with oxygen activated Cu/Ni/Pt wires inside, reactor temperature 960 °C] and a GC Combustion III Interface (ThermoQuest Finnigan, Bremen, Germany). The gas chromatograph (GC) was fitted with a GS-Carbonplot capillary column (30 m × 0.32 mm i.d., d_f 1.5 μm ; Agilent, Santa Clara, USA) and a PorraPlot capillary column (25 m × 0.25 mm i.d., d_f 8 μm ; Varian, Lake Forest, USA). Both columns were coupled using a press fit connector.

A tank of high purity carbon dioxide (carbon dioxide 4.5, Messer Griesheim, Frankfurt, Germany) with a known $\delta^{13}\text{C}$ value of -23.6‰ (VPDB) was used as the working reference gas. All $\delta^{13}\text{C}$ values obtained from analysis of methane were corrected using three CH_4 working standards (isometric instruments, Victoria, Canada) calibrated against IAEA and NIST reference substances. The calibrated $\delta^{13}\text{C}$ values of the three working standards in ‰ vs. V-PDB were $-23.9 \pm 0.2\text{‰}$, $-38.3 \pm 0.2\text{‰}$ and $-54.5 \pm 0.2\text{‰}$.

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



All $^{13}\text{C}/^{12}\text{C}$ -isotope ratios are expressed in the conventional δ notation in per mil versus V-PDB, defined as (Eq. 1):

$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \right) - 1 \quad (1)$$

3 Results

3.1 Temperature dependence

The first experiment was designed to determine the temperature dependence and the required activation energy of CH_4 formation in a deciduous forest soil (SL), a coniferous forest soil (SG) and a sphagnum peat sample (PH). Samples were incubated at temperatures ranging from 30 to 90°C. Methane emissions reached $7.11 \pm 0.59 \text{ ng g}^{-1} (\text{dw}) \text{ h}^{-1}$, $1.19 \pm 0.15 \text{ ng g}^{-1} (\text{dw}) \text{ h}^{-1}$ and $1.12 \pm 0.16 \text{ ng g}^{-1} (\text{dw}) \text{ h}^{-1}$ at 90°C for PH, SG and SL, respectively (Fig. 1). Whereas CH_4 release could be observed for PH and SL at 30°C and 40°C respectively (Table 1), CH_4 release from SG was only measurable above 50°C. Soil SHA which had a similar organic carbon content to soils SL and SG (Table 1) was also investigated and CH_4 emissions of $0.45 \pm 0.02 \text{ ng g}^{-1} (\text{dw}) \text{ h}^{-1}$ at 70°C were observed. For all samples the temperature curves showed an exponential increase of CH_4 emissions with temperature. Interestingly, the results found for the soil and peat samples (Fig. 1) showed a similar pattern to those reported by Keppler et al. (2006) and Vigano et al. (2008) for heated plant matter. Whereas biotically mediated reactions usually have their optimum temperatures between 25 and 40°C (Dunfield et al., 1993) the observed strong increase in CH_4 emissions over the whole temperature range from 30 to 90°C supports a chemically driven process. Furthermore, sterile peat samples (exposed to γ -radiation) showed similar or slightly higher emissions of CH_4 when compared to untreated peat samples. The fact that the emissions were not reduced in the sterile sample is further evidence for a non-microbial pathway. The slightly higher emissions observed for some of the

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sterile samples may possibly be ascribed to CH₄ production during the sterilisation process.

Since humic substances are usually the main constituents of organic-rich soils commercially available lignin and humic acid were investigated for CH₄ release.

5 These substances, with an organic carbon content of 49.5% and 43.5% respectively, when similarly heated up to 90 °C showed even higher CH₄ emissions (at 30 °C 0.1 ± 0.01 ngg⁻¹ (dw)h⁻¹ for lignin and at 90 °C 18.3 ± 0.4 and 6.6 ± 0.9 ngg⁻¹ (dw)h⁻¹ for lignin and humic acid, respectively) than the organic rich soil PH. The similar dependence of CH₄ formation in soils and organic soil components on temperature strongly suggests that the organic soil fraction is the source of CH₄ thermally produced in soils.

10 The experimental data obtained from samples SL, SG and PH were used to draw Arrhenius plots for CH₄ formation (Supplement Fig. S1). The activation energies (E_a) for CH₄ formation, calculated from these plots, yielded values of 50.1 kJ mol⁻¹ for SL, 77.5 kJ mol⁻¹ for SG and 79.2 kJ mol⁻¹ for PH. These activation energies, being higher than 50 kJ mol⁻¹, provide supportive evidence of an abiotic process (Schönknecht et al., 2008). Since adsorption/desorption processes of CH₄ can occur with organic materials, it was considered that in this instance desorption might explain the observed emissions upon heating of the soil samples. Therefore, a series of experiments were performed to test such a possibility. From these it was found that a desorption process did not give rise to significant CH₄ fluxes from any of the soil samples employed in this study except when exceptionally high levels of CH₄ were added (12 500 ppm, see Supplement). These results are in accordance with the findings of Kirschbaum and Walcroft (2008) who reported no significant desorption of CH₄ from plant matter and concluded that desorption is not a quantitatively important artefact contributing to observed aerobic CH₄ fluxes in dry plant leaves.

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.2 Effect of wetting and drying

Many surface soils and sediments are frequently subjected to changing precipitation and evaporation conditions and as a consequence undergo changes in water content. In extreme cases these conditions range from droughts to flooding events, including anthropogenic influences on the water budget like damming rivers or drainages for land reclamation. It is therefore important to study the effect of sample water content on the release of CH₄. This was investigated in an experiment where soil samples were exposed to repeated cycles of wetting and drying. The sample PH emitted up to five times more CH₄ after addition of water, compared to the dried sample when incubated at the same temperature (Fig. 2). Interestingly, this increase appeared to be independent of the amount of water added, when the water content of the sample was in the range of 17 to 67%. In a succession of five wetting-drying cycles no decline in CH₄ release rate was observed. A highly significant rise in emissions was noted with increasing temperature ($p < 0.001$). Emissions from dry samples doubled when the temperature was increased from 30 to 50 °C and a similarly strong effect was also observed for the wetted samples at these temperatures.

To rule out the influence of CH₄ consuming bacteria on our findings, a selection of measurements was repeated after addition of difluoromethane (DFM) (Miller et al., 1998) as described in the supplementary section. No differences were observed between samples with and without added DFM. Considerable CH₄ emissions could also be detected after wetting samples of lignin and humic acid, where, respectively, 1.9 ± 0.2 and $3.1 \pm 0.3 \text{ ng g}^{-1} (\text{dw}) \text{ h}^{-1}$ were released (Table 1).

3.3 Effect of hydrogen peroxide

Reactive oxygen species (ROS) such as hydroxyl radicals (HO[•]) have been suggested to play an important role in the release of CH₄ from pectin and might be the driving force in the CH₄ release during UV radiation of plant foliage (McLeod et al., 2008; Messenger et al., 2009). Hydrogen peroxide (H₂O₂) as a precursor of HO[•] is an important reactant

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



in many degradation processes in soils, being abundant due to its release by roots, soil bacteria and white rot fungi (Frahry and Schopfer, 1998; Kersten and Kirk, 1987). We therefore investigated the influence of H₂O₂ on CH₄ emissions from peat PH and soil SHA.

5 Interestingly, it was found that peat and soil responded rather differently following addition of H₂O₂. A strong increase in CH₄ emissions and a linear relationship ($R^2 = 0.99$) with increasing amounts of added H₂O₂ to sample PH (Fig. 3) was observed whereas for soil sample SHA no additional emissions were observed. It is not clear why the soil and peat samples behaved so differently to the addition of H₂O₂. One possible
10 explanation might be related to the differences in the composition of soil SHA and peat PH. Peat consists mostly of organic matter and low mineral content which might make it more prone to be attacked by ROS. Soil, on the other hand, contains other major components such as clay minerals and metal oxides that might more efficiently interact with H₂O₂.

15 Samples of lignin and humic acid were also treated with H₂O₂. Whereas increased CH₄ emissions were observed for humic acid, no elevated emissions were found for lignin. Thus it is evident that the structural composition of the organic matter in soil has a major impact on the CH₄ emissions.

3.4 Effect of ultraviolet radiation

20 Ultraviolet (UV) radiation has been shown to be an important factor for aerobic production of CH₄ from plant tissues and pectin. It was demonstrated that both UV-A (320–400 nm) and UV-B (280–320 nm) induce CH₄ emissions from plant tissue (Vigano et al., 2008; McLeod et al., 2008), with UV-B radiation showing a much stronger effect. Nevertheless, because average UV-A intensities are around 30-fold higher than UV-B values, UV-A is also an important component on a global level for UV induced CH₄ emissions
25 (Bruhn et al., 2009). Thus, the effect of UV radiation on the formation of CH₄ from soil was evaluated. For most experiments we used a total UV-B irradiance of 2 W m⁻²,

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



typical for mid-latitudes at the surface. In the tropics, where the UV-filtering ozone layer is thinner, ambient UV-B irradiances are about 3.7 W m^{-2} (Bernhard et al., 1997).

Measurements at 2 W m^{-2} UV-B and temperatures of 28 to 32°C showed emissions of 0.25 to $4.92 \mu\text{g m}^{-2} \text{ h}^{-1}$ (Table 1), which were linear over two a day period. Methane emission rates were also found to be a function of UV-B intensity. With increasing intensities from 1 to 4 W m^{-2} CH_4 emissions from soil SL increased linearly from 1.33 ± 0.22 to $7.28 \pm 2.75 \mu\text{g m}^{-2} \text{ h}^{-1}$. Emissions from soil SG increased from 0.56 ± 0.12 to $2.75 \pm 0.69 \mu\text{g m}^{-2} \text{ h}^{-1}$ over the same intensity range (Fig. 4).

The combined emission rates under the influence of UV and temperature are similar to those reported for plant foliage (Vigano et al., 2008; Keppler et al., 2008). Interestingly, variations in CH_4 emissions under UV are not correlated to soil organic content (Table 1). However, the emission rates might be influenced by organic photo sensitizers, which have been shown to have a positive effect on CH_4 emissions from pectin (Messenger et al., 2009), or by clay minerals, often described as photo-catalysts (Katagi, 1990; Wu et al., 2008; Kibanova et al., 2011)

3.5 Stable carbon isotope composition of methane emitted from soil

In addition to CH_4 emission rates, the stable isotope composition ($\delta^{13}\text{C}$ values) of the released CH_4 from soil SHA, peat PH, humic acid and lignin were also measured. Heating experiments showed $\delta^{13}\text{C}$ values of -56 to -65% for lignin, -51 to -56% for PH and -42 to -52% for humic acid. Methane emitted from wet samples of lignin, humic acid and peat PH showed $\delta^{13}\text{C}$ values ranging from -53 to -69% with humic acid again being the substrate with the highest (less negative) CH_4 values ($-53.2\% \pm 0.3\%$). The $\delta^{13}\text{C}$ values measured for CH_4 emitted from humic acid and peat PH over a 24 h period following the addition of H_2O_2 were $-54.9 \pm 1.2\%$ and $-60.2 \pm 4.5\%$, respectively.

The $\delta^{13}\text{C}$ values measured for CH_4 emitted during 48h under UV irradiation were $-56.0 \pm 6.0\%$ for lignin, $-63 \pm 3.3\%$ for SHA, $-44.2 \pm 1.4\%$ for PH and $-35.3 \pm 9.4\%$.

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



for humic acid. In summary, the $\delta^{13}\text{C}$ values of CH_4 emitted from soil differed between substrates and experimental conditions and ranged from -35.5 to 69‰ whereas the $\delta^{13}\text{C}$ values for the organic matter of the bulk soil samples were in the range of -22 to -29‰ . Thus, it appears that all treatments caused substantial fractionation between the precursor carbon and emitted CH_4 . Similar $\delta^{13}\text{C}$ values and isotope fractionations have been reported for CH_4 emitted from plant foliage due to UV radiation or upon heating (Vigano et al., 2009). Both the isotopic values reported for the chemical formation of CH_4 from soil and vegetation are commonly also found for terrestrial biogenic sources (Vigano et al., 2009).

4 Conclusions and outlook

Our study shows that there exist several hitherto unknown processes that produce CH_4 in soil and peat which is clearly not related to methanogenic activity. Figure 5 summarizes our results regarding non-microbial CH_4 formation in the aerobic layers of soils and the environmental factors that might control emissions. From our findings we suggest that the abiotic formation of CH_4 through degradation of organic soil matter represents a thus far undiscovered pathway for CH_4 formation in oxic soils. Our results imply that there are at least two different mechanisms for non-microbial CH_4 formation in soils. This can be best distinguished by comparing thermal and UV-B induced CH_4 release. Samples that released only minor amounts of CH_4 when heated or wetted emitted significant amounts when irradiated with UV-B, and vice versa.

The amounts of CH_4 produced at ambient temperatures of 30°C are small but increase considerably with increasing temperature. Wetted samples during the drying and rewetting cycle experiments showed much higher emissions than the dry sample itself at low temperatures. Assuming that the first five centimetres of the soil horizon account for most of the CH_4 production, the emission rates from dry and wet soil at 30 to 40°C (Table 1) would correspond to emission rates of 0 to $18\mu\text{g m}^{-2} \text{h}^{-1}$, assuming a dry bulk density of 1.5g cm^{-3} for soil and 0.1g cm^{-3} for

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



peat (Minkinen and Laine, 1998). These emissions increase up to an order of magnitude when the soil surface temperature reaches 50 to 70 °C. Although these temperatures are often only observed at soil surfaces in tropical and savannah regions, when compared to field measurements from wetlands with observed CH₄ emissions up to 11.9 mg m² h⁻¹ (286.5 mg m⁻² d⁻¹) and calculated average emission rates of 2.1 mg m⁻² h⁻¹ (51 mg m⁻² d⁻¹) (Morrissey and Livingston, 1992; Roulet et al., 1992; Cao et al., 1998), these are relative minor emissions. However, given the large global soil areas and the frequency at which dried and rewetted soils release CH₄, this source can nevertheless be an important factor in aerobic soil organic matter degradation.

The CH₄ emissions under UV light are consistent with findings by Vigano et al. (2008) and McLeod et al. (2008), who showed that UV irradiation drives CH₄ production from dried plant matter. Thus soil organic matter is most likely the precursor of CH₄ emissions observed in our studies. This is supported by CH₄ emissions that were observed when lignin and humic acid were exposed to UV irradiation under the same conditions as that for the soil samples. However, it is interesting that under UV irradiation there was no apparent correlation between CH₄ production and the soil organic matter content. This indicates that other soil components also play a role in CH₄ formation. Organic photosensitisers such as tryptophan (Messenger et al., 2009) or the mineral soil fraction, e.g., clay minerals and metal oxides (Katagi, 1990; Wu et al., 2008; Kibanova et al., 2011) may catalyze surface reactions of organic matter leading to CH₄ formation. This would also be in agreement with the recent observation that meteoritic matter such as carbonaceous chondrites containing only a few per cent organic matter releases large amounts of CH₄ when exposed to UV irradiation (Keppler et al., 2012).

Methane emissions under UV radiation were found to be in the range of 0.25 to 7.28 μg m⁻² h⁻¹ for various soils in the UV-B intensity range of 1 to 4 W m⁻². Again, these emission rates are considerably lower than emissions observed from natural wetlands (Morrissey and Livingston, 1992; Roulet et al., 1992; Cao et al., 1998). However, a large fraction of the terrestrial surface is directly exposed to UV radiation, and this might even increase due to anthropogenic activities leading to deforestation and

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



desertification. Interesting regions for on-site studies of UV induced CH₄ release could be steppes regions, newly deforested land, and freshly ploughed fields, whereas for water mediated CH₄ release flooding plains and irrigation areas in dry climates would be relevant. However, it has to be considered that more than 90% of CH₄ formed within soils is oxidised by methanotrophic bacteria before it reaches the atmosphere (King, 1990). Methane uptake into aerated temperate forest soils ranges from 10 to 204 μg m⁻² h⁻¹, depending on soil type, temperature and water saturation (Born et al., 1990; Castro et al., 1995; King, 1997). Field measurements regarding the temperature and water mediated CH₄ emissions may thus be impaired by methanotrophic consumption. In contrast direct photolysis of soil organic matter will occur at the upper soil surface at maximum depths of 0.2 to 0.4 mm and indirect photolysis processes might affect the soil down to 2 mm depth (Hebert and Miller, 1990). Thus CH₄ formation induced by UV irradiation at the soil surface might lead to direct CH₄ emissions to the atmosphere. It will be a challenge to differentiate between microbial and non-microbial sources in the field.

Hydrogen peroxide was found to have a positive effect on CH₄ production from peat. Levels of H₂O₂ in soils are influenced by the activity of plant roots, fungi and bacteria (Schönknecht et al., 2008; Miller et al., 1998). As the release of H₂O₂ from living organisms is often a defence mechanism, the amount released might be affected by organism density in the soil and the level of stress applied by (changing) environmental factors. All effects shown to increase CH₄ production might gain importance in the course of climate change considering predicted changes in temperatures, precipitation levels and evaporation rates. Flood plains and other environments with strong fluctuations in the water budget might be of particular interest. Further investigations will be essential to fully understand the biogeochemical cycle of CH₄ in soils and its relevance for the atmosphere

BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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BGD

9, 11961–11987, 2012

Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Non-microbial
methane formation in
oxic soils**

A. Jugold et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Non-microbial
methane formation in
oxic soils**A. Jugold et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Non-microbial methane formation in oxic soils

A. Jugold et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Non-microbial methane formation in oxic soils

A. Jugold et al.

Table 1. Organic carbon content, pH value and CH₄ emissions from dry and wetted samples heated at 30 and 40 °C and under UV irradiation of different soils and soil components.

Sample	pH	C _{org} [% (dw)]	Methane emission				UVB radiation [μg m ⁻² h ⁻¹] (2 W m ⁻²)
			Dry (30 °C)	Dry (40 °C)	Wet (30 °C)	Wet (40 °C)	
Sphagnum peat (PH)	3.7	49.2 %	0.05 ± 0.02 ^a	0.05 ± 0.00 ^a	0.19 ± 0.01	0.41 ± 0.01 ^a	0.76 ± 0.24
Sphagnum peat, sterile (PHS)	3.7	49.2 %	0.11 ± 0.15	0.03 ± 0.02	0.32 ± 0.09	0.52 ± 0.03	n.m.
Deciduous forest soil O _h (SW)	7.4	23.4 %	n.d.	n.d.	0.23 ± 0.02	0.24 ± 0.06	0.25 ± 0.13
Coniferous forest soil A _h (SG)	7.2	5.0 %	n.d.	n.d.	n.d.	0.04 ± 0.01	1.73 ± 0.41
Deciduous forest soil A _h (SL)	4.4	4.0 %	n.d.	0.09 ± 0.02	0.06 ± 0.01	0.10 ± 0.04	4.92 ± 1.46
Deciduous forest soil A _h (SHA)	6.7	5.8 %	n.d.	0.08 ± 0.03 ^a	n.d.	0.20 ± 0.05 ^a	0.50 ± 0.13
Humic acid (HA)	5.5	43.5 %	0.06 ± 0.02	0.82 ± 0.06	0.18 ± 0.03	3.10 ± 0.34	0.80 ± 0.17
Lignin (LN)	9.6	49.5 %	0.1 ± 0.01 ^a	0.33 ± 0.01 ^a	0.65 ± 0.02	1.89 ± 0.20 ^a	0.40 ± 0.11
Lignin sterile (LNS)	9.6	49.5 %	n.d.	0.39 ± 0.03	1.45 ± 0.48	2.70 ± 0.57	n.m.

Subscript h indicates soil horizon, C_{org} is organic carbon content, PH is peat Hille, Germany; SW is soil Häverstädt, Wiehen Mountains, Germany; SG is soil Gonsenheim, Germany; SL is soil Lerchenberg, Germany; SHA is soil Hainich, Germany; n.d. is not detectable (rate cannot be provided as increase in headspace CH₄ was less than 0.02 ppm); n.m. is not measured; ^a data from Hurkuck et al. (2012). Data show mean value ± SD (*n* = 3–5).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Non-microbial
methane formation in
oxic soils**

A. Jugold et al.

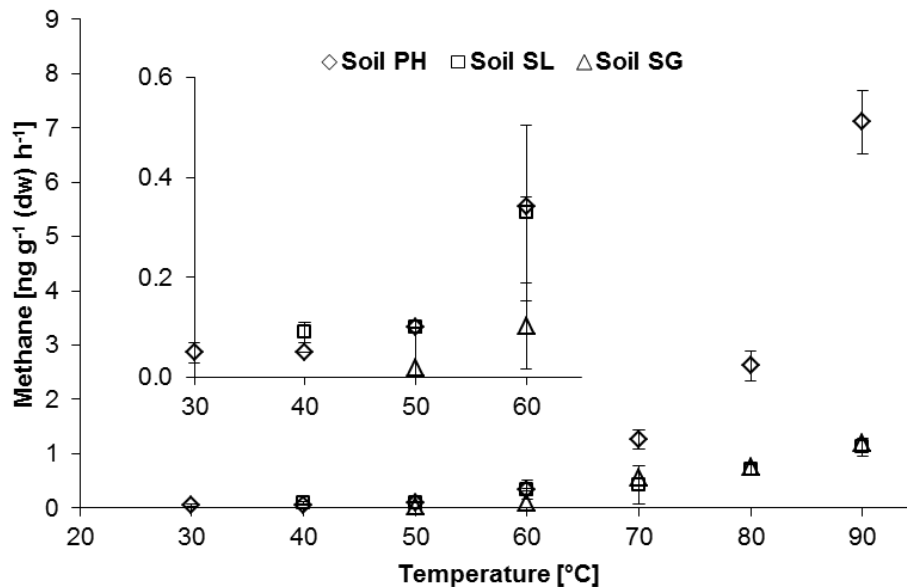


Fig. 1. Formation of CH₄ from soil with increasing temperature. Temperature dependence of CH₄ emissions from peat PH, soil SL and soil SG. Data show mean value ± SD (*n* = 5). Inset shows magnified area between 30 and 60 °C.

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Non-microbial
methane formation in
oxic soils**

A. Jugold et al.

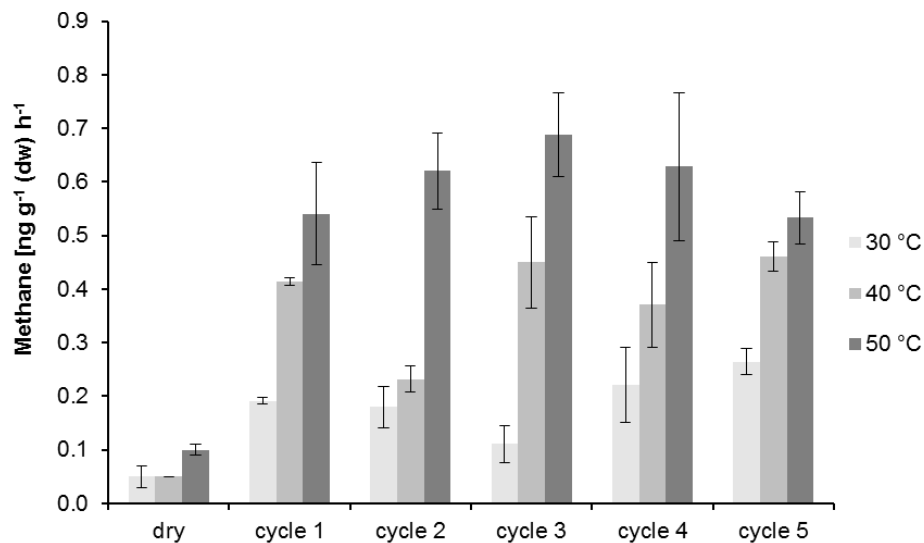


Fig. 2. Methane formation from wetted and dry peat samples. Effect of repeated wetting and drying cycles on CH₄ release from peat PH at 30, 40 and 50 °C. Data show mean value ± SD ($n = 5$).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



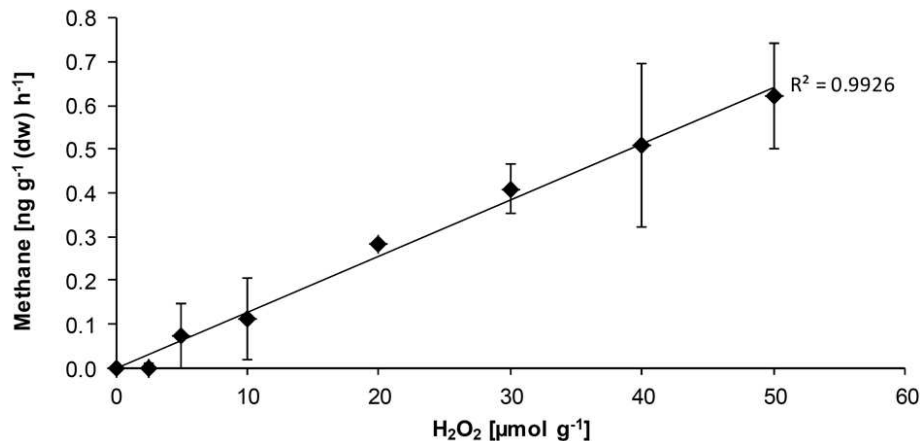


Fig. 3. Relationship between CH₄ emission from peat PH and added amount of H₂O₂. Data show mean value ± SD ($n = 3$, except 20 μmol ($n = 1$)). Incubation: 24 h at 30 °C.

**Non-microbial
methane formation in
oxic soils**

A. Jugold et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



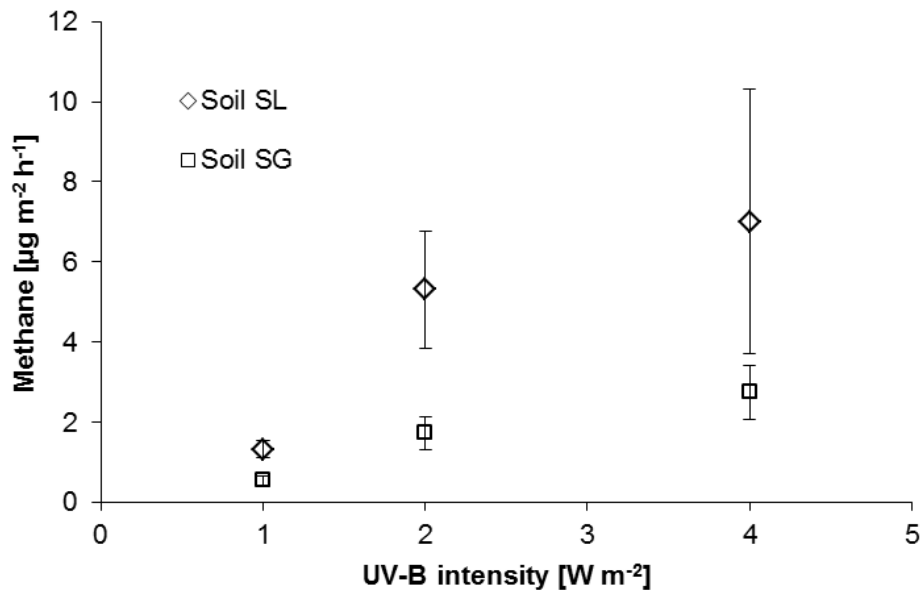


Fig. 4. Relationship between CH_4 emissions from soils SL and SG and UV-B intensity. Data show mean value \pm SD ($n = 3$).

**Non-microbial
methane formation in
oxic soils**

A. Jugold et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



