Abiotic methane formation in oxic soils

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Erklärung

Hiermit versichere ich gemäß § 10 Abs. 3d der Promotionsordnung vom 24.07.2007, dass ich die als Dissertation vorgelegte Arbeit selbst angefertigt und alle benutzten Hilfsmittel (Literatur, Apparaturen, Material) in der Arbeit angegeben habe. Die als Dissertation vorgelegte Arbeit wurde in der Zeit von November 2007 bis Dezember 2012 am Max-Planck-Institut für Chemie in der Arbeitsgruppe ORCAS angefertigt.

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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, some potentially abiotic sources from the biosphere have been discovered in the past few years, starting with methane emissions from plants and plant litter up to the recent discovery of methane production in saprotrophic fungi.

Also methane fluxes from aerobic soils have been observed for decades but no alternative source to methanogenesis has been identified so far.

This work aims to provide evidence for non-microbial methane formation in soils under oxic conditions. It was found that soils release methane upon heating and other environmental factors like ultraviolet irradiation, and drying-rewetting cycles. The chemical formation of methane during degradation of soil organic matter represents an additional source in soil that helps to understand the methane cycle in aerobic soils. Although the emission fluxes are relatively low when compared to those from aerobic soil sources like wetlands, they may still be important in warm and wet regions subjected to ultraviolet radiation. Therefore this methane source might be highly sensitive to global climate change.

Zusammenfassung

Methan ist an vielen chemischen Prozessen in der Atmosphäre beteiligt und hat großen Einfluss auf ihren Strahlungshaushalt. Bis vor kurzem wurden als natürliche biologische Quellen ausschließlich mikrobielle Prozesse beim Abbau organischer Stoffe in Betracht gezogen. Allerdings sind in den letzten Jahren einige potentiell abiotische Quellen in der Biosphäre entdeckt worden, angefangen bei der Methanproduktion in Pflanzen und pflanzlichem Detritus bis hin zur Methanbildung in saprophytischen Pilzen.

Auch aus aeroben Böden, die bislang allgemein als Methansenken gelten, werden seit Jahrzehnten immer wieder Methanemissionen beobachtet. Bislang wurde jedoch keine weitere Quelle als Alternative zur Methanogenese identifiziert.

Diese Arbeit hat zum Ziel, einen Nachweis für nicht-mikrobielle Bildung von Methan in Böden unter oxischen Bedingungen zu erbringen. Es wurde festgestellt, dass Böden beim Erhitzen und durch andere Umweltfaktoren wie UV-Bestrahlung und Vernässung Methan emittieren. Eine Beteiligung von methanogenen Archaen konnte dabei durch verschiedene Verfahren ausgeschlossen werden. Die chemische Bildung von Methan beim Abbau organischer Substanz im Boden könnte eine weitere Quelle im Boden sein, die benötigt wird, um den Methan-Kreislauf in aeroben Böden vollständig zu erfassen. Obwohl die Emissionsraten aus den aeroben Böden relativ niedrig sind im Vergleich zu aeroben Quellen wie Feuchtgebieten, könnte die abiotische Methanbildung in feuchtwarmen Klimaten mit höherer UV-Einstrahlung eine wichtige Quelle sein. Deshalb ist auch zu erwarten, dass die Dimension dieser Quelle auch vom Klimawandel beeinflusst werden wird.

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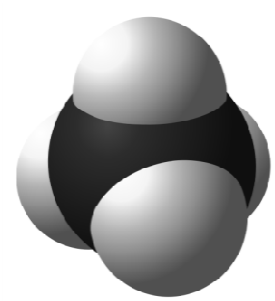
1 Methane

1.1 Methane in the atmosphere



Methane (CH_4) is the most abundant reduced organic gas in the atmosphere. It is also the third most important greenhouse gas after carbon dioxide (CO_2) and water vapour (H_2O). Regarding the atmospheric concentrations of CH_4 and CO_2 the influence of CH_4 on global warming seems comparatively small, but the global warming potential of one molecule of CH_4 is about 25 times as effective as that of CO_2 on a 100 year timescale leading to a radiative forcing by CH_4 of 0.48 W m^{-2} which is about 30 % of that by CO_2 (Lelieveld et al., 1998). With an average atmospheric lifetime of 12 years (Forster et al., 2007) it is one of the long lived greenhouse gases.

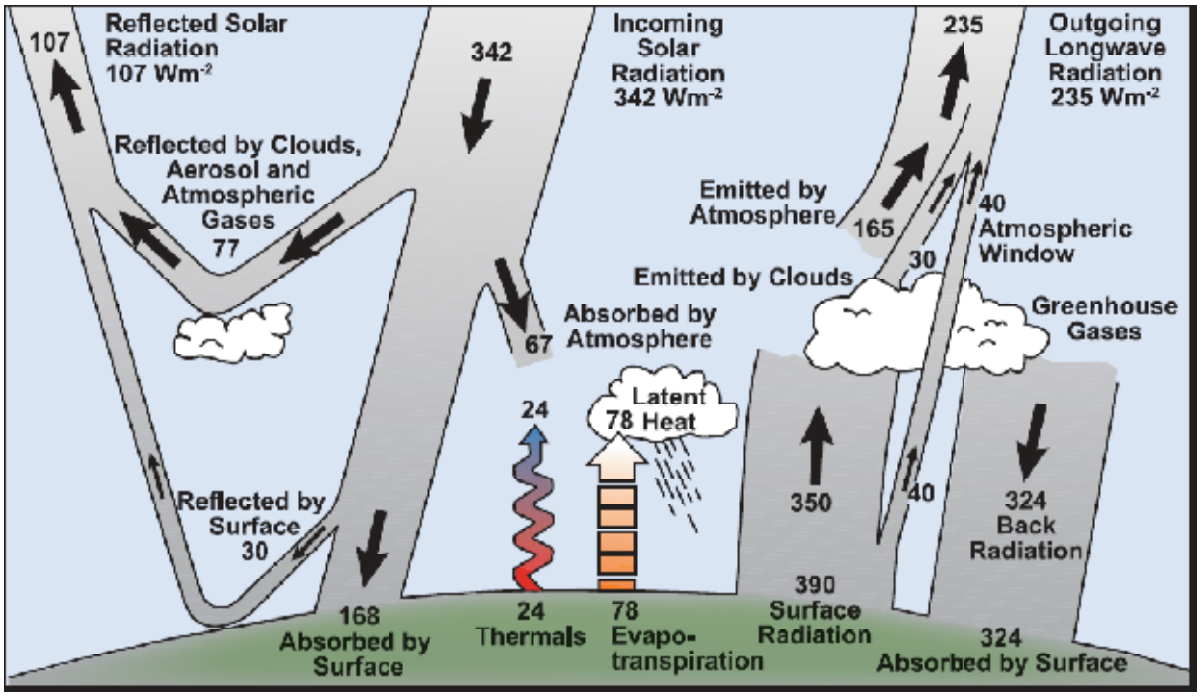


Fig. 1-2: *The Greenhouse effect as part of earth's radiation balance* (Le Treut et al., 2007).

The greenhouse effect describes the influence, which the interaction of radiation and matter has on the energy balance of the atmosphere. The atmosphere itself is mostly transparent for short-waved radiation as emitted by the sun. On the earth's surface part of this short-waved radiation is reflected but most of it is absorbed and

transformed to long-wave or infrared radiation. This thermal radiation is reemitted to the atmosphere which it could pass and be emitted into space if it was not absorbed by the greenhouse gases (Fig. 1-2). This effect is known as radiative forcing, to which CH_4 contributes about 20 % of all long lived greenhouse gases (Fig 1-3).

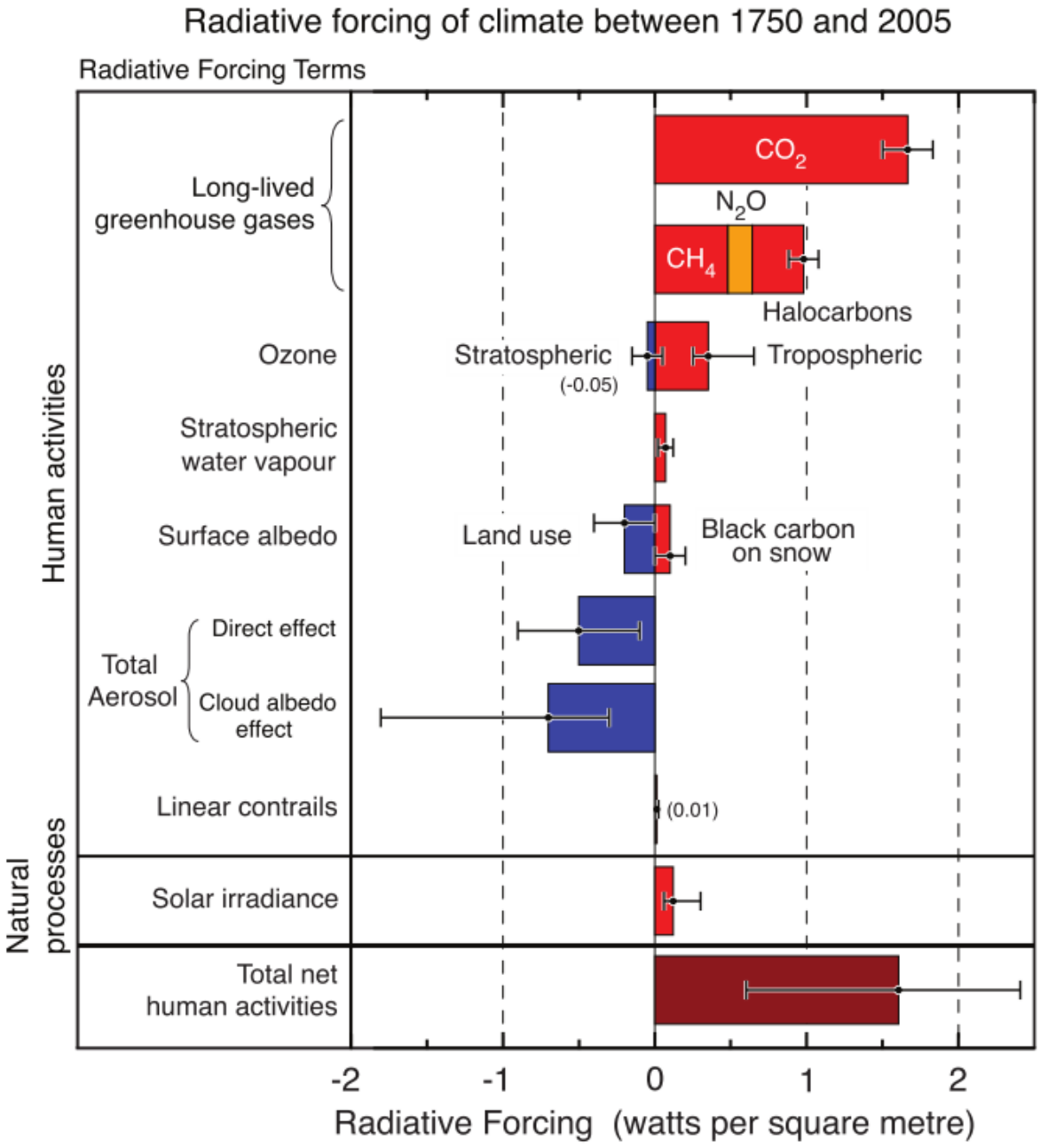


Fig. 1-3: *Radiative forcing agents in the atmosphere; the effect of human activities between 1750 and 2005 (Forster et al., 2007).*

Until the beginning of the industrial revolution, the mixing ratio of CH_4 in the atmosphere was lower than 800 ppb. In the past 250 years, the concentration has more than doubled to today's concentration of about 1.8 ppm (Fig 1-4).

On a global scale, the CH_4 concentration differs between northern and southern hemisphere. The average concentration is higher in the northern hemisphere because it not only holds two thirds of the land masses, but is also home to the developed countries. These are responsible for most anthropogenic methane emissions like extensive agriculture, waste management and fossil fuel combustion.

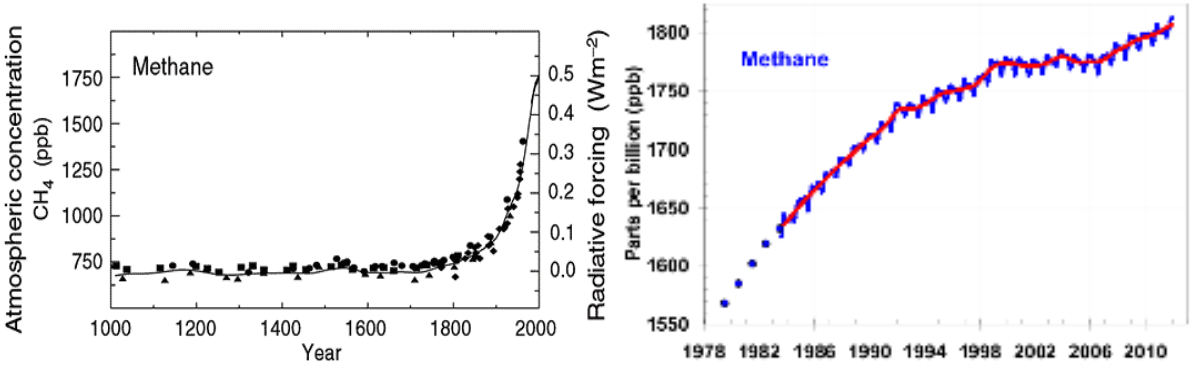


Fig. 1-4: *development of atmospheric methane concentration over the past 1000 years (modified from Ehhalt & Prater, 2001) and since 1980 (NOAA).*

1.2 Sources of Methane

Atmospheric CH_4 originates from both anthropogenic and natural sources. Both groups can be further divided in abiotic and biological sources.

Natural abiotic CH_4 sources are volcanic activity, forest fires and serpentinisation in the earth's mantle (Etiope & Klusman, 2002; Crutzen & Andreae, 1990). Better known are the natural biotic sources: Methane production via methanogenesis in the intestinal tracts of ruminants and insects, especially termites, and in anoxic soils of natural wetlands (Hackstein & Stumm, 1994; Sanderson, 1996; Wang et al., 1996).

Anthropogenic abiotic sources include coal mining, fossil fuel production and burning, and manmade forest fires, but also biotic sources are known to be caused or enhanced by anthropogenic activities (Crutzen & Andreae, 1990; Lelieveld, 1998). Methanogenesis occurs not only in anoxic soils or animal guts, but also in the anoxic milieu existing in landfills (Jones et al., 1983). The sources from anoxic soils and

ruminants have increased due to agricultural use; the most important sources are rice fields and intensive livestock farming.

1.2.1 Methanogenesis

Methanogenesis is the production of methane by methanogenic archea in an anoxic milieu. It occurs under strictly anaerobic conditions mainly in wetland soils and rice paddies, intestinal tracts of termites and ruminants and in human and agricultural waste. In aerobic soils the microbial community degrades organic matter by oxidation to CO_2 to gain energy. In anoxic environments, where oxidation with oxygen from O_2 or oxygen rich compounds is not possible, microorganisms draw their energy from the degradation of organic matter to CH_4. This pathway is not catalysed by a single species of microbes, but by an association in which different microorganisms are specialized on different degradation steps from organic matter to CH_4. The final step, the formation of CH_4 can only be accomplished by methanogens (Thauer, 1998). Five orders of methanogenic archea are known: *Methanobacteriales*, *Methanococcales*, *Methanomicrobiales*, *Methanopyrales* and *Methanosarcinales*. All of them use methanogenesis as their only way of energy production. The fermentation of acetate (Eq. 1-1, step 2.1) can only be accomplished by the last group, *Methanosarcinales*. The other four reduce the carbon compound with H_2 or H^+ (Eq. 2, step 2.2 and 2.3).

All preceding steps are performed by bacteria that often also play a role in sulphate reduction.

1.1) $Glucose + 2H_2O \rightarrow 2CH_3COO^- + 2H^+ + 2CO_2 + 4H_2$

1.2) $Glucose + 2H_2O \rightarrow 2CH_3COO^- + 2HCOO^- + 4H^+ + 2H_2$

2.1) $CH_3COO^- + H^+ \rightarrow CO_2 + CH_4$

2.2) $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$

2.3) $4HCOO^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O$

$Glucose \rightarrow 3CO_2 + 3CH_4$ (net reaction)

Eq. 1-1: Reactions in the microbial metabolism leading to CH_4 production. After Thauer (1998).

The hydrogen, which is needed in the last step can be acquired either from geological sources or is excretet by the soil fauna where it is produced by bacterial communities in the guts of insect larvae and other soil organisms.

1.2.2 Methane production in aerobic environments

Until recently, the only biogenic CH_4 source was thought to be methanogenesis. But Keppler et al. (2006) demonstrated that plants produce CH_4 also under aerobic conditions. This provided a suitable explanation for the methane emissions over the Amazonian rain forest, observed earlier in satellite measurements (Frankenberg et al., 2005). In the ensuing years the scientific community has critically debated the existence of this vegetation source (Dueck et al., 2007; Ferretti et al., 2007; Kirschbaum et al., 2007; Keppler & 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 attempted to provide alternate explanations for the observed release of CH_4 from plants or disprove it at all (Nisbet et al., 2009; Kirschbaum & Walcroft, 2008; Terazewa et al., 2007).

However, observations have provided unambiguous evidence that several different pathways have to exist by which CH_4 is generated under aerobic conditions without microbial activity (Wang et al., 2008; Keppler et al., 2008; McLeod et al., 2008; Brüggemann et al., 2009; Bruhn et al., 2009 & 2012; Messenger et al., 2009; Cao et al., 2008; Quaderi & Reid, 2009). In early attempts to elucidate the details of the mechanism, methoxy groups of plant pectin have been verified to be a precursor compound of aerobic CH_4 emissions from detached plant foliage (Vigano et al., 2008; Keppler et al., 2008; McLeod et al., 2008; Bruhn et al., 2009). In their latest review Bruhn et al. (2012) conclude that pectin is a precursor of plant released CH_4, but that it is one precursor among others. Temperature and UV-light have been identified as environmental factors that control CH_4 emission from dried plant matter (Vigano et al., 2008; Keppler et al., 2008; Lee et al., 2012). Recently, Althoff et al. (2010) could describe an abiotic reaction mechanism for aerobic CH_4 formation. Methane formation could be proven in a reaction of ascorbic acid, ferrihydrit and hydrogen peroxide. In further studies this reaction was complemented by the addition of several potential methyl donor compounds of which methionine and methionine

sulfoxide caused the highest increase in CH_4 formation. This could be transferred from the model system to *in vitro* and *in vivo* experiments where ^{13}C labelled methionine also acted as precursor for CH_4 formation both from plant cell culture and intact tobacco plants (Althoff, 2012). Another recently discovered CH_4 source is the aerobic formation in saprotrophic fungi (Lenhart et al., 2012).

1.2.3 Previous observations of methane formation in aerobic soils

Aerobic soils are known to be a sink for atmospheric methane, consuming around 30 Tg CH_4 each year (Ehhalt & Prater 2001) by the way of methanotrophic oxidation (see chapter 1.3.2). Nonetheless, methane emissions from oxic soils have been observed as early as 1988 (Hao et al., 1988). These observations, like all others of CH_4 production in oxic soils so far (Megonigal & Guenther, 2008; Andersen et al., 1998; von Fischer & Hedin, 2007), have been attributed to methanogenesis by lack of alternative explanations. Anaerobic microsites as a refuge for methanogenes were offered as a possible explanation (Peters & Conrad, 1995). However, in experiments by Kammann et al. (2009) soil cores emitted up to 4.6 µg CH_4 kg^{-1} d^{-1} even after homogenization and thus destruction of potential anoxic microsites. Rimbault et al., (1988) showed that oxic eubacteria produce CH_4 in trace quantities. Nevertheless, von Fisher & Hedin (2007) discussed that methanogens as the sole source for CH_4 in oxic soils have to be regarded critically. Their stable carbon isotope studies indicate that our understanding of CH_4 formation in oxic soils is still incomplete and that there is a lot more to be taken into account than just presence or absence of methanogens and oxygen.

Non-microbial methane formation in oxic soils and from soil components could be shown in studies by Jugold & Keppler (2009) and by Hurkuck et al. (2012) and in the experiments described in chapter 6 of this thesis (Jugold et al., accepted).

1.3 Sinks of Methane

The annual mean sink of atmospheric CH_4 is estimated with 570 Tg (Ehhalt & Prater, 2001). The by far largest sink for atmospheric CH_4, the reaction with OH radicals accounts for over 90% of CH_4 removal. Most of it (80%) is consumed in the troposphere, but 7-11 % of the oxidation also occurs in the stratosphere (Forster et al., 2007; Lelieveld et al., 1998; Levy, 1973).

A second important sink is the consumption in soils (Born et al., 1990). The strength of this sink is strongly dependent on environmental influences.

A further atmospheric sink is the photolytic reaction with free chlorine (Platt et al., 2004; Lassey et al., 2011; Levine et al., 2011).

1.3.1 Reaction with OH radicals in the atmosphere

The dominating sink for atmospheric CH_4 is the tropospheric reaction with OH radicals in which CH_4 is oxidised to CO_2. This process accounts for 85-90% of atmospheric methane removal (Ehhalt & Prater, 2001). The reaction can be described as a photolytical one, even if methane is not dissociated photolytically itself. Photolysis is important in the formation of its reaction partner, the hydroxyl radical, which is formed by photolytic dissociation of ozone (O_3) and the reaction of the resulting excited O with water vapour.

Photolysis of ozone and origin of OH radicals:

$$O_3 \xrightarrow{h\nu(\lambda<310nm)} O_2 + O(^1D)$$
$$O(^1D) + H_2O \longrightarrow \mathbf{2 \cdot OH}$$
$$O(^1D) + M \longrightarrow O(^3P) + M$$
$$O_3 \xrightarrow{h\nu(\lambda<1180nm)} O_2 + O(^3P)$$
$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$

Photochemistry of methane:

$$CH_4 + \cdot OH \longrightarrow \cdot CH_3 + H_2O$$
$$\cdot CH_3 + O_2 + M \longrightarrow H_3CO_2\cdot$$

In presence of NO_x

$$H_3CO_2\cdot + NO \longrightarrow H_3CO\cdot + NO_2$$
$$H_3CO\cdot + O_2 \longrightarrow HCHO + HO_2\cdot$$
$$HO_2\cdot + NO \longrightarrow \cdot OH + NO_2$$
$$NO_2 \xrightarrow{h\nu} NO + O(^3P)$$
$$O(^3P) + O_2 + M \longrightarrow O_3 + M \ (M = N_2, O_2)$$
$$CH_4 + 4O_2 \longrightarrow HCHO + H_2O + 2O_3 \quad \text{(net reaction)}$$

Eq. 1-2: Reactions in the atmosphere that lead to the formation of hydroxyl radicals and to the decomposition of methane (taken from Vigano 2010).

1.3.2 Methanotrophy in soils

Uptake of atmospheric CH_4 into aerated soils is based on bacterial methane oxidation (methanotrophy) in the soils, maintaining a CH_4 gradient between atmosphere and soil pore space. The global annual CH_4 uptake by soils has been calculated to be 30 ± 15 Tg a^{-1} (Ehhalt & Prather, 2001) and a similar conclusion was reached with a model by Curry (2007) who estimates 28 (9-47) Tg a^{-1} global soil uptake. Bornet al., (1990) speak of 5.6 – 58.2 Tg a^{-1} global soil uptake.

Methanotrophy means the oxidation of CH_4 by bacteria. The methane oxidation in methanotrophs is catalised by enzymes known as methane monooxigenases (MMO) who oxidise CH_4 to methanol (CH_3OH) which is further oxidised to formaldehyde by methanol dehydrogenase (Fig. 1-5). There are two types of MMO, the sMMO which uses NADH + H^+ as an electron donor and pMMO which uses cytochrome *c*.

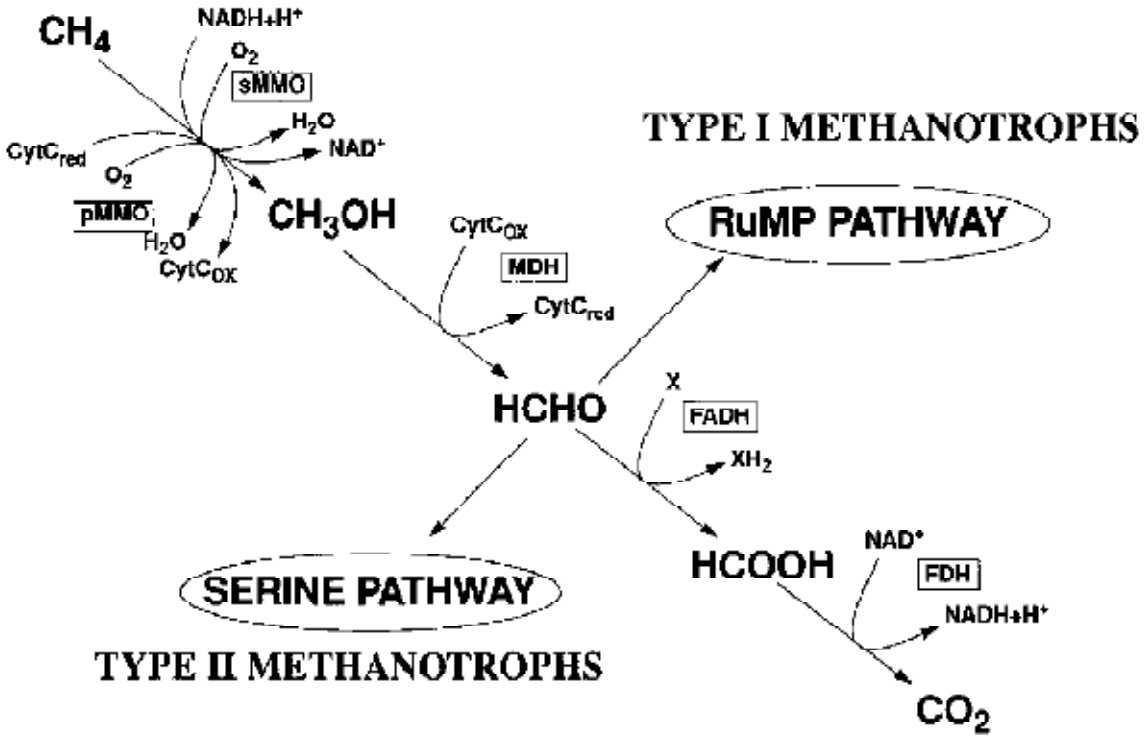


Fig. 1-5: *Pathways for the oxidation of methane and assimilation of formaldehyde. Abbreviations: CytC, cytochrome c; sMMO/pMMO, methane monooxigenases; MDH, methanol dehydrogenase, FADH, formaldehyde dehydrogenase; FDH, formate dehydrogenase (Hanson & Hanson, 1996).*

Methanotrophs belong to the six genera *Methylomonas, Methylobacter, Methylococcus, Methylomicrobium, Methylocystis* and *Methylosinus* of which the first four belong to the type I methanotrophs and the latter two are type II methanotrophs. The two types of methanotrophy are distinguished by their pathway for formaldehyde fixation. In type I methanotrophs formaldehyde is fixated in the cell material via the RuMP pathway, explained in Fig. 1-6a and type II methanotrophs fixate formaldehyde via the serine pathway, explained in Fig. 1-6b.

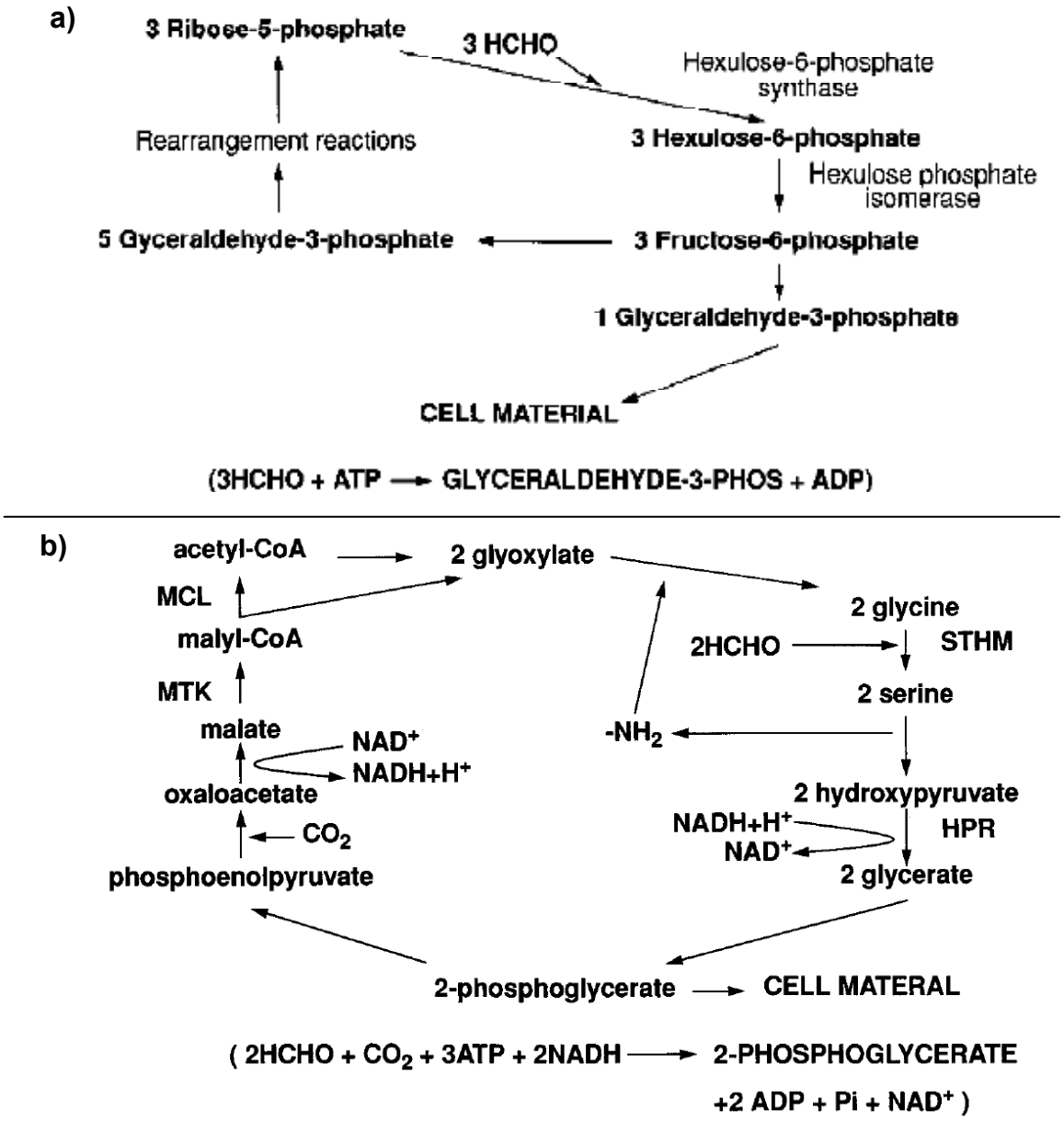


Fig. 1-6: *Pathways for formaldehyde fixation. a) RuMP pathway, b) serin pathway (Hanson & Hanson, 1996).*

Besides CH_4 uptake from the atmosphere, methanotrophy is also responsible for the fact that around 90 % of the methanogenically formed CH_4 from the anaerobic soil layers is already being oxidised while passing through the aerobic layer on its way to the soil surface (King, 1990). A strong reduction of the CH_4 flux to the atmosphere occurs.

Methane oxidation in the soil is influenced by water, temperature, pH, diffusion barriers, ammonium inhibition and bacterivores (Mancinelli, 1995; Schlesinger, 1997; King, 1997). Both, too low and too high water contents show a negative influence on CH_4 oxidation capacities. When it is too dry, the methanotrophic bacteria suffer, when the water content is too high, soil diffusion and thus transport of CH_4 to the bacteria is limited. Other diffusion barriers like layers of clay also limit the microbial access to methane and oxygen.

Temperature has also an important effect on methanotrophs. Most methanotrophic communities in soil have a temperature optimum around 25 °C (Hanson & Hanson, 1996) but CH_4 oxidation also occurs below 10 and over 35 °C. The optimum for methanotrophic bacteria specialized on extreme habitats can differ significantly.

An important factor influencing CH_4 oxidation in agricultural soils is ammonium inhibition. Soils with high nitrogen concentrations are limited in their CH_4 oxidation capacity. The complete process of nitrogen species inhibiting CH_4 oxidation is not completely resolved, but it seems that multiple effects are responsible (King & Schnell, 1994; Schnell & King, 1994). Ammonium (NH_4^+) can be oxidised by MMO like CH_4. Both the intermediate hydroxyl amine (NH_2OH) and the end product nitrate (NO_2^-) disturb the methane oxidation pathway. NH_2OH works potentially as an inhibitor for MMO and nitrate inhibits formate dehydrogenase. The inhibitory effects can be observed immediately. A long term effect is possibly based on a shift in the microbial populations from methanotrophs to pure ammonium oxidisers.

The inhibition of MMO can also be of use in a scientific context. A widely used technique to measure methane oxidation rates is to determine the flux of CH_4 in a chamber before and after adding an inhibitor like acetylene (C_2H_2), fluoromethane (CH_3F) or difluoromethane (CH_2F_2, DFM). The most effective and most specific of these inhibitors is DFM, which does not inhibit methanogenesis like C_2H_2 does under certain circumstances and it is not degraded by MMO as fast as CH_3F. It competes at

the MMO reaction sites with CH_4, but cannot be oxidized by the enzyme. The inhibiting effect of DFM on methane oxidation is reversible. (Miller et al., 1998)

1.4 Isotopic source signatures of methane

Stable isotopes are variants of a chemical element that differ by their atomic mass. This is caused by a different number of neutrons in the nuclei. In contrast to radioactive isotopes, they do not decay.

Methane molecules consist of carbon and hydrogen. Both elements occur in nature with two stable isotopes: ^{12}C (abundance 98.99 %) and ^{13}C (1.11 %) for carbon, H (99.985 %) and D (0.015 %) for hydrogen/deuterium.

Because the heavier isotopes are so rare, only variants with single substituted isotopes can be measured precisely enough to be of use for stable isotope analysis.

More commonly used than the abundance is the ratio r of the heavier to the lighter isotope $^{n+1}X/^{n}X$. In case of carbon it would read:

$$R = \frac{^{13}C}{^{12}C}$$

(Eq. 1-3)

This ratio can be further transformed into the δ notation by:

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

(Eq. 1-4)

Values of $\delta^{13}C$ are usually calculated relative to the values for the VPDB (Vienna Pee Dee Belemnite), which has been established as an equivalent to the original PDB. The original Pee Dee Belemnite (*Belemnitella americana*) was a fossil found in the PeeDee Formation in South Carolina. Its $^{13}C/^{12}C$ ratio is among the highest ever found in a natural material and it was therefore established as the standard on which the VPDB scale is based. The VPDB scale is also used for oxygen isotope ratios of carbon-based substances.

Values of $\delta\ ^{2}H$ (‰) are usually given in relation to that for Vienna Standard Mean Ocean Water (VSMOW). The first Standard Mean Ocean Water (SMOW) was created from a mixture of various distilled ocean water and snow samples from all over the world. It was later recalibrated and VSMOW is now used as a reference for both hydrogen and oxygen isotope ratios.

The analysis of stable isotope composition is useful to identify precursor compounds of the respective products and to examine reaction pathways. Table 3-1 shows the $\delta^{13}C$ and $\delta^{2}H$ values of methane from different natural and anthropogenic sources.

Source	Source strength [Tg CH_4 yr^{-1}]	$\delta^{13}C$-CH_4 [‰]	$\delta\ ^{2}H$-CH_4 [‰]
Biomass burning	30	-24	-228
Coal	33 ± 5	-36	-140
Gas	70 ± 14	-43	-185
Gas hydrates	10	-60	-200
Plants	5 – 25	-58	-275
Plants (UV)	2 – 5	-59	-334
Rice	69 ± 12	-63	-320
Ruminants	58	-60	-300
Waste	40 ± 8	-52	-300
Wetlands (boreal)	100 ± 30	-65	-330
Wetlands (tropical)	200 ± 50	-58	-330

Table 1-1: *Source strength, $\delta^{13}C$ and $\delta^{2}H$ values of atmospheric methane. (taken from Vigano, 2010).*

2 UV degradation of organic matter

2.1 Solar UV radiation

Ultraviolet (UV) light covers the wavelength range from 10 nm, where x-rays end, up to 400 nm, where the wavelength range of visible light starts. The wavelength range from 100 – 10 nm is called extreme UV (EUV). The UV light, that is part of the solar radiation, is usually divided into three subspecies, UV-A (400 – 315 nm), UV-B (315 – 280 nm) and UV-C (280 – 100 nm). Of these three only UV-A and UV-B reach the earth's surface, because UV-C and part of UV-B are blocked by the ozone layer where they lose their energy in the photolytical dissociation of O_3 to O_2 and O·.

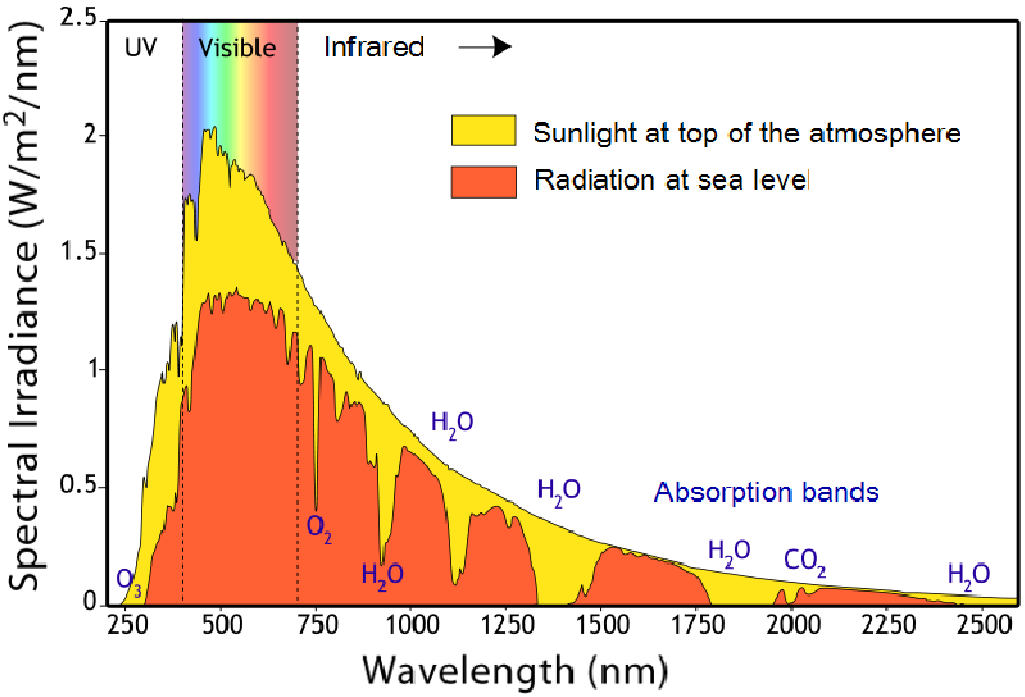


Fig. 2-1: *Solar radiation spectrum at the top of the atmosphere and at sea level.*

Typical ambient (non-weighted) summer UV-B irradiances near the Earth surface range from 2 W m^{-2} at mid-latitudes to 3.7 W m^{-2} in the tropics (Bernhard et al., 1997).

2.2 UV degradation of organic matter and its potential role as a methane source

Photolysis is an important degradation pathway for organic compounds in the environment leading to the release of both CO_2 and CH_4. For arid areas, where little biological degradation can be found, it has been suggested to be the major degradation pathway for plant litter (Austin & Vivanco, 2006) but it has also been proposed that a light-induced increase in litter degradability is a more important mechanism for photodegradation than the direct light-induced mass loss (Foereid et al., 2010).

Solar UV radiation poses a strong influence on biogeochemical cycling by affecting the composition of microbial communities in soil as well as in aquatic biotopes. These influences are based either on direct effects of UV radiation on the microbial organisms, but also on effects on the plant metabolism that leads to changes in plant litter structure and root exudates (Zepp et al., 2007).

Ultraviolet radiation has been shown to be a prominent factor for aerobic production of CH_4 from plant tissues and pectin. It was demonstrated that both UV-A (320-400 nm) and UV-B (280-320 nm) induce CH_4 emissions from plant tissue (Vigano et al., 2008, McLeod et al., 2008) with UV-B radiation showing a much stronger effect. Nevertheless, as average values of UV-A are around 30-fold higher than UV-B values, UV-A is also an important component on a global level for UV induced CH_4 emissions (Bruhn et al., 2009).

In a study using deuterium labelled plant pectin, Keppler et al. (2008) could show that the CH_4 released by UV radiation originated from the pectin's methoxy groups. Other plant components which were found to emit CH_4 und UV light in a study by Vigano et al. (2008) were lignin and cellulose, which is of particular interest for the elucidation of a possible pathway as cellulose does not have any methoxy groups.

Lignin has long been known to be susceptible to photodegradation. It is an unwanted effect in wood based goods, where it is responsible for discolouring of paper and weathering of plastic products and construction wood (Andrady et al., 2011), as well as a desired effect employed in the treatment of paper mill effluents (Villaseñor et al., 1996). Despite the strong scientific interest, so far the destruction of the educt and the range of possible solid products have been in the focus more than the range of gaseous products, including CH_4.

2.3 UV catalytic properties of minerals

Photodegradation on the soil surface is an effect long known in pesticide research (Katagi, 2004).

Clay minerals like kaolinite have been shown to promote the photolytic degradation of several organic pollutants in aqueous and gaseous media (Kibanova et al., 2009, 2011). The photolytic degradation is positively influenced by adsorption of the pollutants to the clay surfaces. Secondary degradation by active oxygen species might also play a role as it is known that OH· radicals form on clay mineral surfaces under UV radiation (Katagi, 2004). The same promotion might apply for the photodegradation of soil organic matter in presence of clay minerals at the soil surface.

Titanium dioxide (TiO_2), also promotes photolytic degradation of organic pollutants, similar to clay minerals. This effect is most probably based on light scattering on the TiO_2 surfaces and the formation of singlet oxygen (Ksibi et al., 2003). The photocatalytic properties of TiO_2 are being used by the paper industry in the UV treatment of waste water from pulp mills to degrade lignin in the effluents (Dahm & Lucia, 2004; Villaseñor et al., 1996). Next to TiO_2 zinc oxide (ZnO) is also known to exhibit photocatalytic abilities (Kansal et al., 2008). This suggests the possibility that several oxides in soil might catalyse photodegradation of soil organic matter.

3 Soils

Soils are formed by weathering of a source rock, new- or reformation of minerals, degradation of organic detritus, humification and chemical transport. Most soils can be divided into different layers, typically with a layer of organic detritus on the top (O-horizon) and an organic rich horizon below (A-horizon), that is formed mostly from degradation products of the vegetational detritus. The lowest layer is often the underlying source rock and a mostly mineralic horizon (C-horizon) that is still in contact with the source rock from which it was formed by weathering. The horizon in the middle (B-horizon) is often dominated by clay minerals which derive from further weathering of the mineralic soil components in the C-horizon.

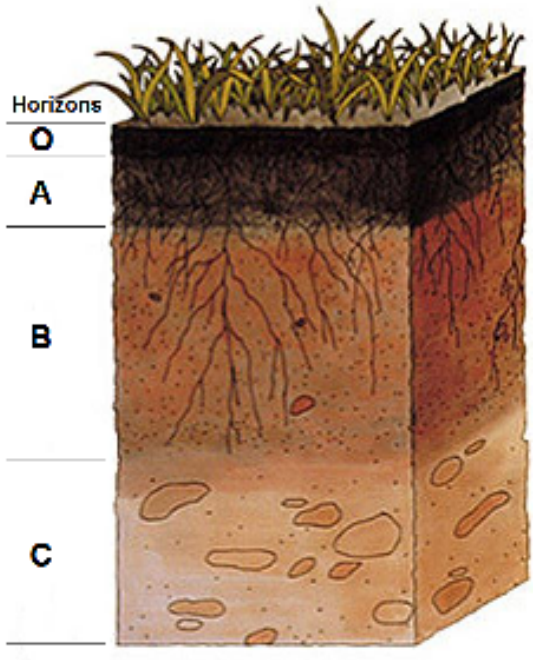


***Fig. 3-1**: Schematic of a soil profile.*

Depending on the source rock, the vegetation and climatic factors, the expression of the layers differs and different soils can be distinguished. Within the soil, the soil components form structures with more or less pore space, which is filled with either air or water. The soil air can differ substantially in composition from the atmosphere above the soil surface as it is influenced by soil organisms, roots, degradation of

organic matter and chemical weathering of minerals. In the same way the pore water can be enriched with dissolved salts or soluble organic substances.

The soil constituents can be divided into soil organic matter and anorganic/mineralic constituents, which are mostly oxides and silicates. An important group among the latter are the clay minerals, a subgroup of the phyllosilicates, which take part in many processes in soil chemistry.
Different processes lead to the formation of peat. Peat is a highly organic soil and is build up from plant material that is converted into humic substances under anaerobic conditions. The content of further components depends on the conditions under which the peat bog was formed. An ombrotrophic bog receives all its water and nutrients solely from precipitation. It is a slightly acidic environment, due to the lower pH of rainwater and the lack of buffering minerals. In contrast minerotrophic fens are fed by streams or lakes, are supplied with a higher mineral input and show lower acidity or even alkaline conditions.
The soils used in this study should give a broad cross section on temperate forest soils and show a high vegetational variation between sampling points. In addition an ombotrophic bog was sampled to extend the range to highly organic soils with negligible mineral content. Moreover the organic matter in sphagnum peat consists of humified substances, whereas for the forest soils different types of lignin where expected to account for most of the organic.

3.1 Soil organic matter

As organic compounds in soil we regard all dead substances of floral or faunal origin and their organic products in the soil and on its surface. (Scheffer & Schachtschabel, 1998). Next to the solid organic substances also dissolved organic matter (DOM) is part of the organic soil compounds.

3.1.1 Formation/Origin

Components of the lightly degraded detritus are often saccharides, peptides, amino acids, proteins and fractions of larger cell components like cellulose and lignin. Primary soil organic matter is degraded mostly by a variety of soil organisms ranging from bacterial communities to earthworms, millipeds and insect larvae. Depending on

the numbers and the activity of the detritivores and the nature of the detritus, it can be turned over quite rapidly.

Pektin and sugars are rare among the soil organic matter as they are the most easily degradable compounds.

In contrast, lignin is the most stable of the primary organic soil compounds and is therefore often found in humic substances. In microbial or fungal degradation a metabolisation of lignin on its own is not possible because of its low energy content. A co-metabolism with sugars or cellulose, which provides easier available energy, is needed. Further lignin can only be degraded in aerobic environments. Therefore anaerobic sediments are often enriched in lignin. Due to its stable, partly aromatic structure even in aerobic soils, most lignin will only be partly mineralized. The aromatic part of the structure is transformed into humic like substances and integrated into humic acid structures.

Humic substances are highly molecular, persistent organic compounds. The origin of humic substances is the humification of organic matter that like lignin can only be partly mineralized. In most cases the active groups of the compounds are mineralized and the aromatic backbone is integrated into larger molecules. Humic substances are divided into humic acids which are unsoluble in water but soluble in alkaline solutions and the water soluble fulvic acids.

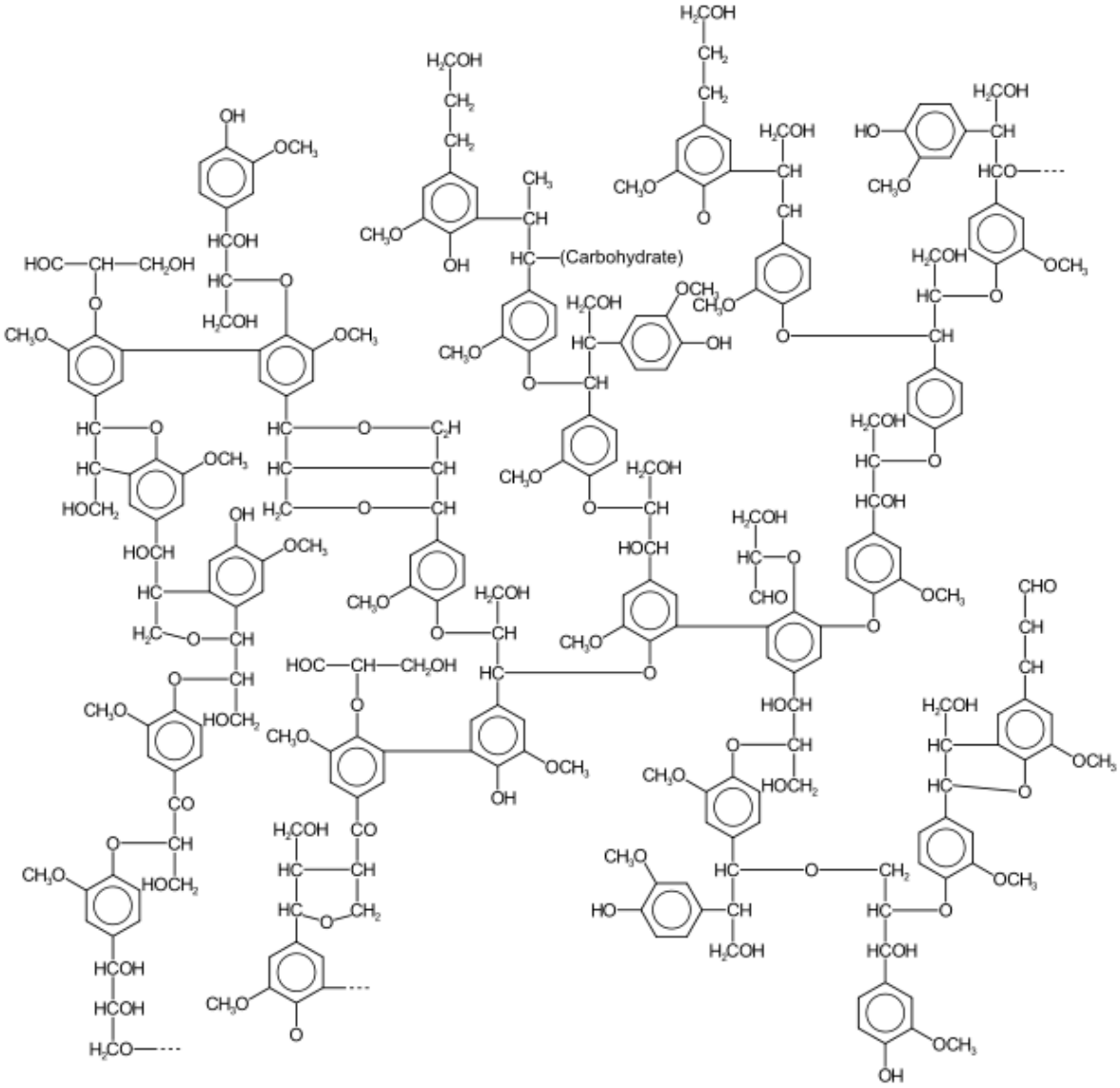


Fig. 3-2: *Example of a lignin structure.*

The lignin structure is a variable composition of three modules: p-cumaryl alcohol, coniferyl alcohol and sinapyl alcohol. They differ in their number of methoxyl groups and are partly specific for different plant groups. Coniferylalcohol with only one methoxyl group is the main constituent of lignin in coniferous wood. Together with sinapyl alcohol, which has two methoxyl groups, it forms the lignin in deciduous trees. P-cumaryl alcohol, which is characterized by the absence of methyl groups is common in the lignin of monocotyledonous plants which contains all three alcohols.

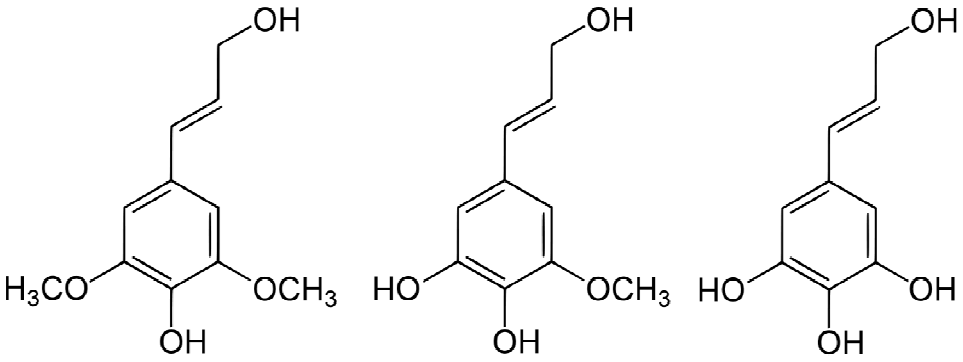


Fig. 3-3: *The three major lignin components sinapyl alcohol, coniferyl alcohol and p-cumaryl alcohol (from left to right).*

3.1.2 Function

Humic substances are macromolecules with a large surface and numerous reaction sites. Water and other molecules as well as ions can be bound reversibly. Organic matter therefore plays an important role in the nutrition budget of the soil as it not only releases nutrients when it is further degraded, but also retains nutrients released during the weathering of mineralic compounds and water in the soil and keeps them available for plants. Their positive influence on the water budget is also caused by their large size which leads to increased pore space in the soil. Humic substances also account for some of the buffer capacity of a soil by stabilizing the soil pH.

3.2 Oxides and Hydroxides

The most common oxide in soils is quartz (SiO_2) which derives as primary mineral from the source rock or in minor quantities is brought into the system by aerial transport. Despite its quantity, quartz does not contribute to soil chemistry as it is rather inert. The most important oxides and hydroxides with respect to soil chemistry are the metal oxides and hydroxides of iron and manganese and in tropical soils also aluminum hydroxides.

3.2.1 Formation and structures

Iron(III)oxides are primarily weathering products. They remain stable in the soil as long as the millieu is aerobic. In anaerobic environments they take part in the microbial degradation of organic substances, where they function as electron acceptors. In this process the iron is being reduced and dissolved. The Fe^{2+} ions can

be transported through the soil until they reach aerobic areas where they mineralize in Fe(III) oxides again.

Iron from oxides and hydroxides is most easily available for redox reactions from those minerals with the lowest crystallinity. Thus the availability of iron from low crystalline or amorphous ferrihydrite is excellent, but iron from crystalline haematite and goethite seldom takes part in redox reactions.

The stability of iron minerals is not only dependent on the available oxygen but also on the pH in the soil environment.

3.2.2 Functions in soil

Iron oxides and hydroxides are important redox reaction partners in many processes in soils. One example is the function of Fe(III)oxides as electron acceptors in the microbial degradation of organic compounds (Chapter 3.2.1), another one the buffer function of iron hydroxide in soils at very low pH (around pH 2).

$FeOOH + 3\ H^+ + 4\ H_2O \rightarrow [Fe(H_2O)_6]^{3+}$

3.3 Clay minerals

Clay minerals derive from weathering of primary silicates (mainly feldspars) and are a major component of soils and sediments.

3.3.1 Structure

Clay minerals can be divided into two groups by structural differences. In 1:1 layer silicates an octahedron layer alternates with a tetrahedron layer. In the 2:1 layer silicates, an octahedron layer is sandwiched between two tetrahedron layers. The latter group, which also contains smectit and vermiculite, contains exchangeable cations or water between the tetrahedron octahedron sandwiches.

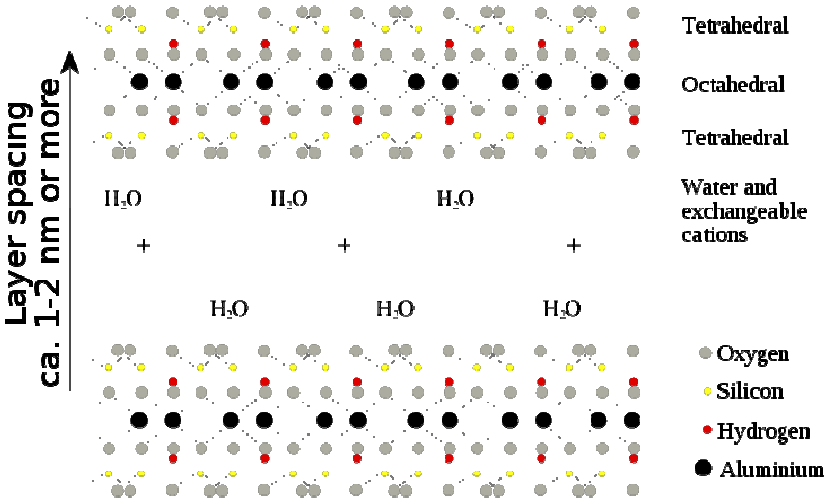


Fig. 3-4: *Structure of montmorillonite, a 2:1 layer silicate.*

Fig. 3-5: *Vermiculite, a 2:1 layer silicate.*

3.3.2 Functions in soils

Clay minerals are an important compound in soil. They can adsorb cations and molecules and are therefore important for the budget of vegetational available nutrients in the soil. Further, those with a high swelling capacity, as found in smectit, vermiculite or montmorillonite for example, play an important part in the water retention capacity of soils. By adsorbing cations and whole molecules, clay minerals also provide reaction surfaces for chemical processes. Clay minerals are often also found to form humus-clay-complexes with the humic soil components.

They also have a function as buffer in the soil and buffer around pH 4 by exchanging cations from their water layer for protons:

$$Clay\text{-}O^-M^+ + H^+ \rightarrow Clay\text{-}O^-H^+ \; M^+$$

4 Research aims

At the beginning of my thesis work I postulated that non-microbial CH_4 formation occurs in oxic soils. With this I oppose the common opinion that in soils only methanogenic formation in anoxic milieu is possible.

The hypothesis is based on previous findings by Keppler et al. (2006) that CH_4 is emitted from plant material under oxic conditions. Their findings started an on-going debate among plant and atmospheric scientists on the general possibility of CH_4 formation under oxic conditions.

Methane formation in oxic environments has not only be reported for plants but some observations of methane emissions have also been reported from oxic soils (Hao et al., 1988; Megonigal & Guenther, 2008; Andersen et al., 1998; von Fischer & Hedin, 2007), but have so far not been linked to a possible oxic and non-microbial methane source.

The main goals of this study are to provide proof for aerobic, non-microbial methane production from soils, investigate different environmental influences and to find first clues on a possible pathway and precursors.

The experiments described in chapter 6 were designed to address these questions by testing different soil types and soil components for their ability to release CH_4 under the influence of varying temperature, moisture, UV intensity, hydrogen peroxide levels and soil pH. Additional experiments were carried out to exclude possible artefacts by methanogenesis, methanotrophy or sorption processes on the sample surface.

5 Material and Methods

5.1 Samples

To address the main question of this study, whether there is methane formation in soils under oxic conditions, it was necessary to use a variety of soils in the experiments. Therefore six 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 (N 49° 57' 47'', E 8° 11' 01''). 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 (N 50° 0' 24.4", E 8° 11' 50.3"). 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.

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

Soil SHT is the clay rich horizon of the *terra fusca* from the same sampling site as SHA.

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 in the Wiehen Mountains (N 52° 15' 17.4", E 8° 52' 29.5").

Soil SB originates from Crossgar, N-Ireland and is a sample of an Oh-horizon of a deciduous forrest soil.

Peat PH was sampled at the peat bog "Großes Torfmoor" near Hille, Germany (N 52° 19' 23.7" E 8° 42' 34.7"). The top 10 cm of *sphagnum* peat was collected as a bulk sample. The top layer consisting of fresh *sphagnum* plants was removed prior to sample preparation. Subsamples were sterilised by gamma irradiation and autoclaving (described in 5.4.3).

5.2 Reagents

In addition to the soil samples some organic and some mineralic substances where used in the experiments to act as model soil compounds.

Lignin, humic acid, and vermiculite were obtained from Sigma-Aldrich (Taufkirchen, Germany).

Doubly distilled water (dd H_2O) was prepared with an ELGA UHQ-IIMK3.

5.3 Reaction vials

Reaction vials, 360 ml

Sample incubation took place in 360 ml glass vials 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).

Reaction vials, 40 ml

For some preliminary studies, sample incubation took place in 40 ml screw cap vials sealed with a hole type screw cap (Supelco) containing a PTFE/silicone septum (Supelco).

UV reaction chambers

The UV reaction chambers are in-house made glass chambers with a quartz glass lid and a side port for headspace sampling. They have a volume of 200 ml and an inner diameter of 6 cm. The irradiated surface measures 19.63 cm^2.

For the investigation of methane emissions under UV irradiation a UV reaction cell (Althoff, 2012) was built by the workshop and glass workshop of the MPIC.

It consists of a cylindrical glass body with a wide brim at the top and a sideport at one third of the height. The sideport is sealed with an ultra-torr fitting with a septum and allows multiple sampling from the gas phase during the experiment.

The UV cell (Fig. 5-1) has an inner diameter of 5 cm and a volume of 206 ml. The cell is closed with a UV transparent quartz glass lid and made air tight by a rubber O-ring (inner rubber ring). Both are held in place by a collar which is screwed tight from below the brim of the cell and above the lid. A second rubber ring (outer rubber ring) protects the quartz glass from too much pressure from the collar. To eliminate UV-C

radiation below 295 nm, a cellulose diacetate (CDA) film, which serves as a UV-C filter, is placed between the quartz glass plate and the outer rubber ring.

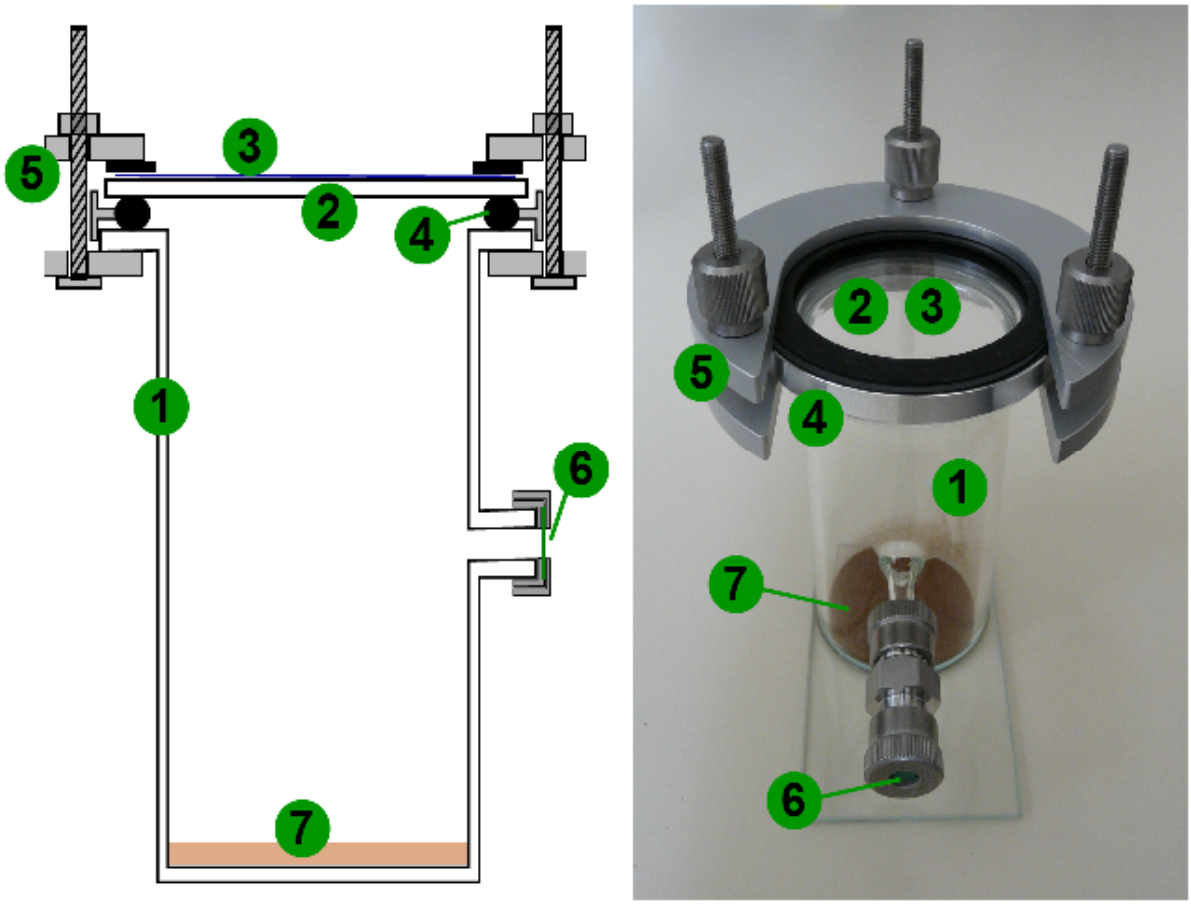


Fig. 5-1: *Scheme and photo of UV reaction cell. (1) glass body, (2) quartz-glass lid, (3) cellulose diacetate film, (4) inner rubber seal, (5) collar, (6) septum, (7) sample.*

5.4 Sample preparation

5.4.1 Lyophillisation

In preparation for the experiments all soil samples were freeze dried using an Alpha 1-2 LDplus freeze dryer (Christ, Germany, Version 1.26). The main drying is conducted at 0.63 mbar and -25 °C.

5.4.2 Homogenisation

The freeze dried samples were homogenized using an ELTA UM105 electronic coffee grinder.

5.4.3 Sterilisation

Sterilisation of soil samples was either performed in an Advantage-Lab AL02-03 autoclave (T: 121 °C, p: 1 bar, t: 10 min) or by exposure to γ-radiation using a ^{60}Co source (dose, 25 kGy; dose rate, 2.2 kGy h^{-1}; temperature, 4 °C).

5.5 Analytical instruments

5.5.1 GC-FID

For the quantitative evaluation of CH_4 emissions headspace samples from the reaction vials were analysed with GC-FID (Gas chromatograph with flame ionisation detector). In these experiments a Shimadzu GC-14B and a Varian GC-FID of similar setup were used.

In gas chromatography the sample gas is transported through a column by a carrier gas flow. In the column, the gas molecules (mobile phase) interact with the column filling (stationary phase). The duration of this interaction depends on chemical and physical properties, which are specific for each compound. Therefore the different compounds are separated and reach the detector after specific retention times.

For all experiments except the UV experiments the Shimadzu GC-14B was used. A gas mixtures containing 8.905 ppm CH_4 and an air sample with a known CH_4 content of 1.905 ppm were used as reference standards.

The temperature in the GC oven of the Shimadzu GC is set to 125 °C isothermal. The column used for separation is a 2 m high grade steel column. It has an inner diameter of 3.175 mm and as filling a 5A 60/80 molecular sieve from Sigma Aldrich. Using the Shimadzu GC-14B a precision of +/- 11 ppbv can be reached.

For the UV studies CH_4 concentrations were determined with a GC-FID (Varian STAR 3400 CX) of similar setup with the same column and filling. The oven temperature of the Varian GC is 80 °C isothermal. An air sample with a known CH_4 content of 1.736 ppm was used as a reference standard.

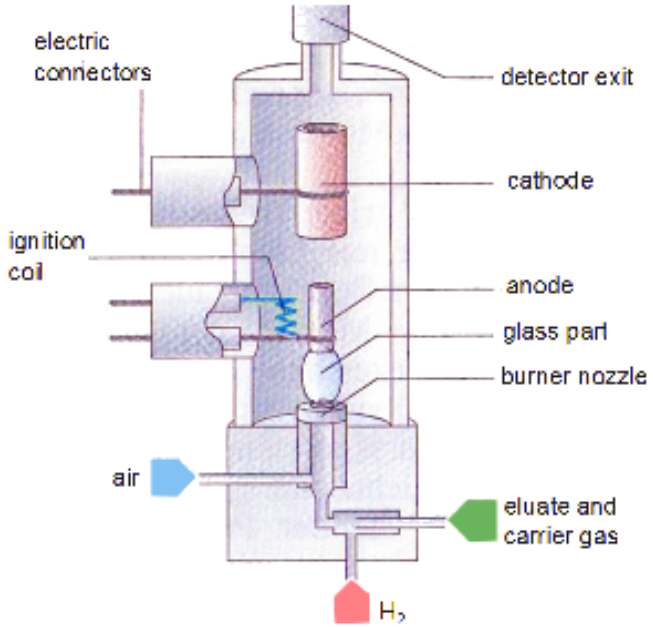


Fig. 5-2: *Scheme of flame ionization detector (FID). Modified from Schwedt (1996).*

Measurement procedure at the GC FID

With a gas tight syringe, a 5 ml gas sample is drawn from the headspace of the reaction vial. This is injected through the septum of the injection port into the sample loop. Both systems work with a sample loop with a defined volume of 2 ml. A six-point valve (VICI) changes the loops connections to the injection port and the carrier gas flow (Fig. 5-3). In position A (injection position) the loop is connected to the injection port and an open piece of tubing. Excess gas leaves through this exit. Switching the valve into position B, the measuring position, connects the sample loop with the carrier gas flow and allows the 2 ml gas sample to be carried into the system. When switching into measuring position, chromatogram plotting is started simultaneously, either manually (Shimadzu GC-14B) or automatically (Varian). The gas (carrier gas + sample gas) flows through the column, where it is separated, and then to the flame ionisation detector, where it is first mixed with hydrogen and air and then burned in a glass chamber (Fig. 5-2). The ionisation of the gas in the flame leads to an increase of current between the electrodes of the collector. This increase in the voltage is measured and the signal is passed on to the computer, where it is plotted in the chromatogram.

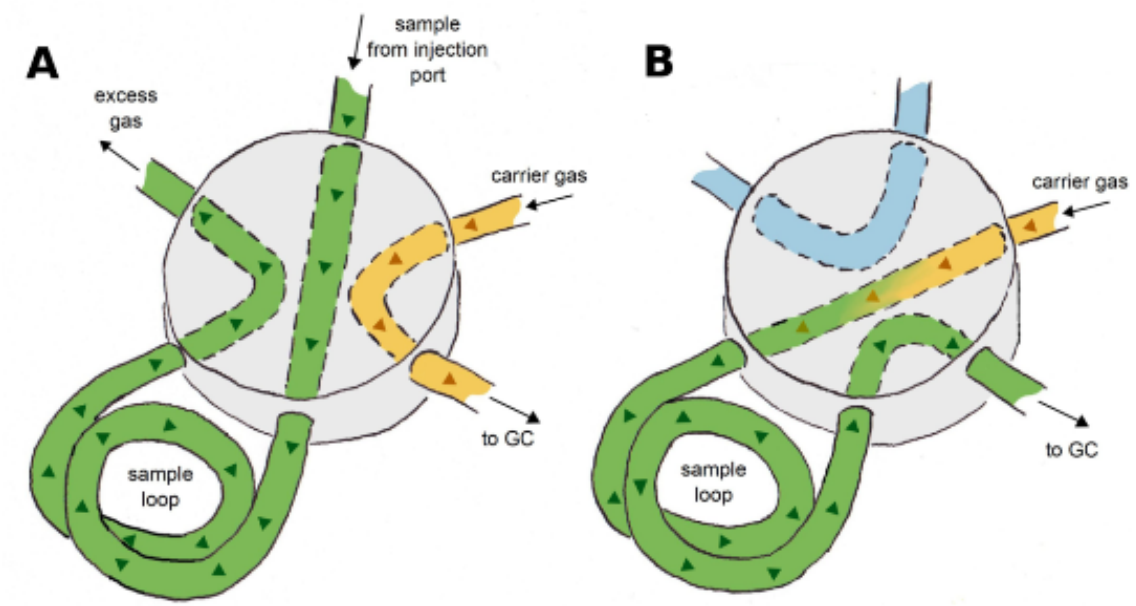


Fig. 5-3: *Scheme of six-port sample valve in sampling position (A) and measuring position (B).*

5.5.2 Determination of carbon content with SC Analyser and by loss on ignition

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 Belfast (SB) the organic carbon content was determined by loss on ignition. Therefor the weight loss of 1 g sample material was determined after two hours at 600 °C (n=3). Half of the loss was assigned to organic carbon combustion.

5.5.3 $\delta^{13}C$ sample analysis with PreCon-GC-C-IRMS

The PreCon-GC-C-IRMS is a gas chromatography combustion isotope ratio mass spectrometer supported by a cryogenic pre-concentration unit (Fig. 4-4).

In the preconcentration unit the sample vial is connected to an evacuated sample loop with a volume of 40 ml, but at first separated by a valve. By opening the valve 40 ml of the headspace gas is sucked into the sample loop. On its way the sample passes a CO_2 trap (Ascarite II). A sixport valve (Fig. 4-3) connects the loop with the carrier gas flow. From the sample loop the gas sample is flushed trough a first trap consisting of a 1/8” stainless steel tube without filling, which is cooled to -150°C for the removal of water and CO_2 residues. It is then flushed to a second trap, a 1/8” stainless steel tube filled with Hayesep D and cooled to -130 °C, for trapping of CH_4.

After 10 min. trap 2 is heated to 50 °C within 10 s to release CH_4 back into the gas flow. CH_4 is then trapped again on a focus trap. This is a 0.5 m PoraPlot column with an inner diameter of 0.25 mm, placed in liquid nitrogen at –196 °C. After 10 min of cryofocussing the trap is lifted out of the dewar and CH_4 can be transported into the GC unit.

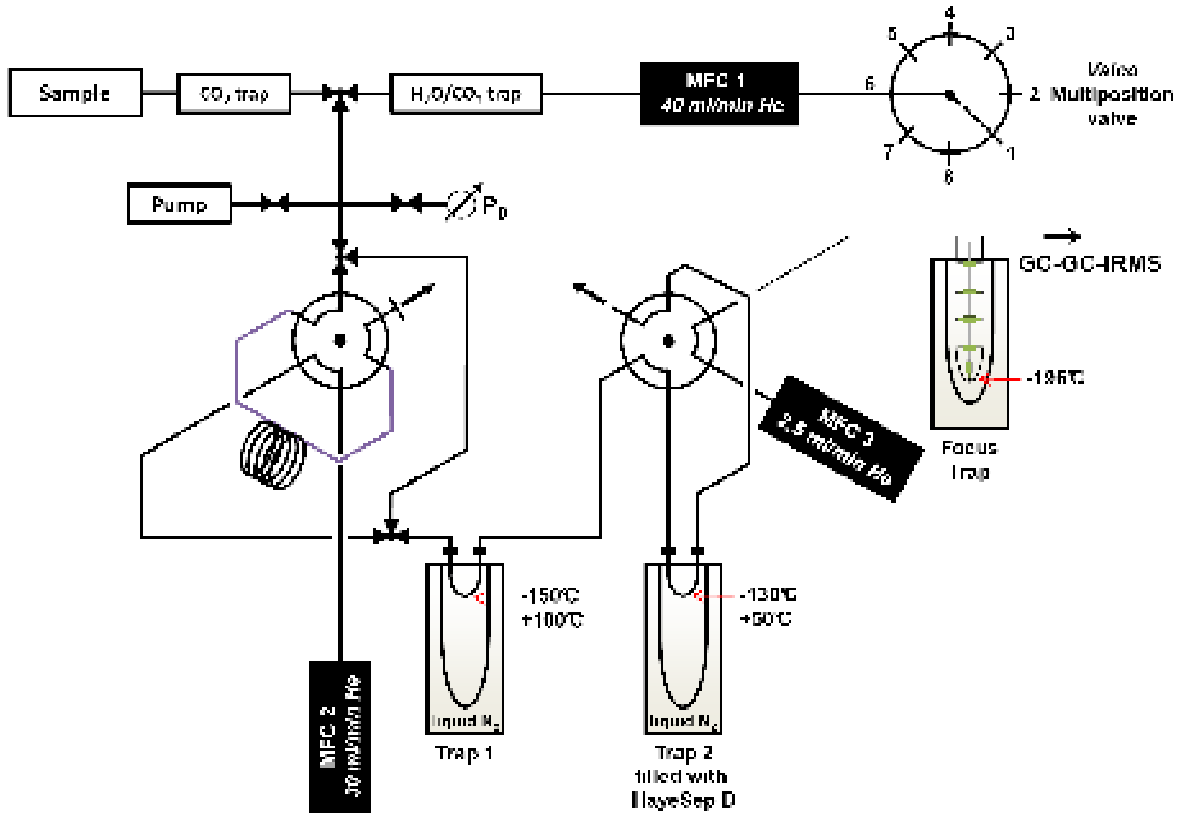


Fig. 5-4: *Scheme of the cryogenic pre-concentration unit. MFC = mass flow controller; P_0 = pressure gauge.*

The gas chromatograph (HP 6890N, Agilent, Santa Clara, USA) is fitted with a GS-Carbonplot capillary column (30 m x 0.32 mm i.d., d_f 1.5 µm; Agilent, Santa Clara, USA) and a PoraPlot capillary column (25 m x 0.25 mm i.d., d_f 8 µm; Varian, Lake Forest, USA). The oven temperature is kept at 30 °C.

After passing the GC, the separated analytes reach the oxidation reactor which consists of an Al_2O_3 ceramic tube with a length of 320 mm and 0.5 mm inner diameter, filled with oxygen activated, twisted Cu/Ni/Pt wires and is kept at 960 °C. In the reactor NiO oxidises the organic compounds of the sample. This reaction is catalysed by platinum and NiO is reduced in the process to Ni but is immediately

oxidised again by CuO. The reactor can be regenerated by reoxidising the reduced Cu_2O.

The resulting CO_2 is then passed on to the DeltaPlusXL IRMS (ThermoQuest Finnigan, Bremen, Germany) where it is separated based on its mass charge ratio.

Depending on the oxidised carbon isotopes from the sample and the different oxygen isotopes they can be oxidised with, the resulting CO_2 molecules have a mass of either 44 ($^{12}C^{16}O^{16}O$), 45 ($^{13}C^{16}O^{16}O$; $^{12}C^{17}O^{16}O$) or 46 ($^{12}C^{16}O^{18}O$; $^{12}C^{17}O^{17}O$). These masses are separated in the IRMS and detected separately (Fig. 5-5).

From the masses 44 and 45 the $^{12}C/^{13}C$ ratio can be calculated after subtracting the ^{17}O Anteil of mass 45 wich can be calculated from mass 46 because the $^{17}O/^{18}O$ ratio is constant in natural samples. The amount of $^{12}C^{17}O^{17}O$ (mass 46) is neglectably small and does not influence the calculation.

With this system it is possible to measure δ13C values of samples with mixing ratios down to 100 ppbv.

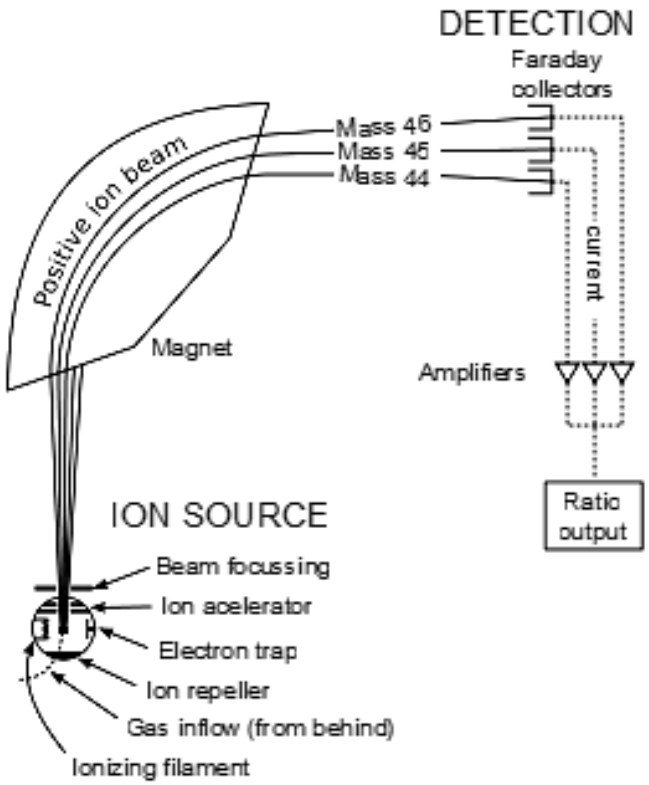


Fig. 5-5: *Schematic of an IRMS detector (USGS).*

Three working standards (isometric instruments, Victoria, Canada) with $\delta^{13}C$ values (in ‰ vs. V-PDB) of -23.9 ± 0.2 ‰, -38.3 ± 0.2 ‰ and -54.5 ± 0.2 ‰ were employed in the measurements to correct the values acquired from CH_4 analysis. Additionally high purity carbon dioxide gas (carbon dioxide 4.5, Messer Griesheim, Frankfurt, Germany) with a known $\delta^{13}C$ value of -23.6 ‰ (VPDB) is used as the reference gas.

5.6 UV Experiments

Ultraviolet (UV) radiation has been shown to be an important factor for aerobic production of CH_4 from plant tissues and pectin. It was therefore important to address the possibility of UV-induced CH_4 formation from soil material in the experiments.

Typical ambient (unweighted) summer UV-B irradiances at Earth surface range from 2 W m^{-2} (mid latitudes) to 4 W m^{-2} (tropics) (Bernhard et al., 1997). Due to absorption of shortwave radiation in the atmosphere the solar UV spectrum that reaches the earth surface ranges from 295-480 nm.

5.6.1 UV lamp set up

In the laboratory experiments the UV source is an Osram Vitalux 300W light bulb. The intensity of the UV-B irradiance from the Vitalux UV lamp is adjusted by the distance between lamp position and sample surface. The spectrum of the lamp, however, starts already at 250 nm and thus contains some UV-C radiation as well. Therefore it is important to block wavelengths of the range of 250-295 nm.

The solution to this problem is to add a layer of cellulose diacetate film which excludes wavelengths below 295 nm. A combination of the Vitalux UV Lamp with the cellulose diacetate film is considered to simulate solar UV irradiance on the earth surface.

Two UV reaction cells (described in chapter 5.3.1) can be placed under the lamp simultaneously. They are loaded with 1-5 g of sample material each. This amount depends on the sample density and has to be sufficient to cover the bottom of the chamber completely. One cell is covered with a non-UV transmitting glass plate to act as a control. The area under the lamp is cooled by two 12 V fans for the irradiation period to keep the temperature inside the cells at 29-32 °C. The larger volume of 206 ml allows to sample from the same cells at different time points.

5.6.2 Spectral comparison of Osram UV lamps.

The observation that the Osram Vitalux lamps differed from each other in their spectra would probably have led to differences in the promotion of CH_4 formation in soils under otherwise same conditions and the same total UV-B. To compensate this the phenomenon was monitored and considered in the experiments. Spectra of all four lamps were plotted and compared. Peaks of maximum intensities appeared at the same wavelengths but their ratios differed between the lamps. Lamp spectra can be found in the Appendix (App 1-1).

6 Experiments and Results

One major topic is the possibility of non-methanogenic oxic methane production in soils. A second one is the influence of different environmental factors on the process. The samples where therefore subject to experiments with varying temperature, moisture, UV intensities and H_2O_2 levels, described in the following chapter. Additional experiments were performed to exclude possible artefacts in the measurements such as sorption/desorption processes, methanotrophy and methanogenesis.

6.1 Influence of temperature

6.1.1 Temperature dependency of CH_4 emissions from soils

The experiment was designed to determine the temperature dependency of CH_4 formation in several forest soils (SHA, SG, SL) and a sphagnum peat sample (PH). The samples were incubated at temperatures ranging from 30 to 90 °C and the amounts of CH_4 generated were measured after 24 hours of incubation. For peat PH CH_4 emissions ranged from 0.05 ± 0.02 ng g^{-1} (dw) h^{-1} at 30 °C to 7.11 ± 0.59 ng g^{-1} (dw) h^{-1} at 90 °C. Three soil samples, SHA, SG and SL, with an organic carbon content between 4.0 and 5.8 %, were also investigated (see Table 6-1). For all samples measured the temperature curves showed an exponential increase of CH_4 emissions with rising temperature (Fig 6-1).

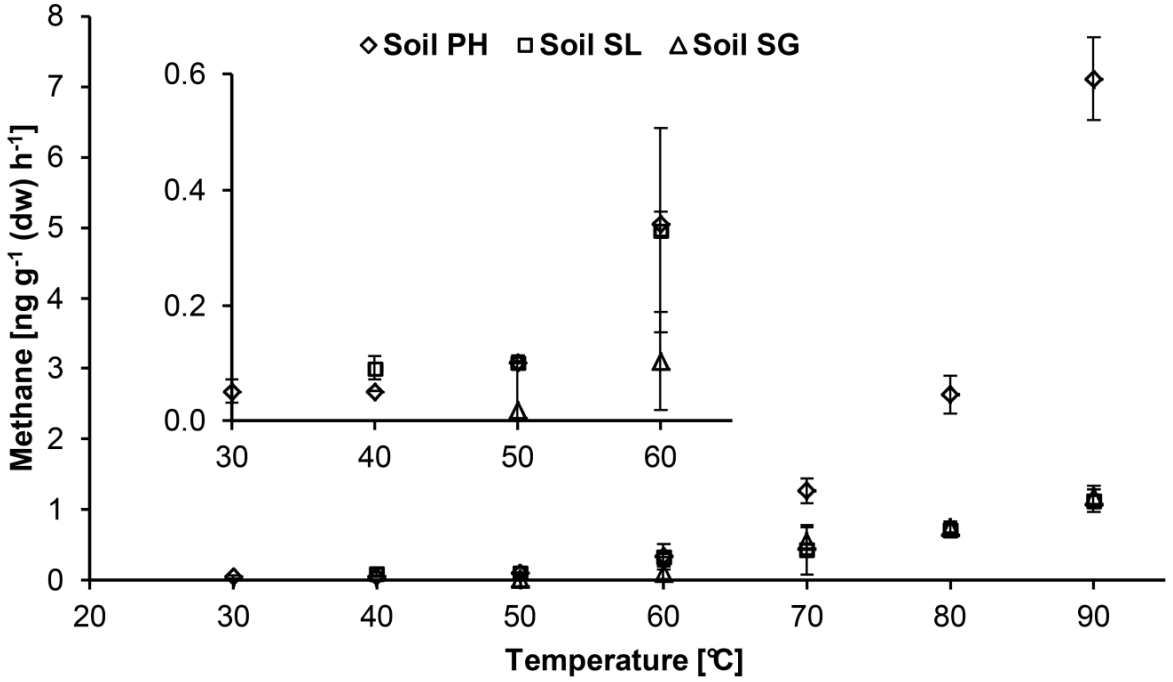


Fig. 6-1: *Formation of CH_4 from soil with increasing temperature. Temperature dependence of CH_4 emissions from peat PH, soil SL and soil SG. Data show mean value ± SD (n=5). Inset shows magnified area between 30 and 60 °C.*

6.1.2 Temperature curve for organic soil compounds

In addition to the soil samples two organic model compounds, lignin and humic acid, were investigated for their potential to release CH_4 under elevated temperatures.

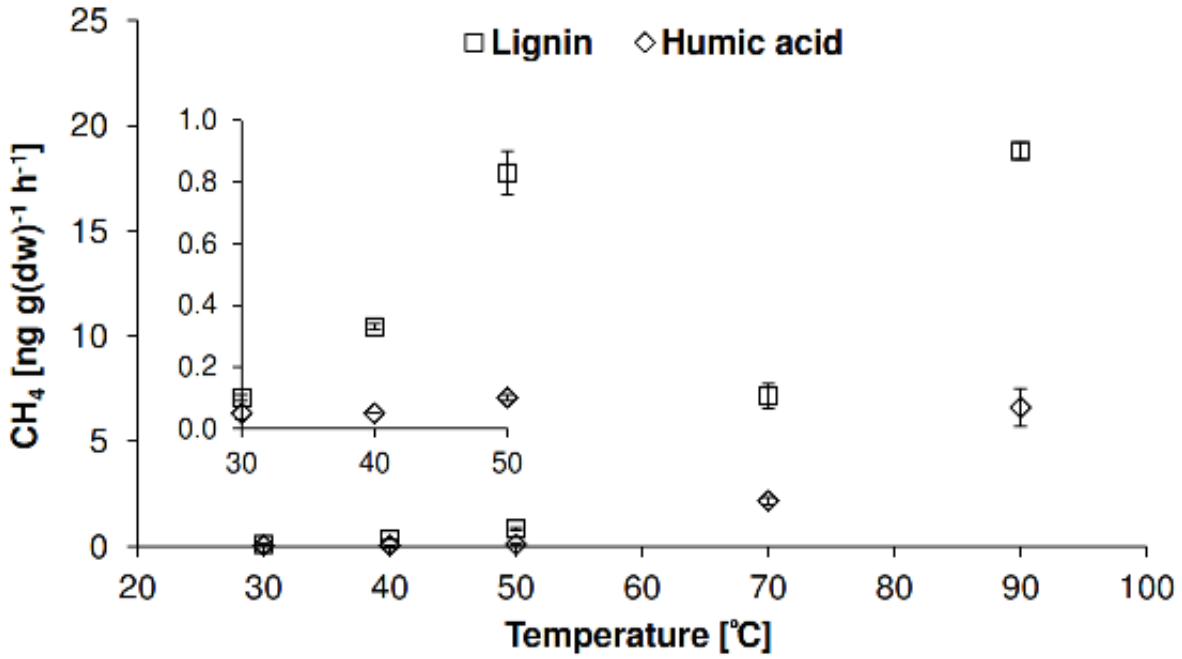


Fig. 6-2: *Formation of CH_4 from organic soil components with increasing temperature. Temperature dependence of CH_4 emissions from lignin and humic acid. Data show mean value ± SD (n=5). Inset shows magnified area between 30 and 50 °C.*

These substances, with an organic carbon content of 49.5 % and 43.5 % respectively, were also heated up to 90 °C and showed even higher CH_4 emission increases (at 30 °C 0.1 ± 0.01 ng g^{-1} (dw) h^{-1} for lignin and at 90 °C 18.3 ± 0.4 and 6.6 ± 0.9 ng g^{-1} (dw) h^{-1} for lignin and humic acid, respectively) than the organic rich peat PH.

6.1.3 Arrhenius plot

The experimental data from temperature experiments on samples SL, SG and PH as well as lignin and humic acid was used to draw Arrhenius plots for CH_4 formation (Fig. 6-3 and 6-4), because the activation energy (E_a) that can be calculated from an Arrhenius plot can indicate whether an abiotic or an enzymatic reaction occurred. Activation energies below 50 kJ mol^{-1} are considered to be an indicator for biological reactions, whereas E_a above this value are strong evidence for an abiotic reaction

(Schönknecht et al., 2008). The activation energies for CH_4 formation from each material are listed in Table 6-1. They range from 50.1 to 84.1 kJ mol^{-1}.

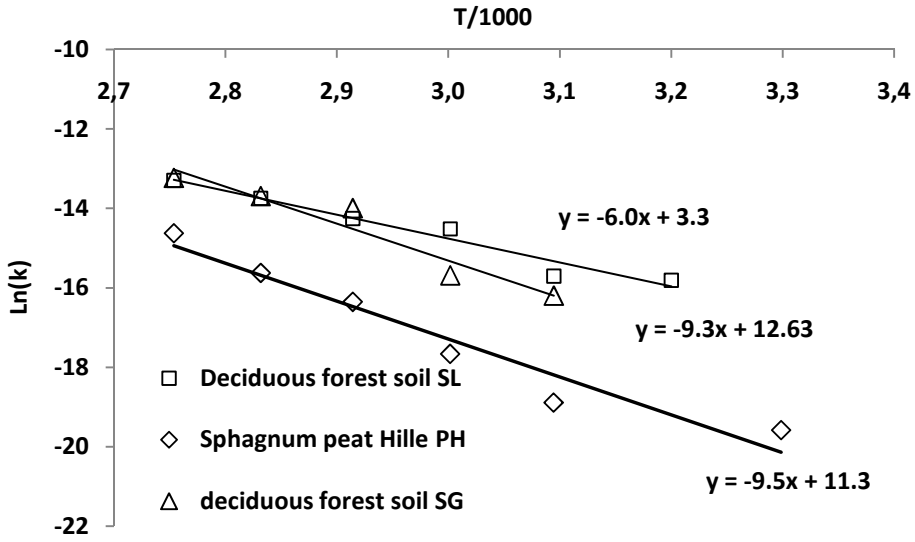


Fig. 6-3: *Arrhenius plot for the temperature experiments on peat PH and the soils SL and SG.*

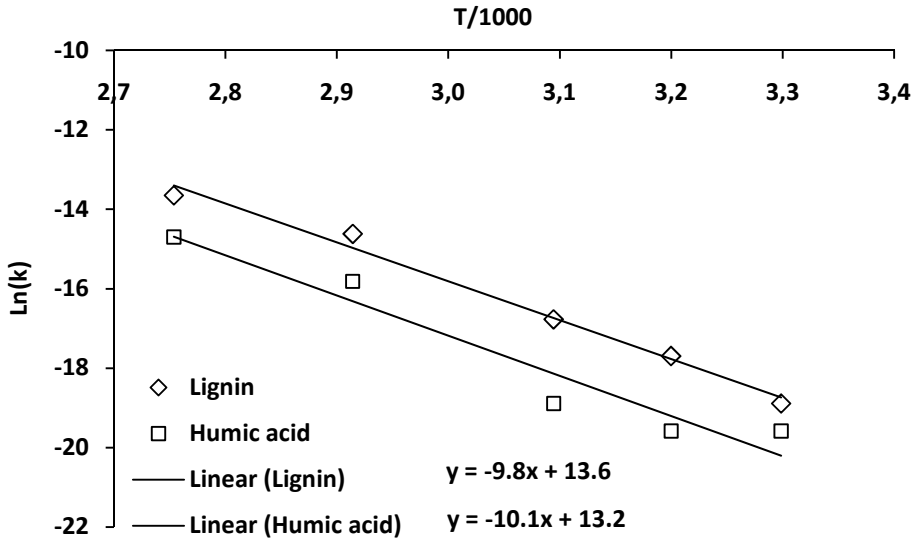


Fig. 6-4: *Arrhenius plot for the temperature experiments on lignin and humic acid.*

Sample	Corg [% dw]	CH_4 [ng g(dw)$^{-1}$ h^{-1}]					Act. energy e_a [kJ mol^{-1}]
		30 °C dry	40 °C dry	50 °C dry	70 °C dry	90 °C dry	
Sand (quartz)	< 0.20	-	n.d.[b]	-	n.d.[b]	-	-
Vermiculite	< 0.20	-	n.d.[b]	-	n.d.[b]	-	-
Lepidocrocite	< 0.20	-	n.d.[b]	-	n.d.[b]	-	-
Sphagnum peat	49.24 ± 0.25	0.05 ± 0.02[b]	0.05 ± 0.01[b]	0.1 ± 0.01	1.87 ± 0.11[b]	7.11 ± 0.59	79.2
SHA	5.82 ± 0.05	n.d.	0.08 ± 0.03[b]	-	0.45 ± 0.02[b]	-	-
SHT	1.98 ± 0.01	n.d.	0.03 ± 0.00[b]	-	0.19 ± 0.02[b]	-	-
Deciduous forest soil O_h (SW)	23.4 %	n.d.	n.d.	-	-	-	-
Coniferous forest soil A_h (SG)	5.0 %	n.d.	n.d.	0.06 ± 0.05	0.55 ± 0.19	1.19 ± 0.15	77.5
Deciduous forest soil A_h (SL)	4.0 %	n.d.	0.09 ± 0.02	0.10 ± 0.00	0.43 ± 0.35	1.12 ± 0.16	50.1
Pectin	38.93 ± 0.34	-	0.08 ± 0.03[b]	-	2.99 ± 0.16[b]	-	-
Cellulose	42.45 ± 0.24	-	0.00 ± 0.03[b]	-	0.02 ± 0.00[b]	-	-
Humic acid (HA)	43.5 %	0.06 ± 0.02	0.82 ± 0.06	-	2.16 ± 0.18	6.60 ± 0.60	84.1
Lignin (LIG)	49.55 ± 0.67	0.10 ± 0.01[b]	0.33 ± 0.01[b]	0.83 ± 0.07[b]	7.14 ± 0.59[b]	18.8 ± 0.40	81.5

Table 6-1: *Methane emissions from dry material at different temperatures and calculated activation energies.*

± represents the standard deviation (SD; n=3-5), dw = dry weight, n.m. = not measured, [b] data from Hurkuck et al., (2012)

6.1.4 Correlation of CH_4 emissions to C_{org}

The experimental data shown in Table 6-1 was used to plot CH_4 emissions under UV-B irradiation against the organic carbon content of the sample materials.

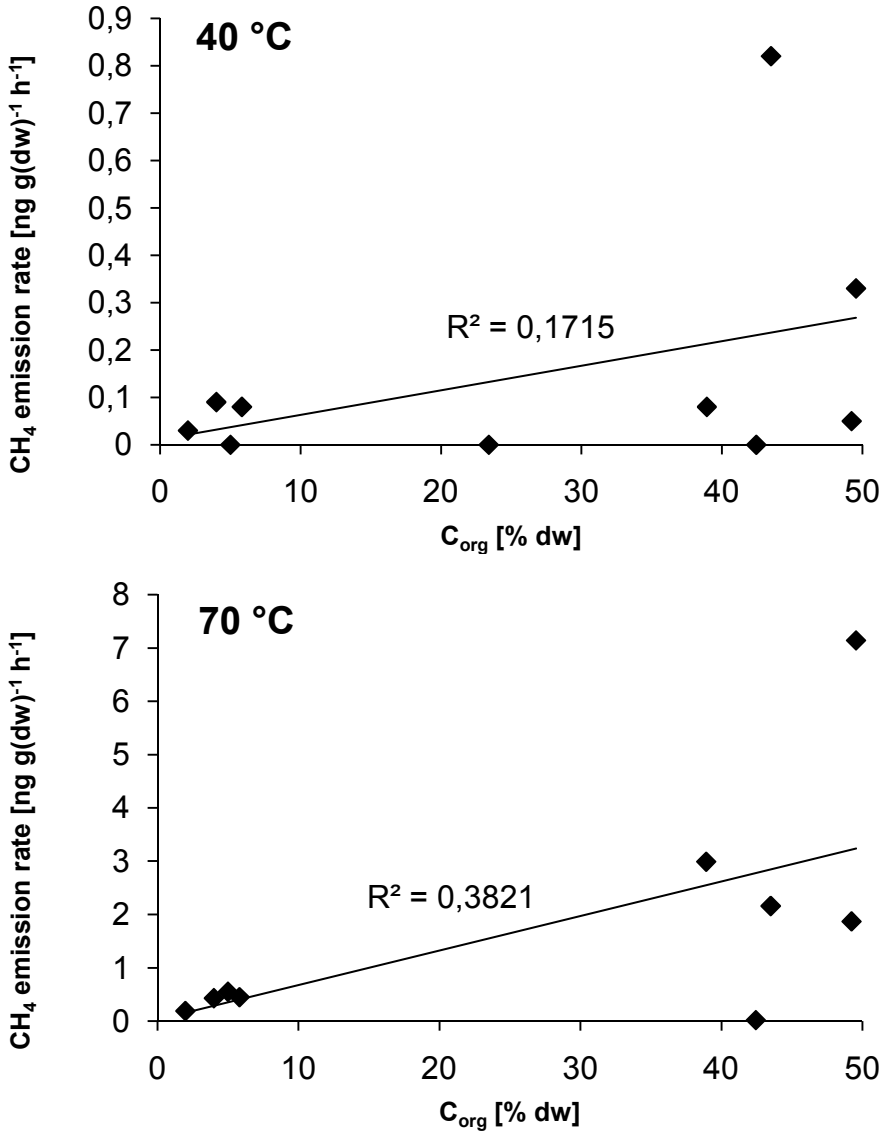


Fig 6-5: *Comparison of sample carbon content and CH_4 emission rates at 40 and 70 °C.*

The plots show no evidence for a linear correlation of C_{org} and CH_4 emission (Fig. 6-5).

6.2 Influence of water

6.2.1 Methane release from dried soils and organic samples after addition of water

The intention for the following experiments was to study the effect of soil moisture on CH_4 release from different samples and at different temperatures.

5 g of sample were infused with 10 ml water and incubated for 24 h at 30 and 40 °C. For some materials the experiments were also performed at 50 and 70 °C.

Wet samples showed without exception higher CH_4 emissions than dry samples. For wet samples also a temperature dependency could be observed (Table 6-2).

Sample	pH	Corg [% dw]	CH_4 [ng g(dw)$^{-1}$ h^{-1}]			
			30 °C wet	40 °C wet	50 °C wet	70 °C wet
PH	3.7	49.24 ± 0.25	0.19 ± 0.01	0.41 ± 0.01	0.54 ± 0.10	6.24 ± 0.39 [b]
SHA	6.7	5.82 ± 0.05	n.d.	0.20 ± 0.05 [b]	-	0.97 ± 0.10 [b]
SHT	7.1	1.98 ± 0.01	n.d.	n.d.	n.d.	0.18 ± 0.01 [b]
SW	7.4	23.4 %	0.23 ± 0.02	0.24 ± 0.06	-	-
SG	7.2	5.0 %	n.d.	0.04 ± 0.01	-	-
SL	4.4	4.0 %	0.06 ± 0.01	0.10 ± 0.04	-	-
Pectin	-	38.93 ± 0.34	-	0.20 ± 0.02 [b]	-	6.69 ± 0.52 [b]
Cellulose	-	42.45 ± 0.24	-	0.04 ± 0.02 [b]	-	0.20 ± 0.02 [b]
Humic acid (HA)	5.5	43.5 %	0.18 ± 0.03	3.10 ± 0.34	-	-
Lignin (LIG)	9.6	49.55 ± 0.67	0.65 ± 0.02[b]	1.89 ± 0.20[b]	3.10 ± 0.43[b]	7.74 ± 0.77[b]

Table 6-2: *Methane emissions from wet material at different temperatures and pH values for wet materials.*

6.2.2 Correlation of CH_4 emissions to C_{org}

The CH_4 emission rates given in table 6-2 were plotted against the organic carbon content of the respective samples (Fig. 6-6). When data for all samples is plotted (Fig 6-6a), no evidence for a linear correlation of CH_4 emissions to C_{org} can be derived. If the database is restricted to soil samples (Fig 6-6b), a trend towards a linear correlation is noticeable.

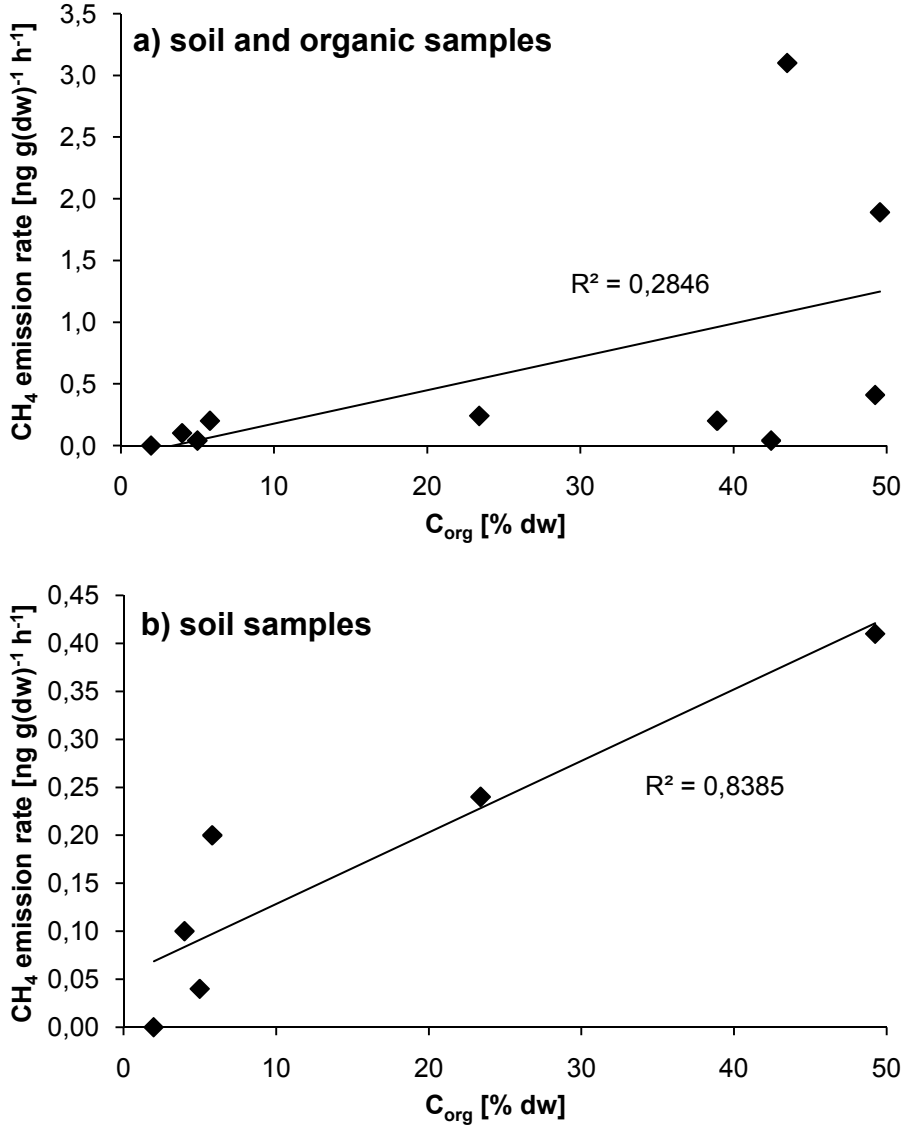


Fig 6-6: *Correlation of sample carbon content and CH_4 emission rates in wet samples at 40 °C.*

6.2.3 Dependency on water content

To determine the dependency on water content, sets of peat PH (5 g) were supplemented with 1, 5 and 10 ml doubly distilled water (resulting in water contents of 16.7, 50 and 66.7 %) and incubated at 30 °C for 24 hours. The addition of 1 ml water resulted in a still mostly dry, powdery sample with a small area of moist, clumped peat. 5 ml however were enough to moisten a large fraction of the sample. In this set the sample was completely moist after the incubation. The addition of 10 ml sufficed to wetten the whole sample instantly with a little of free water being left.

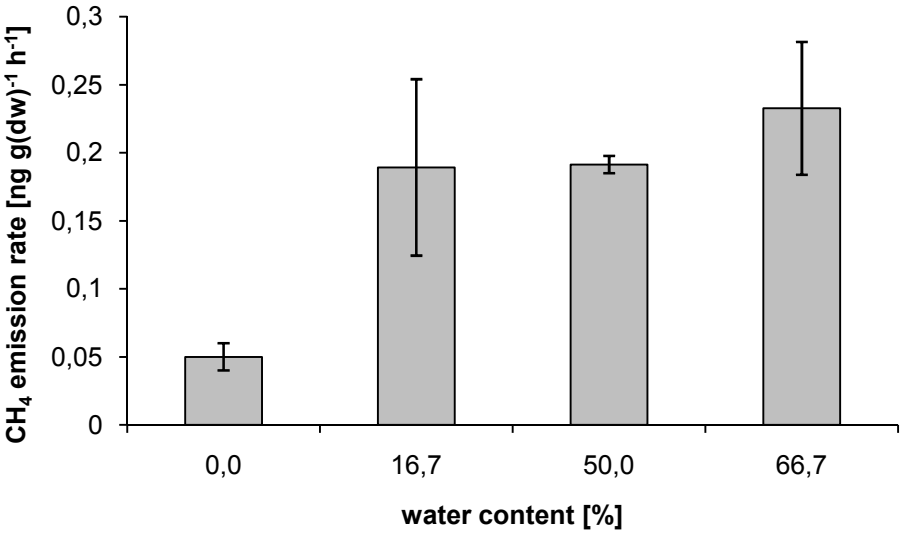


Fig. 6-7: *Methane emissions from the different moisture steps and from dry material. Temperature = 30 °C, Error bars indicate standard deviation (n=5).*

The results (Fig. 6-7) show, that the amount of added water is not crucial for the extent of methane emission. The only important factor is the absence or presence of water, at least for the ratios used in the experiments.

6.2.4 Drying-rewetting-cycles:

In most natural environments soils are subject to cycles of varying precipitation and evaporation. The effect of consecutive changes in the water availability on the processes leading to CH_4 emissions was investigated with the following experiments.

Peat PH

Peat PH (5 g in 360 ml screw cap vials, n=5) was incubated for 24 h at 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 the headspace was analysed for CH_4 content. The samples were frozen and freeze dried directly after each measurement. After being rewetted and incubated, the headspace was analysed again for CH_4. This cycle was repeated at least five times at all temperatures. At 40° C it was repeated ten times to see if a decrease of CH_4 emission could be observed, but emissions remained in the range of 0.5 ng $g(dw)^{-1}$ h^{-1} for all cycles.

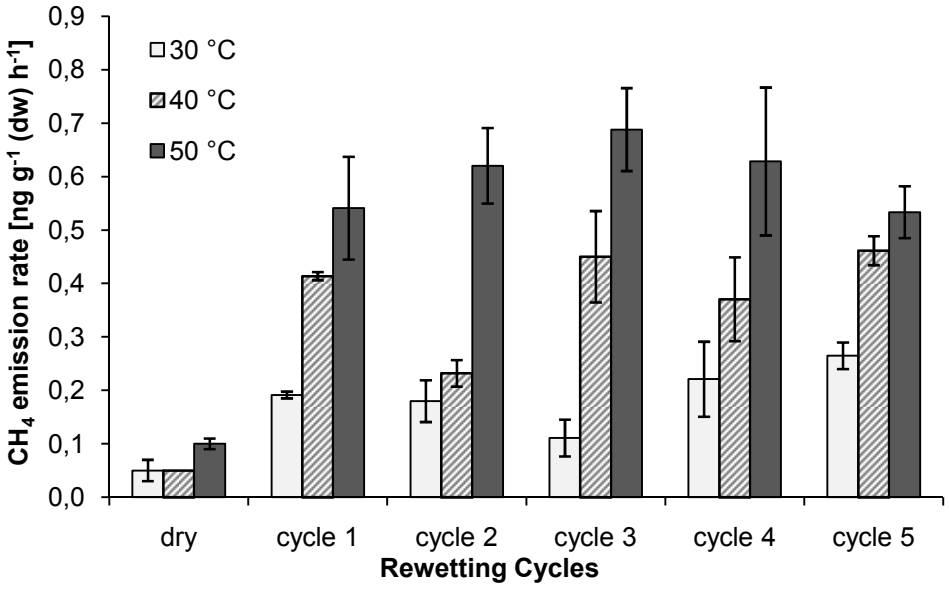


Fig. 6-8: *Emissions from dry material and rewetting cycles 1-5 at different temperatures from peat PH. Error bars indicate standard deviation (n=5).*

Soil Häverstädt and Lignin

The experiment was repeated with 5 g of soil "Häverstädt" and with 5 g Lignin (360 ml screw cap vials, n=5).

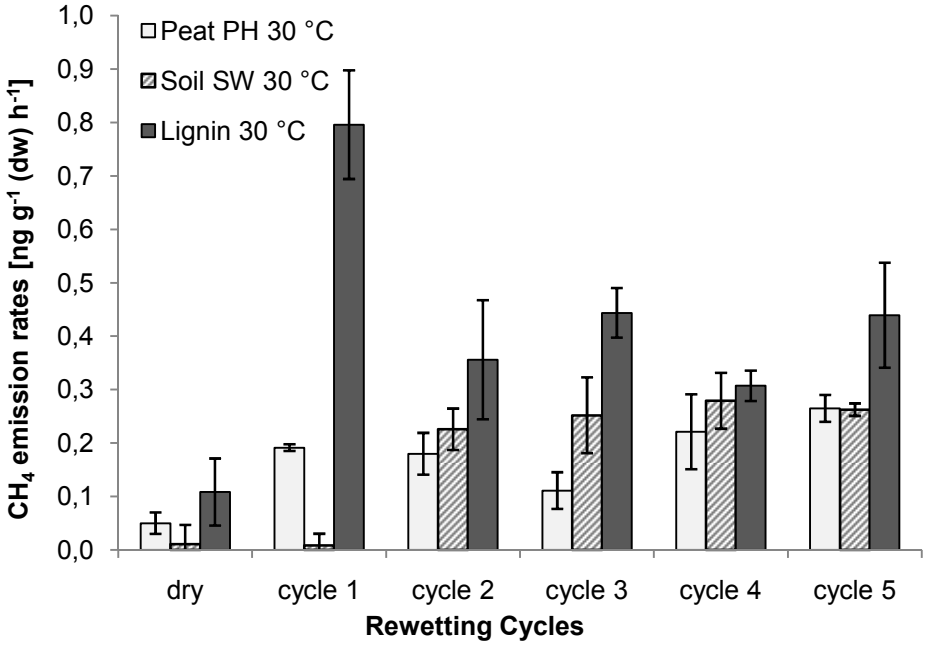


Fig. 6-9: *Emissions from peat PH, soil SW and lignin, from dry materials and rewetting cycles 1-5 at 30 °C. Error bars indicate standard deviation (n=5).*

Most interesting in the rewetting cycles using SW (soil Wiehen) at 30 °C is the observation that methane emission did not start until the second cycle but then stayed around 0.25 ng $g(dw)^{-1}$ h^{-1}. This effect could also be seen in a repetition of the experiment.

The lignin samples show a different behaviour: The CH_4 emission is highest in the first cycle (seven times the dry value) and then declines to a lower rate in the second (three times the dry value) which then stays constant for all following cycles.

6.3 Influence of pH

Different environmental factors influence the acidity of soils. To determine a possible influence of pH on CH_4 formation, the experiments with wet peat (PH) (Chapter 6.2.1) and wet soil (SB) were repeated with acidic to neutral solutions with a pH-value between 3.7 to pH 7. Suspensions of PH and SB in water showed pH values of 3.7 and 4.8 respectively. With the replacement of water with NaOH according to an afore determined titration curve (Table 6-4), the pH was shifted to less acidic values in the other sets. Quintets of the samples were incubated for 5 h at 40 °C prior to measurements.

pH	sample	µl NaOH (1M)	µl H_2O
4.82	0.5 g SB	0	2500
5.51	0.5 g SB	125	2375
6.04	0.5 g SB	200	2300
7.03	0.5 g SB	350	2150
3.69	0.5 g PH	0	2500
5.01	0.5 g PH	475	2025
5.99	0.5 g PH	950	1550
7.09	0.5 g PH	1650	850

Table 6-3: *Proportions of NaOH, soil, and dd H_2O for experiments with different initial pH values.*

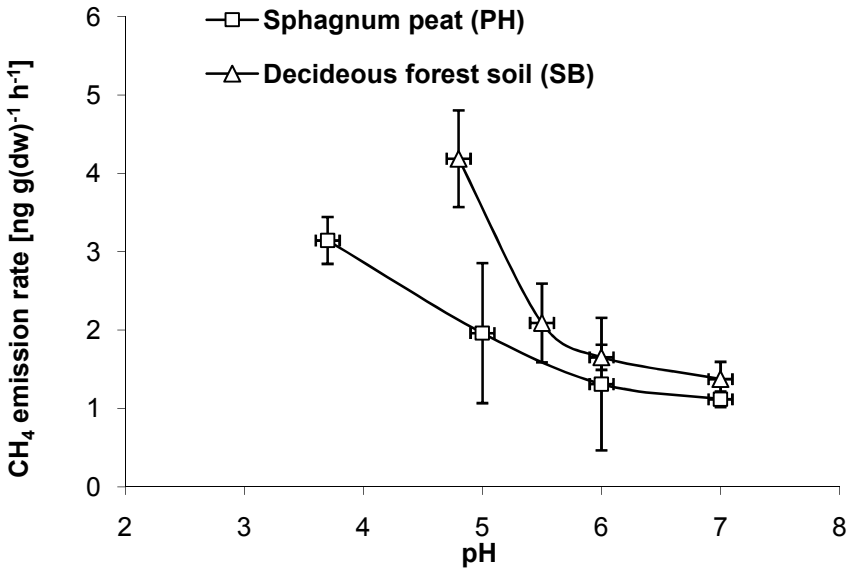


Fig. 6-10: *Influence of pH on CH_4 emissions from soil SB and peat PH. Error bars indicate standard deviation (n=5).*

A prominent influence of pH on CH_4 emissions could be observed for the soil (SB), where the reaction leading to CH_4 emissions seems to be promoted by acidic environments. In the peat samples a similar trend can be observed (Fig. 6-10).

6.4 Influence of hydrogen peroxide

The main sources of hydrogen peroxide (H_2O_2) in soils are microbial activity, root exudates and fungi. It is a common reaction partner for many processes in soils. Therefore it was considered highly possible that it plays a role during non-microbial CH_4 formation and turns out to be an environmental factor influencing the production rates. The following experiments were designed to evaluate a possible influence of H_2O_2 on CH_4 formation in soils.

6.4.1 Peat and soil

Eight batches of five vials (volume 360 ml), each containing 5 g of peat Hille (PH), were prepared. The samples were supplemented with 10 ml aqueous solution of varying H_2O_2 concentrations (0-25 mM). They were closed immediately after introduction of the solution and incubated for 24 h at 40 °C. The batch that was supplemented with doubly distilled water was used as background and the mean of its methane emission was substracted from the values obtained from the vials containing H_2O_2. The same experiment was performed with the sample material soil Hainich (SHA).

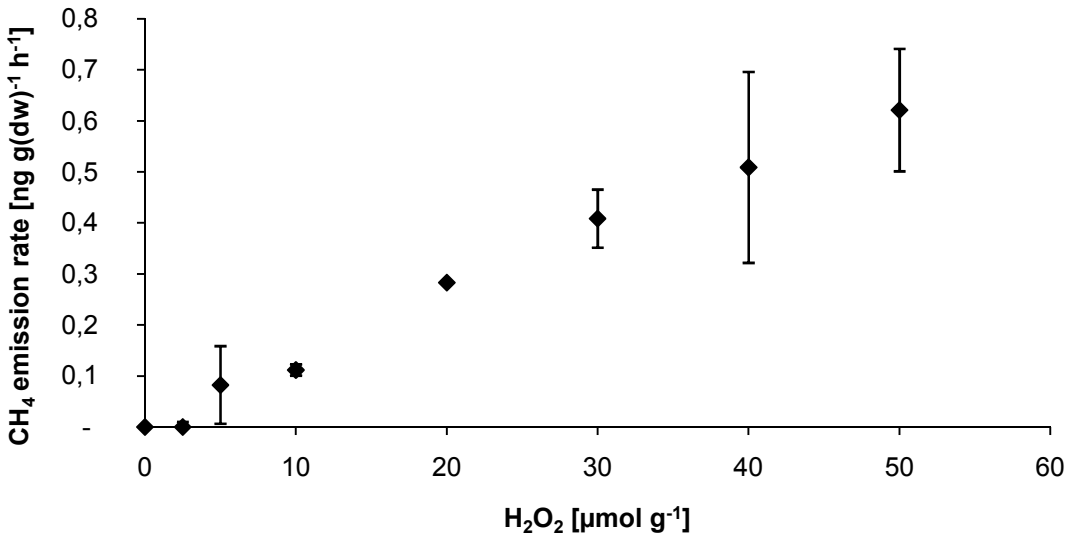


Fig. 6-11: *Relationship between CH_4 emission from peat PH and added amount of H_2O_2. Data show mean value ± SD (n=3, except 20 µmol (n=1)). Incubation: 24 h at 30 °C.*

It was found that peat and soil responded rather differently following addition of H_2O_2. A strong increase in CH_4 emissions and a linear relationship (R^2 = 0.99) with increasing amounts of added H_2O_2 to sample PH (Fig. 6-11) was observed whereas for soil sample SHA no additional emissions could be measured.

6.4.2 Lignin and humic acid

The experiment was repeated with a batch (n=5) containing 5 g lignin and one containing 5 g humic acid. Both were supplemented with 10 ml aqueous H_2O_2 solution (25 mM) and a batch of three samples of each material, supplemented with 10 ml doubly distilled water, was used as background. No increase in CH_4 emission could be shown for lignin, but for humic acid 0.54 ± 0.19 ng $g(dw)^{-1}$ h^{-1} were released additionally in the vials containing H_2O_2 compared to those supplemented with pure water.

6.4.3 Temperature dependency of the reaction with hydrogen peroxide

To investigate whether the reaction with H_2O_2 is still relevant at ambient temperatures the experiment was repeated at 22, 30 and 40 °C using 0.5 g peat (PH) in a 40 ml screw cap vial and 1 ml of a 50 mM H_2O_2 solution.

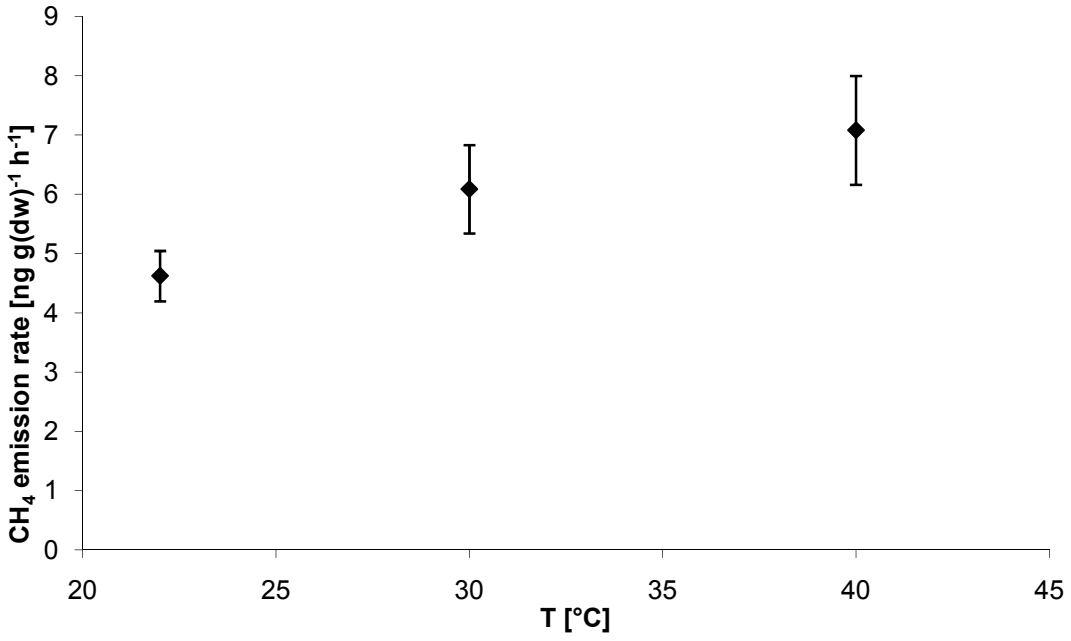


Fig. 6-12: *Effect of temperature on CH4 emissions from peat supplemented with H_2O_2. Data show mean value ± SD (n=3). Incubation time: 5 h.*

The data show that CH_4 formation from the reaction of H_2O_2 with soil or peat is temperature dependent, but also that at ambient temperature CH_4 emissions can still be observed (Fig. 6-12).

6.5 Influence of UV irradiation

UV irradiation has previously been shown to be a driving force in abiotic degradation of organic matter (Austin & Vivanco, 2006). The following experiments were designed to investigate whether UV driven degradation processes lead to CH_4 formation and to research interaction with other factors like soil composition and moisture.

6.5.1 Dry material under UV

A variety of soil samples and peat samples were irradiated with UV-B intensities of 2 Wm^{-2} which equals ambient summer UV-B irradiances at Earth surface at mid-latitudes. The emission rates were calculated from the measured CH_4 headspace concentrations before irradiation and after 24 h. The emissions ranged from 0.50 ± 0.13 µg m^{-1} h^{-1} to 4.92 ± 1.46 µg m^{-1} h^{-1} for the natural samples and from 0.40 ± 0.11 to 0.80 ± 0.17 µg m^{-1} h^{-1} for the organic model compounds (Table 6-5).

Sample	**pH**	**C_{org} [% (dw)]**	**dry (30 °C) [ng g(dw)$^{-1}$ h^{-1}]**	**UV-B radiation (2 W m^{-2}) [µg m^{-1} h^{-1}]**
Sphagnum peat (PH)	3.7	49.2 %	0.05 ± 0.02	0.76 ± 0.24
Deciduous forest soil O_h (SW)	7.4	23.4 %	n.d.	0.25 ± 0.13
Coniferous forest soil A_h (SG)	7.2	5.0 %	n.d.	1.73 ± 0.41
Deciduous forest soil A_h (SL)	4.4	4.0 %	n.d.	4.92 ± 1.46
Deciduous forest soil A_h (SHA)	6.7	5.8 %	n.d.	0.50 ± 0.13
Humic acid (HA)	5.5	43.5 %	0.06 ± 0.02	0.80 ± 0.17
Lignin (LIG)	9.6	49.5 %	0.1 ± 0.01	0.40 ± 0.11

Table 6-4: *Methane emission rates under UV-B radiation*

6.5.2 Correlation CH_4/ C_{org}

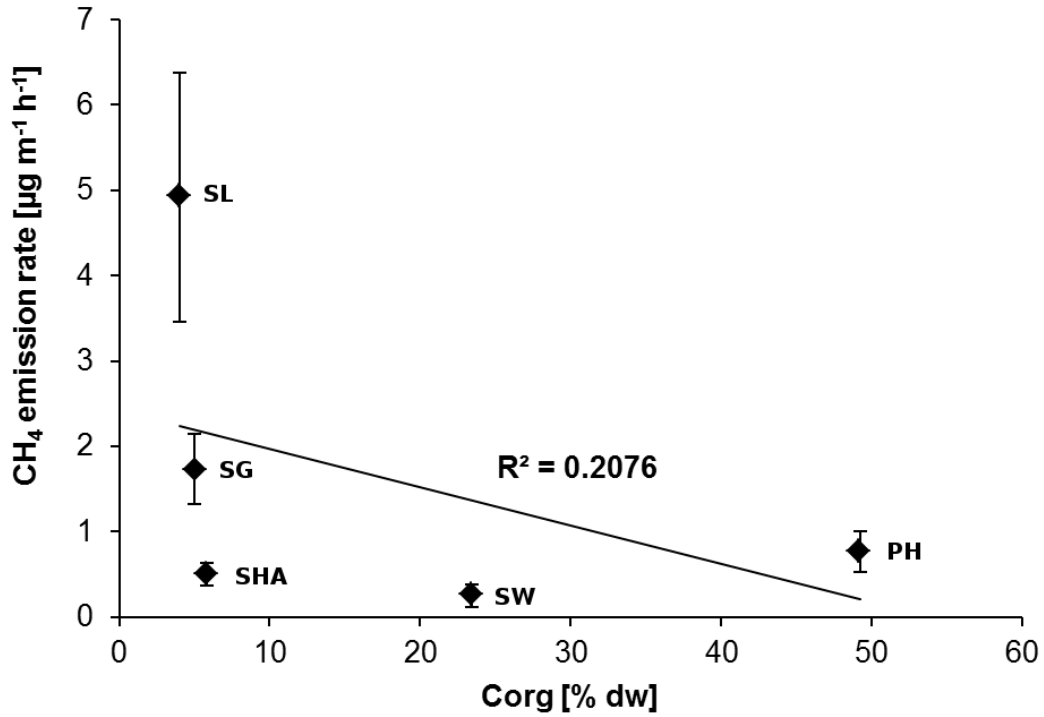


Fig. 6-13: *Correlation of organic content of sample material with CH_4 emissions under UV-B irradiation (2W).*

In Fig. 6-13, the CH_4 emission rates are plotted against the samples carbon contents. The CH_4 emission rates are not linked to the organic content of the sample material (R^2 = 0.21).

6.5.3 Comparison of non-UV-B samples (controls) with dark incubated samples

The control samples in all UV-experiments are covered with non-UV-B transmissive glass. In contrast to the samples from the temperature experiments which were incubated in the dark, these samples are irradiated by the full lamp spectrum minus UV-B and some UV-A. To see whether the visible light or the remaining UV-A radiation cause CH_4 emissions in the control samples, the results from lignin control samples were compared to those obtained in the temperature experiments. The comparison (Fig 6-14) shows emissions for the non-UV-B samples at 32 °C which would also be expected from a sample incubated in the dark at the same temperature. No additional emissions are caused by either visible light or UV-A.

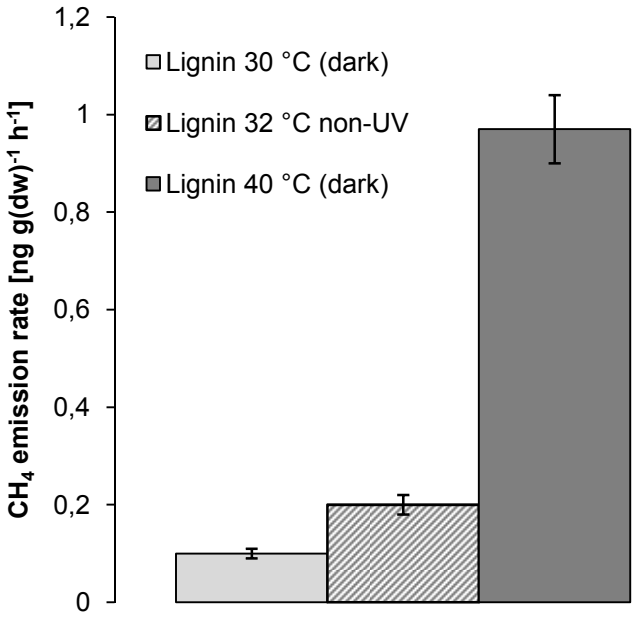


Fig. 6-14: *Comparison of emission rates from the control sample (non-UV) to emission rates from temperature experiments (dark). Error bars indicate standard deviation (n=3 for non-UV, n=5 for temperature experiment).*

6.5.4 Comparison of UV-B treated samples with dark incubated samples

Thermally and irradiation driven CH_4 formation seem to have a different mechanism as both methods show different effectivity in the samples. Highest emissions under UV-B radiation of 2 W m^{-2} were detected from samples that showed no emissions after low temperature incubation (SL and SG). On the other hand, the sample showing highest emissions after low temperature incubation (lignin) was found to release the lowest emissions in the UV experiments (Table 6-5; Fig. 6-15).

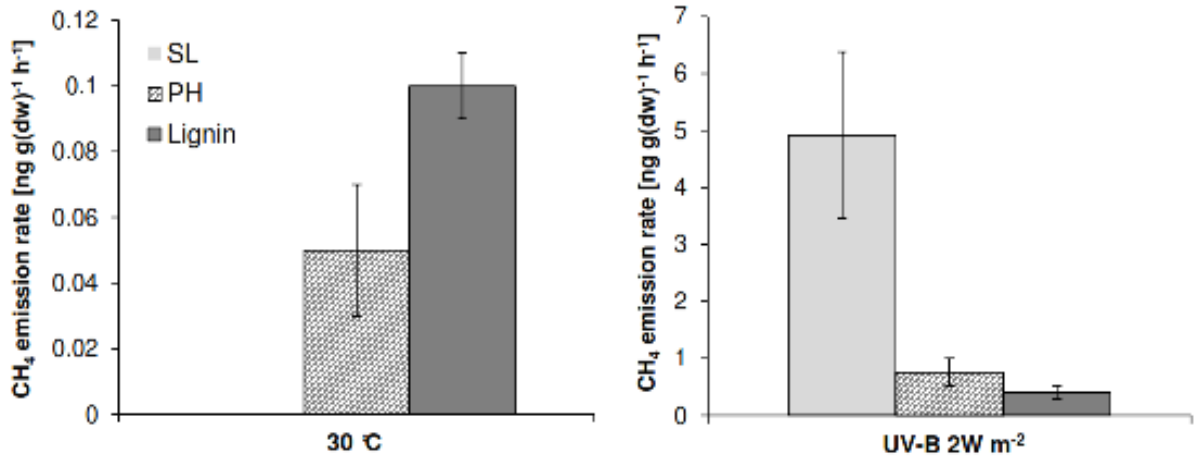


Fig. 6-15: *Comparison of dark incubated samples (left) with UV-B treated samples (right).*

6.5.5 Wet material under UV

This experiment was executed to evaluate a possible influence of soil water content on the CH_4 emission rates under UV-B irradiation.

The UV reaction cells were loaded with 5 g of soil SG and 3 ml doubly distilled water. Four cells were covered with 2 mm quarz glass and four with three layers of 3 mm normal, non-UV-B-transparent glass each. All reaction cells were placed under UV lamps in a distance that resulted in an UV-B irradiation intensity of 2 W m^{-2}, the same as for the experiments with dry soil under UV-B (chapter 5.6.1). Measurements of CH_4 concentrations in the headspace after 24 hours showed no difference between UV-B irradiated samples and the control group or between this experiment and the emissions from wet soil SG incubated at 30 °C (Table 6-2).

6.5.6 UV intensity

To evaluate the relationship between UV intensity and CH_4 emissions, samples of lignin, soil SL and soil SG were irradiated in the UV reaction cells with set intensities of 1, 2 and 4 W m^{-2} UV-B and the corresponding UV-A values. The experiments were performed in triplicates.

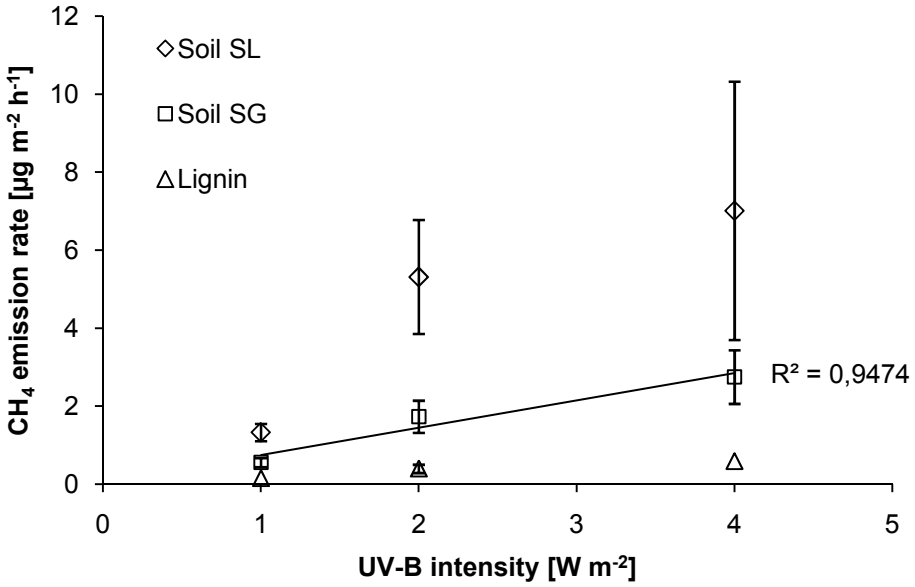


Fig. 6-16: *Intensity dependency of CH_4 emissions from lignin and soils SL and SG. Error bars indicate standard deviation (n=3).*

Methane emission rates were found to be increasing with UV-B intensity. With increasing intensities from 1 to 4 W m^{-2} CH_4 emissions from soil SG increased linearly from 0.56 ± 0.12 to 2.75 ± 0.69 µg m^{-2} h^{-1}. Emissions from soil SG increased from 1.33 ± 0.22 to 7.28 ± 2.75 µg m^{-2} h^{-1} over the same intensity range (Fig. 6-15). Humic acid and lignin showed CH_4 emissions when irradiated with UV-B light but the emissions were not as high as the emissions for some soils despite the higher amount of potential organic precursors (ch. 6.3).

6.5.7 Clay minerals

Comparison of the CH_4 emission rates from several soils under UV light showed, that the emission rates are not linked to the amount of organic (% C_{org}) the soils contain. Therefore an additional experiment was designed to evaluate a possible influence of clay minerals on the CH_4 emission rates under UV-B irradiation as described in chapter 2.3.

In the first experiment eight UV reaction cells were filled with 2 g vermiculite each. This resulted in a filling height of 0.7 cm. Four cells were covered with quartz glass, four with three layers of window glass each. Of both groups two cells were placed under a UV lamp in a distance of 35 cm and a lamp with a distance of 70 cm. Methane concentrations in the cells were measured after 24 hours of irradiation. No CH_4 emissions could be detected.

In the experiment humic acid and kaolin were infused with water (1:1:4) and shaken for 24 h with 300 rpm. The suspension was then lyophilised. Of the resulting powder 2.5 g were used per UV reaction vial and irradiated for 48 h with an UV-B intensity of 2 W m^{-2}. No elevated CH_4 emissions could be observed compared to pure humic acid.

6.6 Stable carbon isotope composition of methane emitted from soil

The stable isotope compositions ($\delta^{13}C$ values) of the released CH_4 from soil SHA, peat PH, lignin and humic acid under the conditions of experiments 5.1.1, 5.2.1, 5.5.1 and 5.4 were measured using a GC-C-IRMS system (see chapter 5.4.3). Methane emissions from heating experiments showed $\delta^{13}C$ values of −56 to −65 ‰ for lignin, −51 to −56 ‰ for PH and −42 to −52 ‰ for humic acid. In the experiments with wet samples, CH_4 emitted from lignin, humic acid and peat PH showed $\delta^{13}C$ values ranging from −53 to −69 ‰. Humic acid was again the substrate with the highest (less negative) CH_4 values (−53.2 ‰ ± 0.3 ‰). Lignin and PH showed $\delta^{13}C$ values of −62.9 ‰ ± 6.5 ‰ and −67.8 ‰ ± 0.3 ‰ respectively. The $\delta^{13}C$ 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±1.2 ‰ and −60.2±4.5 ‰, respectively.

The $\delta^{13}C$ values measured for CH_4 emitted during 48 h under UV irradiation were −56.0 ± 6.0 ‰ for lignin, −63 ± 3.3 ‰ for SHA, −44.2 ± 1.4 ‰ for PH and −35.3 ± 9.4 ‰ for humic acid. Overall, the $\delta^{13}C$ values of CH_4 emitted from soil differed between substrates and experimental conditions. They ranged from −35.5 to −69 ‰ for the CH_4 emissions whereas the $\delta^{13}C$ values for the organic matter of the bulk soil samples and organic materials 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 $\delta^{13}C$ 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).

6.7 Additional experiments

6.7.1 Sterile Samples (autoclaved vs. gamma irradiated)

Methane formation in oxic soils can possibly be of microbial origin. Several hypothesis exist as to whether this happens in anaerobic microsites (Peters & Conrad, 1995) or due to the activity of facultative methanogenic bacteria adapted to oxic environments (Rimbault et al., 1988). It was therefore of importance for this work to show aerobic methane production also in sterilized samples.

Part of peat PH and lignin was sterilized using gamma irradiation. Further subsamples of peat PH and lignin were sterilized by autoclaving.

Some experiments regarding temperature and water dependency were repeated using sterile samples. The water used was autoclaved. The results were comparable to those from non-sterile samples or in some cases higher (see Table 5-6). The higher emissions can be ascribed to CH_4 emissions driven by the highly energetic gamma radiation and the thermic activation during autoclaving. To eliminate these artifacts from the sterilisation processes some sterile samples were freezedried and then incubated as described afore.

This supports the conclusion from chapter 6.1.1 (temperature curve), that CH_4 release upon heating is the result of a chemically driven reaction rather than a biological one.

Only in the case of autoclaved PH and lignin samples at 50 °C the methane emissions were reduced by 50 % compared to non-sterile samples. That might be

due to the fact that autoclaving already released some of the thermically available CH_4 from the sample.

	dry			wet	
	30 °C	**40 °C**	**50 °C**	**30 °C**	**40 °C**
Lignin					
non-sterile	0.10 ± 0.01	0.33 ± 0.01	1.09 ± 0.09	0.65 ± 0.02	1.89 ± 0.20
autoclaved	-	-	0.58 ± 0.01	1.23 ± 0.10	-
gamma irradiated	0.21 ± 0.03	-	-	2.55 ± 0.23	-
Irr. and lyophilised	0.02 ± 0.09	0.39 ± 0.03	-	1.45 ± 0.48	2.70 ± 0.57
PH					
non-sterile	0.05 ± 0.02	0.05 ± 0.01	0.1 ± 0.01	0.19 ± 0.01	0.39 ± 0.04
autoclaved	-	-	0.41 ± 0.04	0.19 ± 0.02	-
gamma irradiated	0.21 ± 0.02	-	-	0.38 ± 0.03	-
Irr. and lyophilised	0.11 ± 0.15	0.03 ± 0.02	-	0.32 ± 0.09	0.52 ± 0.03

Table 6-5: *Emissions from non-sterile, autoclaved, and gamma irradiated samples, with and without water.*

6.7.2 Exclusion of methane oxidation by methane consuming bacteria

A selection of experiments from the water dependency study was repeated to investigate the possible influence of methanotrophic bacteria on the measured CH_4 emissions. For the dry samples and those with a sample:water ratio of 2:1, 1:1 and 1:2 the experiment was repeated with an addition of 20 µl diflouromethane (DFM) per vial. This was done to inhibit CH_4 oxidation by any methanotrophic bacteria (Miller et al., 1998) possibly present in the non-sterile samples. No significant effect was observed after adding DFM, concluding that there were no methanotrophic bacteria active in the lyophilised samples. The measured CH_4 emissions were 0.8 ± 0.2 ng per g (dw) per h without DFM and 0.4 ± 0.02 ng per g (dw) per h with DFM in the dry samples. The wetted samples showed emissions ranging from 1.6 ± 0.1 to 1.9 ± 0.1 ng per g (dw) per h with and without added DFM.

6.7.3 Evaluation of the influence of desorption

It has been suggested, that CH_4 release from plant materials might be a result of CH_4 desorption under low CH_4 environments, e.g. after flushing with CH_4 free air (Kirschbaum et al., 2007).

It has already been shown by Kirschbaum and Walcroft (2008) that desorption does not play a significant role under ambient conditions regarding moisture, temperature and CH_4 concentrations. But whereas Kirschbaum and Walcroft used ambient CH_4 levels for adsorption and investigated the desorption at ambient temperatures under low CH_4 conditions, we forced adsorption to peat at high CH_4 levels of 12,500 ppm, 100 ppm and 10 ppm.

The intention of this experiment was to show, whether the observed CH_4 emissions are indeed formed during the experiments or as an artefact caused by desorption of CH_4, possibly of microbial origin, adsorbed to the material under higher than ambient CH_4 levels in the soil or peat.

The aim was to investigate how much of the adsorbed CH_4 would be desorbed during the lyophilisation process and if the remaining adsorbed CH_4 was a potential cause for artefacts in our measurements.

The peat samples treated with the highest CH_4 levels showed an increased CH_4 release compared to an untreated control group (2.2 ± 0.9 ng per g (dw) per h vs. 0.4 ± 0.1 ng per g (dw) per h). The samples treated with 100 and 10 ppm CH_4 however

showed no significant increase neither before nor after lyophilization. Furthermore samples of kaolinite and sea sand were tested for their adsorption potential of CH_4 using 10 ppm CH_4 but no adsorption/desorption processes could be observed.

6.7.4 Oxygen rich vs. anoxic environment

To see if the non-microbial methane formation in oxic soils depends on oxygen, samples of both peat and soil were incubated under air, oxygen and nitrogen. The experiments were performed at 40 °C and in triplicate. For these experiments 0.5 g material were filled in 40 ml vials. The vials were flushed with either oxygen, synthetic air (~20 % oxygen) or nitrogen.

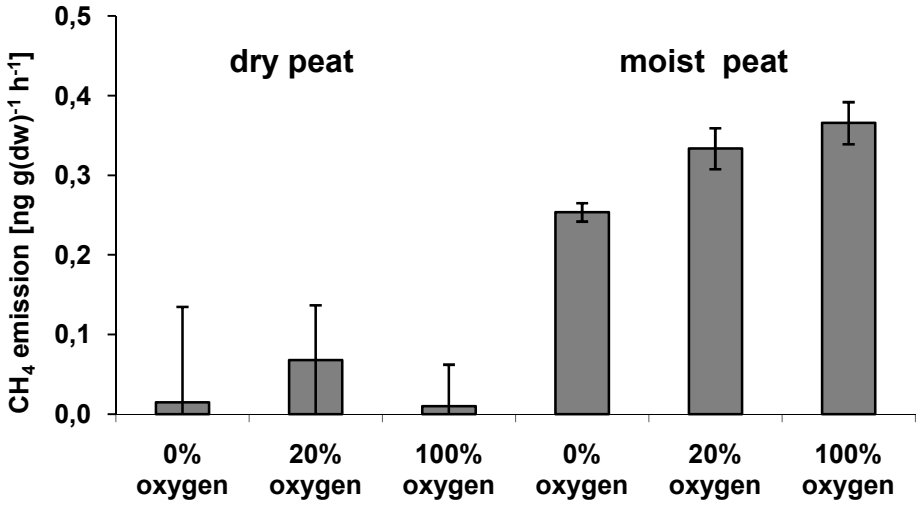


Fig. 6-17: *Influence of oxygen on CH_4 emissions from peat. Error bars indicate standard deviation (n=3).*

The data shows no difference in methane emissions from dry peat at 40 °C under any of the three conditions. In wet samples oxygen might be slightly promoting CH_4 emissions.

6.7.5 Possible effects of sample preparation in the UV experiments

Rough vs. smooth surface

To evaluate whether the surface structure of the milled samples has an effect on the CH_4 yield under UV radiation, the experiment with sample SL under 2 W m^{-2} UV-B was repeated with the only difference that the loosely filled sample was pressed flat in the reaction cell creating a smooth surface. Measurements after 24 h showed emission rates of 4.01 ± 0.70 µg m^{-2} h^{-1} which is comparable within standard deviation to the results for the loosely filled samples (5.31 ± 1.46 µg m^{-2} h^{-1}).

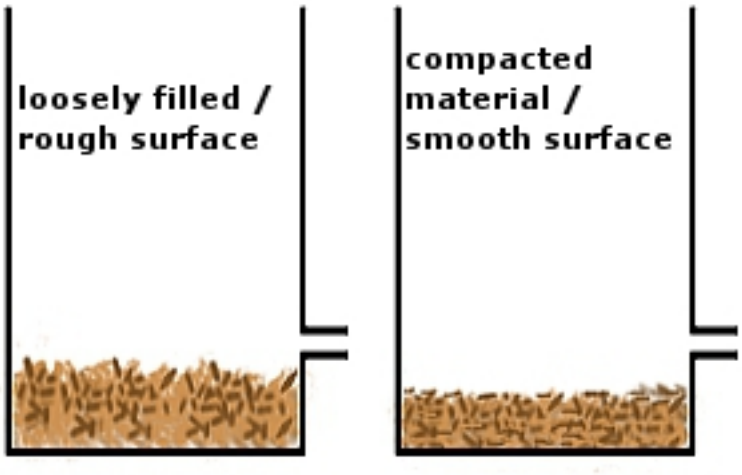


Fig. 6-18: *Scheme of the different surface structures in the experiment.*

Milled vs. unmilled material

To evaluate whether the homogenisation has an effect on CH_4 release under UV radiation, some unmilled material of the sample PH was placed under the UV lamps at 2 W^{-2} UV-B intensity. After the usual irradiation time of 24 h CH_4 measurements showed an emission rate of 0.60 ± 0.19 µg m^{-2} h^{-1}. This is comparable to the emissions found for milled peat (0.76 ± 0.24 µg m^{-2} h^{-1}).

7 Discussion

The three main topics of this thesis are the possibility of aerobic methane production, its response to different environmental influences and to get an idea on a possible pathway.

The results in chapter 6 show that there exist several processes that produce CH_4 in soil and peat which could be proven in this work to be not related to methanogenic activity. The emission rates in the experiments depend upon temperature, moisture, UV intensity and hydrogen peroxide levels. From comparing the influence of the different environmental factors and structural differences of the postulated precursors, some information on the pathways of CH_4 formation could be deduced. Furthermore earlier observations of CH_4 emissions from oxic soils by other scientists (Megonigal & Guenther, 2008; Hao et al., 1988; Andersen et al., 1998; von Fischer & Hedin, 2007; Kammann et al., 2009) might be explained.

Figure 7-1 summarizes the findings regarding non-microbial CH_4 formation in the aerobic layers of soils and the environmental factors that might control emissions. 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. At least two different mechanisms for non-microbial CH_4 formation in soils might exist as can be concluded by comparing thermal and UV-B induced CH_4 release.

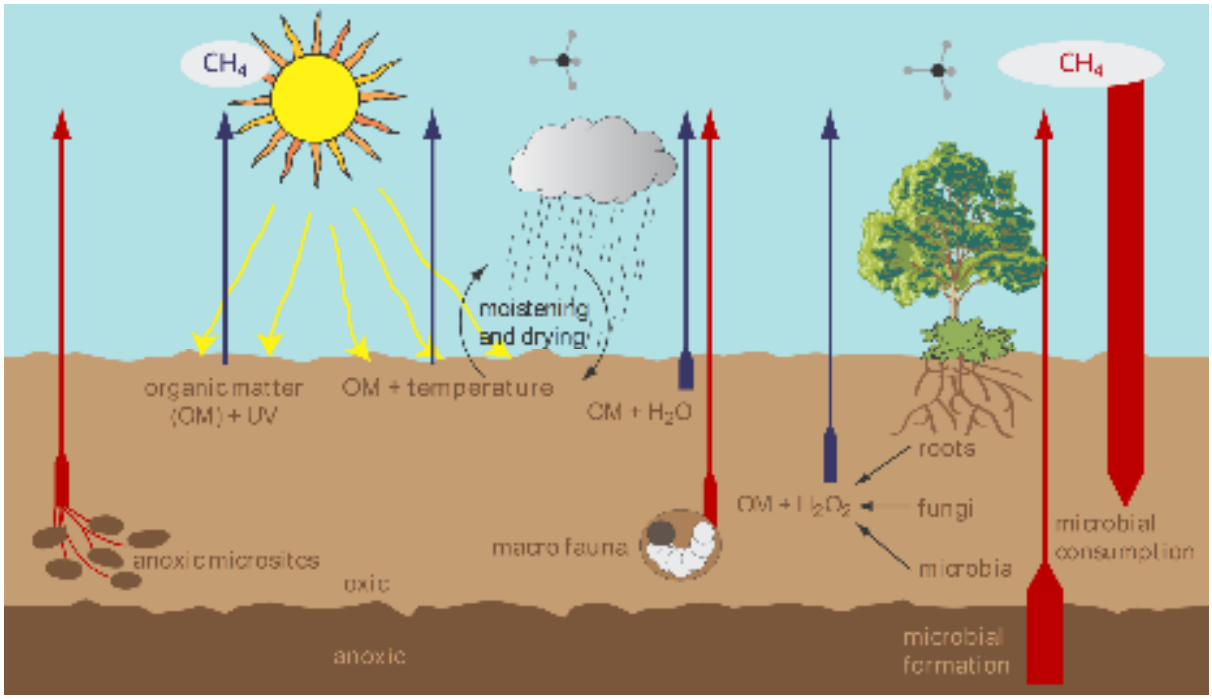


Fig. 7-1: *Scheme of CH_4 cycling in soil including non-microbial (blue) and the previously known microbial sources (red). Environmental factors such as temperature, UV irradiation, drought/wet cycles and formation of hydrogen peroxide produced by biota might control chemical formation of CH_4 in soil.*

7.1 Temperature

Regarding the temperature experiments (chapter 6.1) the amounts of CH_4 produced at ambient temperatures of 30 °C were small, but grew considerably with increasing temperature. They did so exponentially and thus without showing a preferred temperature optimum which would have been expected for a biotic reaction.

Interestingly, these results for the heated soil and peat samples (Fig. 6-1) show a similar pattern as those found by Keppler et al., (2006) and Vigano et al., (2008) for heated plant matter. Whereas biotic mediated reactions have their optimum often at temperatures between 25 and 40 °C the observed strong increase in CH_4 emissions over the whole temperature range from 30 to 90 °C supports the hypothesis for a chemically driven reaction.

Activation energies calculated for the temperature experiments also support the abiotic nature of the reaction: Arrhenius plots showed activation energies (E_a) between 50 and 84.1 kJ mol^{-1} which indicates abiotic formation, as in biotic mediated reactions enzymatic activity lowers the activation energy below 50 kJ mol^{-1} (Schönknecht et al., 2008).

Further evidence for the abiotic nature of the CH_4 emissions can be found in the results from the experiments with sterile samples (6.7.1). Admittedly, preparation of sterile soil samples is difficult (Brock, 1978), but it could be shown in enrichment as well as inhibition experiments with identical material (Jugold et al., accepted) that no methanogens were active in the sterilised peat and lignin samples.

The two organic compounds used in this study (lignin and humic acid) emitted CH_4 in the same fashion as the soil samples. In contrast to that cellulose did not emit methane in similar experiments (Hurkuck et al., 2012). A most obvious structural difference between lignin and humic acid on the one hand and cellulose on the other is the lack of $-OCH_3$ groups in cellulose. These have been suggested and validated as precoursors for abiotic methane formation before (Vigano et al., 2008; Keppler et al., 2008) and this is a further confirmation.

7.2 Water

Wetted samples (chapter 6.2.1) showed much higher emissions than the dry sample itself at low temperatures, but it could also been shown, that the actual water/sample ratio is of minor importance (6.2.2). Water could still be a limiting factor, but at much smaller ratios than tested in the experiments. Another possible explanation might be that water does not take part in the reaction but is needed as a medium for reaction partners.

A second impressive observation is that the methane emission in the drying-rewetting-cycles does not decline with further repetitions as could be expected. A readsorption of atmospheric methane between cycles can be excluded, as the isotopic signature of CH_4 from all experiments differs from the atmospheric background and it could also be shown in experiment 6.7.3, that due to the vacuum conditions in the lyophilisation steps, sorption processes are not an issue. The precursor compound seems to be abundant enough to release CH_4 for more than ten to fifteen cycles and the mechanism seems to need the drying steps to “recharge”.
The different behaviour of lignin samples, from which the CH_4 emission is highest in the first cycle and then declines to less than half of this rate in the second, might indicate that the methoxy groups in the lignin are so readily available for the reaction, that they already show depletion in the second cycle.

The second soil employed in this experiment, soil SW shows a slightly different pattern than the peat and organic substances. It takes two cycles until an increase in CH_4 emissions (compared to dry values) can be observed. One could jump to the conclusion that the reaction takes more time in this sample. However, it is unlikely that it would show a six fold increase in CH_4 release after just twice the time. It is most likely that the reaction needs some form of activation in the material that takes places in the first cycle and enables methane formation or release in the following cycles.

As stated for the heating experiments the organic compounds lignin and humic acid emitted CH_4 in contact with water. Again cellulose, employed in the same experiments by Hurkuck et al., (2012) did not.

7.3 UV

In the experiments described in chapter 6.5, it could be shown that UV irradiation of soil samples and soil organic matter leads to CH_4 emission.

The emission of CH_4 under UV light is in line with findings by Vigano et al., (2008) and McLeod et al., (2008), who showed that UV irradiation is a driving factor for CH_4 production from dried plant matter. Thus soil organic matter is most likely the precursor of CH_4 emissions observed in the experiments with soil under UV light. This is supported by CH_4 emissions that were observed when lignin and humic acid were exposed to UV irradiation under the same conditions as that for the soil samples. In contrast to the findings by Hurkuck et al., (2012) discussed in chapter 7.1 and 7.2, where cellulose showed no CH_4 emissions under elevated temperature or after addition of water, it did emit CH_4 under UV light in studies by Vigano et al., (2008). The CH_4 emissions observed in spite of the lack of methoxy groups in cellulose imply that in addition to the formation from these groups, UV radiation leads to CH_4 formation from other structural components of the organic precursors as well.

Even though the soil organic matter seems to be the precursor of the observed CH_4 emissions, there was no apparent correlation between CH_4 production and the soil organic matter content under UV irradiation (Fig. 6-13, R^2=0.21). This indicates that other soil components also play a role in CH_4 formation. Organic photo-sensitizers 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 CH_4 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 CH_4 when exposed to UV irradiation (Keppler et al., 2012).

Furthermore, UV irradiation had no additional effect on wet samples in the experiments (6.5.3). This is interesting regarding the observation, that UV induced and water mediated CH_4 formation are based on different pathways. In the experiments with added water the precursors are most probably the methoxy groups of the organic components. In the experiments using UV, part of the CH_4 emissions are likely to be based on the split off of methoxy groups as well, as has been shown with isotopically labeled pectin by Keppler et al., (2008), but a second mechanism

cleaving the organic precursors at different positions has also been postulated (Vigano et al., 2009). Maybe the latter one works for cellulose, but not for lignin or UV intensity in the study was reduced to an ineffective level by the water present in the reaction cells. The later can be ruled out considering results of studies concerned with the photodegradation of lignin in kraft black liquor, a waste product of the paper industry, rich in lignin and hemicellulose, and other paper mill effluents (Villaseñor et al., 1996; Ksibi et al., 2003). At first glance their results are in contrast to the findings of this study, that UV has no additional effect on the CH_4 formation from lignin. However, they measured a decline in lignin, but did not investigate the formation of CH_4 and other volatiles. Therefore the possibility remains, that photodegradation of lignin in aqueous solution does not lead to CH_4 formation but to other products, possibly CO_2 and in the following H_2CO_3.

A combination of temperature and UV in the experiments could lead to a higher CH_4 emission than each of them alone, at least it has been shown in studies by Villaseñor et al., (1996) that increased temperatures positively influence the ZnO-catalysed photodegradation of lignin. Their study focused on the decline in lignin and not on possible CH_4 emissions. It would therefore be interesting to repeat their experiments with a focus on the measurement of possible CH_4 and CO_2 emissions. And whereas Villaseñor et al., performed their experiments on kraft black liquor, it would be interesting to perform similar experiments on dry material as well to exclude the effect of water on CH_4 formation.

7.4 Hydrogen peroxide

Reactive oxygen species (ROS) such as hydroxyl radicals (HO•) have been suggested to play a prominent role in the release of CH_4 from pectin and might be the driving force in the CH_4 release during UV radiation of plant foliage (McLeod et al., 2008; Messenger et al., 2009). Hydrogen peroxide (H_2O_2) as a precursor of HO• is an important reactant 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). As the release of H_2O_2 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.

In the experiments described in chapter 5.4 H_2O_2 was found to have a positive effect on CH_4 production from peat (6.4.1) but it was also found that H_2O_2 addition only triggers CH_4 emission from humic acid or soils which organic component is based on humic acid. No emission could be observed from lignin or soil Hainich (SHA).
A possible explanation for the different behaviour of soil SHA and peat PH might be related to the differences in their composition. Peat consists mostly of organic matter with only a minor mineral content which might make it more prone to decomposition by ROS. Soil, especially the one used in the experiment, has a higher mineralic content which includes clay minerals and metal oxides that might interact more readily with H_2O_2 than the organic component.
When treating lignin and humic acid with H_2O_2 (6.4.2) increased CH_4 emissions were only observed for humic acid, not for lignin. It is therefore supposable that the structural composition of the organic matter in soil has a major impact on the CH_4 emissions.

7.5 Implications of measured isotope ratios

The $\delta^{13}C$ values of CH_4 emitted in the experiments differed depending on substrates and experimental conditions. They ranged from −35.5 to −69 ‰ for the CH_4 emissions and thereby differed from values for atmospheric CH_4 (-45 ‰). In comparison the $\delta^{13}C$ values for the organic matter of the bulk soil samples and organic materials were in the range of −22 to −29 ‰. Thus, all treatments seemed to cause isotope fractionation between the substrate and emitted CH_4. Similar $\delta^{13}C$ values and fractionations have been reported for CH_4 emitted from plant foliage due to UV radiation or upon heating (Vigano et al., 2009). The isotopic values reported for the chemical formation of CH_4 from both soil and vegetation are commonly also found for terrestrial biogenic sources as listed in Table 1-1.

7.6 Summary of main findings and implications on possible pathways

These are the main results of all experiments done in this work which provide clues on possible CH_4 formation pathways:

- Non-microbial methane formation in oxic soils exists.
- Activation energies were > 50 kJ mol^{-1} for all materials (Table 6-1), therefore the reaction is abiotic.
- No correlation of emission rates and organic content could be observed in temperature and UV experiments (Fig. 6-5, 6-13).
- The highest releases in temperature and UV experiments came from different samples. (ch. 6.4; Table 6-5; Fig. 6-15).
- Higher emission rates were observed from wet samples than from dry samples (6.2).
- Higher H_2O_2 concentrations led to higher CH_4 emissions in humic acid and peat (6.4).
- A linear relation of UV intensity and CH_4 emission was discovered (6.5.6).
- UV irradiation did not lead to additional emissions in wet samples (6.5.5).
- The abiotic formation of CH_4 in the temperature and water experiments is not influenced by the presence or absence of oxygen (6.7.4).
- Higher emission rates were observed in more acidic set ups (6.3).

Regarding the pathway of non-methanogenic CH_4 formation in soils, these findings can be summed up to the conclusion, that there is most probably more than one mechanism for the non-microbial CH_4 formation from soil material. As stated above (ch. 7.1 and 7.2) the two organic compounds of this study, lignin and humic acid, showed CH_4 emissions under wet and dry conditions, whereas cellulose, does not (Hurkucket al., 2012). On the other hand cellulose does emit CH_4 when irradiated with UV light (Viganoet al., 2009). The formation under UV irradiation must therefore have a different mechanism than the thermally induced and the water mediated reaction.

The thermally promoted and the water mediated reactions most probably involve the separation of a methoxy group. The photolytic CH_4 formation is based on both: split

off of the methoxy groups and cleavages at other, so far unidentified parts of the precursor's structure.

7.7 Implications for global CH_4 production and future trends

The results show that most investigated samples can release CH_4 under ambient conditions. Assuming that the first five centimetres of the soil horizon account for most of the CH_4 production, due to highest fluctuations in temperature and humidity, the emission rates from dry and wet soil at 30 to 40 °C (Table 6-1 and 6-2) would correspond to emission rates of 0 to 18 µg m^{-2} h^{-1}, assuming a dry bulk density of 1.5 g cm^{-3} for soil and 0.1 g cm^{-3} for peat (Minkinnen 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 CH_4 emissions up to 11.9 mg m^{-2} 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), the emissions calculated above are relatively small. However, given the large global areas of natural wetlands and forests of 504 and 3952 million ha respectively (Cao et al., 1998; FAO 2006) and the frequency at which dried and rewetted soils release CH_4, this source can nevertheless be an important factor in aerobic soil organic matter degradation. Furthermore, it can explain the earlier findings of CH_4 emissions from aerobic soils (Hao et al., 1988; Andersen *et al.,* 1998; von Fischer & Hedin, 2007; Megonigal & Guenther, 2008).

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 and calculated for 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 desertification.

When working on CH_4 emissions from natural soils, it always has to be considered that more than 90 % of CH_4 formed within soils is oxidised by methanotrophic bacteria before it reaches the atmosphere (King, 1990). The strong influence of

methanotrophy also leads to CH_4 uptake into aerated soils. 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 CH_4 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 affect the soil down to 2 mm depth (Hebert and Miller, 1990). Thus CH_4 formation induced by UV irradiation at the soil surface might lead to direct CH_4 emissions to the atmosphere. Nevertheless, it will be a challenge to differentiate between microbial and non-microbial sources in the field, not least because methanogenic CH_4 production shows a similar isotopic fractionation as some of the stated non-methanogenic sources.

All effects shown to increase CH_4 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 will be of particular interest and with changes in vegetation cover and variations in UV irradiation reaching the surface (Zepp et al., 2007) the importance of UV degradation will change.

Future trends regarding the water mediated non-microbial CH_4 release from soils would have to be surveyed on regional scales, as the global change in surface hydrology shows a very high spatial variability (Trenberth et al., 2007).

Regarding the effect of temperature on CH_4 emissions from soil, global surface temperatures in general have risen by 0.74 ± 0.18 °C over the past 100 years (Fig. 8-1) in which the rate doubled in the past 50 years. The increase is even higher for terrestrial surface compared to ocean surfaces with 0.27 and 0.13 °C respectively per decade after 1976. (Trenberth et al., 2007)

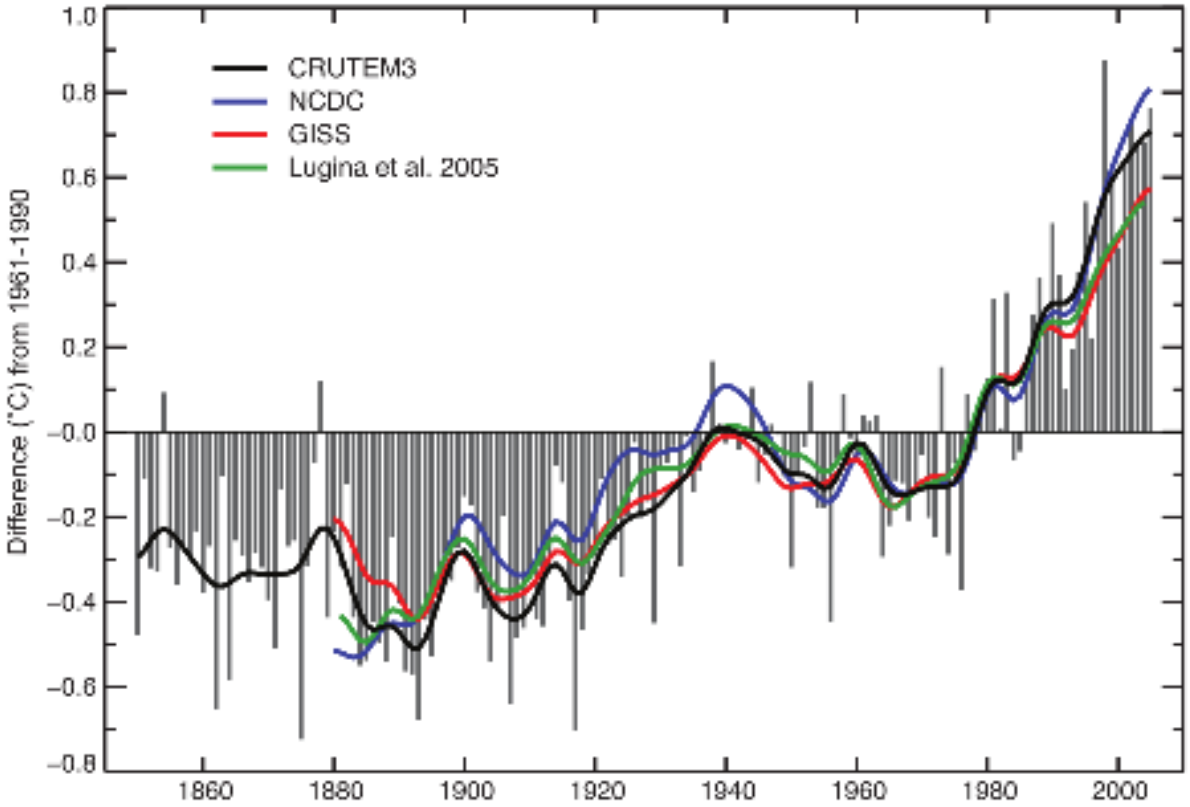


Fig. 7-2: *Trends in global land-surface air temperature 1850-2005 compared to the mean suface air temperature of 1961-1990 (Trenberth et al., 2007).*

Future changes in UV irradiation are hard to predict, because they depend on many factors. In previous decades, the depletion of the stratospheric ozone layer has led to an increase of UV-B radiation, but with an anticipated ozone recovery, UV-B intensities might drop below pre ozone depletion values. Changes in the ozone layer will affect UV-B irradiances differently at different latitudes with highest effects in polar regions and the tropics staying mostly unaffected. This difference will be increased by the additional influence of cloud cover and aerosols. Cloud cover is expected to decline in low latitudes, which are least influenced by ozone recovery, leading to an increase of UV exposure. In high latitudes, cloud coverage is expected to increase, blocking more UV light and adding to the ozone related decline in UV-B intensities (Zepp et al., 2007). This implies, that the regions most affected by desertification and anthropogenic removal of vegetation cover are also those dealing with a potential increase in UV intensities.

8 Outlook

Two main tasks derive from the outcome of this study.

(1) To estimate the full importance of this source for the global methane budget, at present and in future scenarios.

(2) To further unravel the mechanisms behind this novel source.

To be able to estimate the full extent of non-microbial CH_4 formation from oxic soils, a wider variety of soil types has to be surveyed than was possible in this study. Interesting regions for on-site studies of UV induced CH_4 release could be steppes regions, newly deforested land, and freshly ploughed fields, whereas for water mediated CH_4 release flooding plains and irrigation areas in dry climates would be relevant. For soil types and climate zones outside the spectrum evaluated in this study, field measurements should be preceded by laboratory studies on the respective soil. With more underlying data even modelling of this source at present and of future trends could be imagined.

To unravel the mechanisms, model studies using isotopically labeled precursor compounds could be employed. Especially the obvious difference between pathways of thermical and photolytical CH_4 generation promises a good starting point for further investigations.

To clarify the pathway of UV induced CH_4 formation it would be interesting to repeat experiments of Villaseñor et al., (1996) as explained in chapter 7.3 with the modification that dry material should be used in comparison to the kraft black liquor employed in the original experiments. In these experiments possible emissions of CH_4 and CO_2 should be measured and an identification of the remaining fractions of the lignin structure after photodegradation should be aspired.

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Figures

Tables

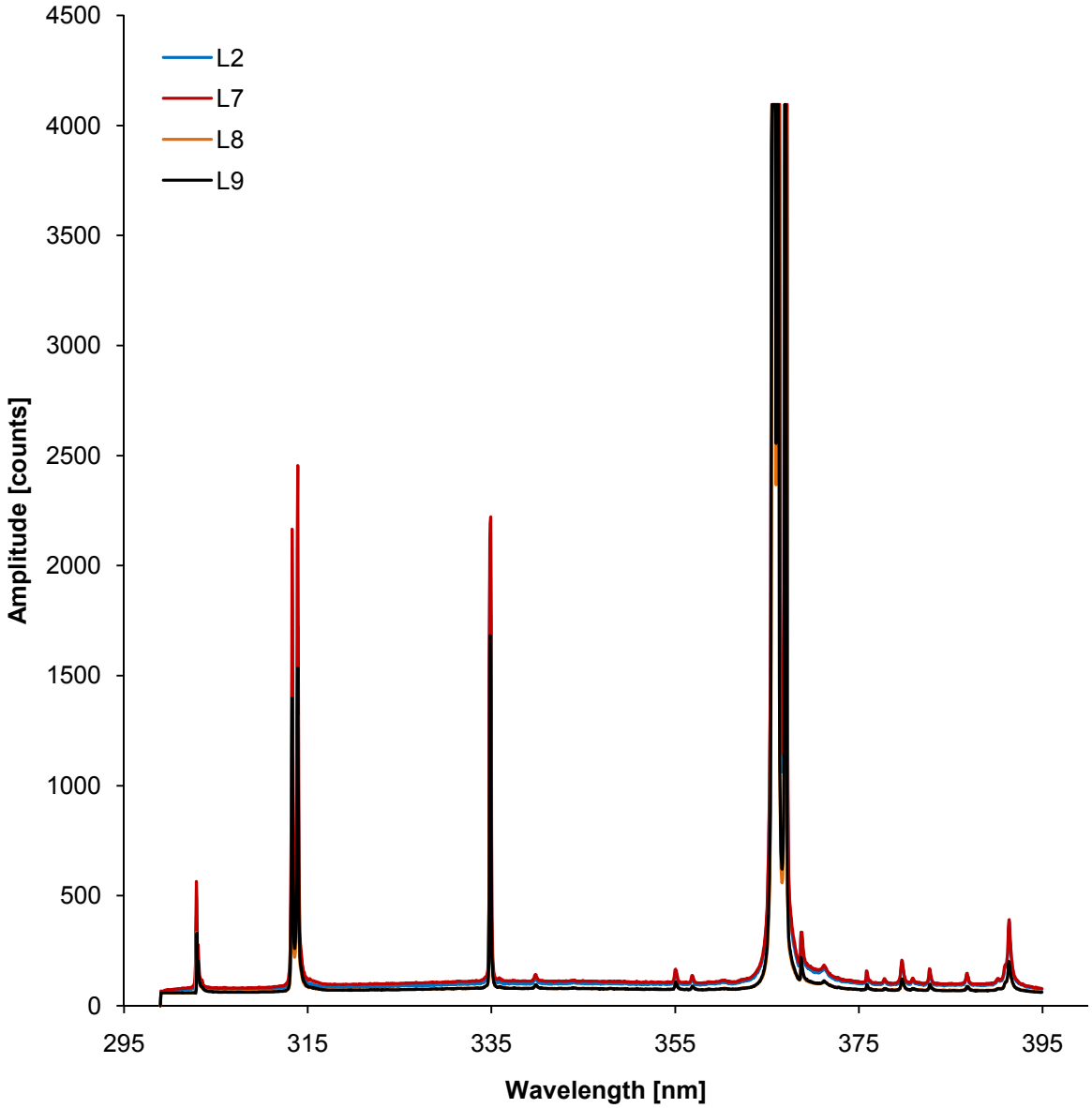
Abbreviations

ADP	adenosine diphosphate
ATP	adenosine triphosphate
CDA	cellulose diacetate
CH_4	methane
CO_2	carbon dioxide
CytC	cytochrome c
dd H_2O	doubly distilled water
DFM	difluoromethane
dw	dry weight
E_a	activation energy
FADH	formaldehyde dehydrogenase
FDH	formate dehydrogenase
H_2O_2	hydrogen peroxide
GC	gas chromatograph
GC-C-IRMS	gas chromatography-combustion-isotope ratio mass spectrometry
GC-FID	gas chromatograph with flame ionisation detector
H^+	proton
H_2O	Water
$H_3CO•$	methoxy radical
$H_3CO_2•$	hydroperoxymethane radical
HA	humic acid
HCHO	formaldehyde
HO•	hydroxyl radical
$HO_2•$	hydroperoxy radical
i.d.	inner diameter
lab air	ambient laboratory air
LIG	lignin
MDH	methanol dehydrogenase
MMO	methane monooxigenase
m/z	mass-charge-ratio
n.d.	not detectable
n.m.	not measurable

N_2	nitrogen
NADH, NAD^+	nicotinamide adenine dinucleotide (reduced and oxidized form)
NaOH	sodium hydroxide
NO_2	nitrogen dioxide
O_2	oxygen
O_3	ozone
P_o	pressure gauge
PH	peat Hille (sphagnum peat sample)
pMMO	persistent methane monooxygenase
ppmv	parts per million (volume)
ppbv	parts per billion (volume)
PreCon	preconcentration unit
PTFE	polytetrafluoroethylene
ROS	reactive oxygen species
SB	soil Belfast (soil sample)
SD	standard deviation
SG	soil Gonsenheim (soil sample)
SHA	soil Hainich, A-horizon (soil sample)
SHT	soil Hainich, T-horizon (soil sample)
SL	soil Lerchenberg (soil sample)
sMMO	soluble methane monooxygenase
SW	soil Wiehen (soil sample)
UV	ultraviolet

Appendix

A.1 UV spectra of the UV lamps



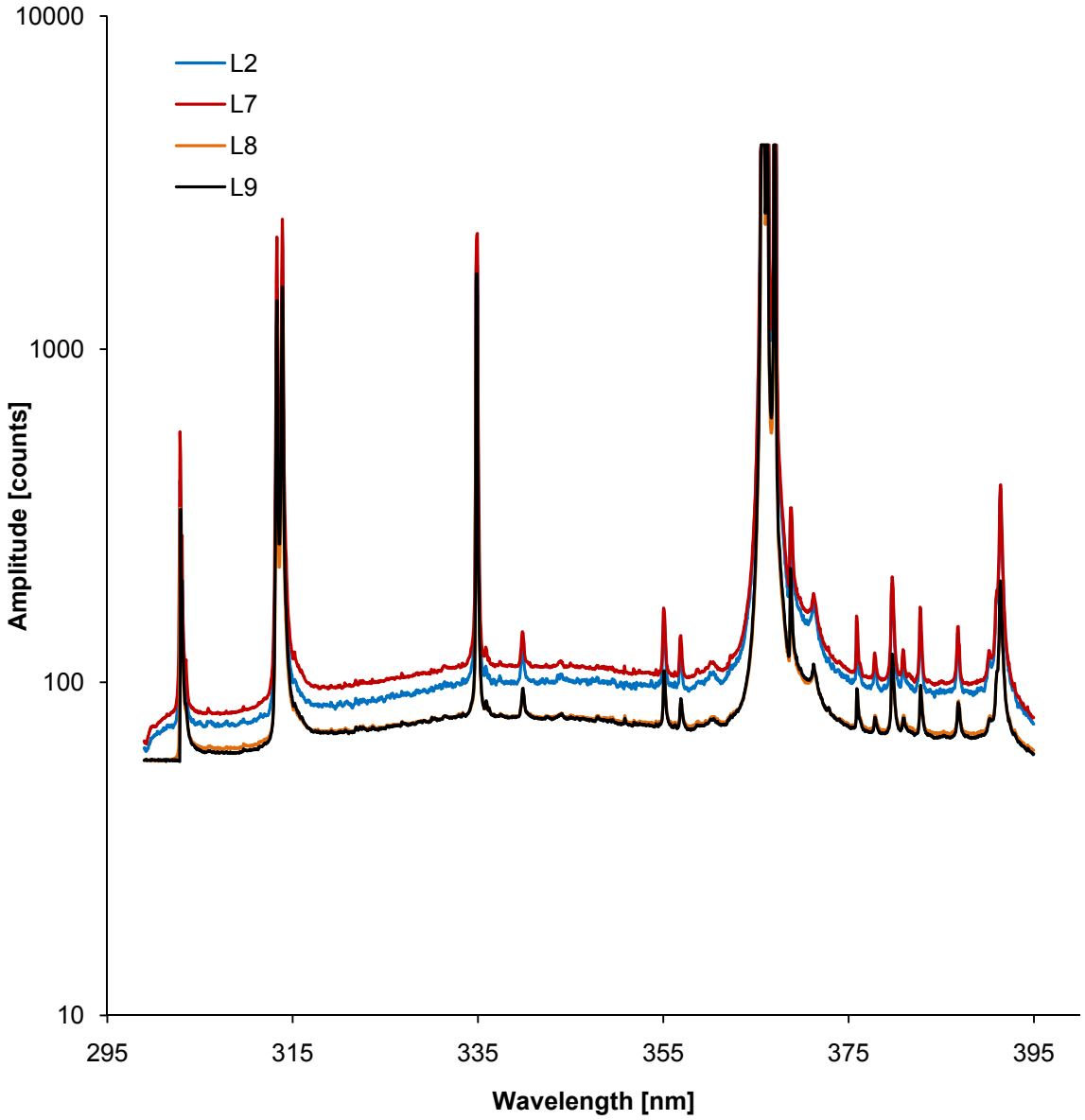


***Fig. A-1**: UV spectra of four Osram Ultra Vitalux lamps employed in the UV studies. Spectra were obtained with a UV-spectrometer (HR2000; Ocean Optics, Dunedin, FL, USA). The spectra were acquired in a distance equaling a UV-B intensity of 1 W m^{-2} for each lamp.*

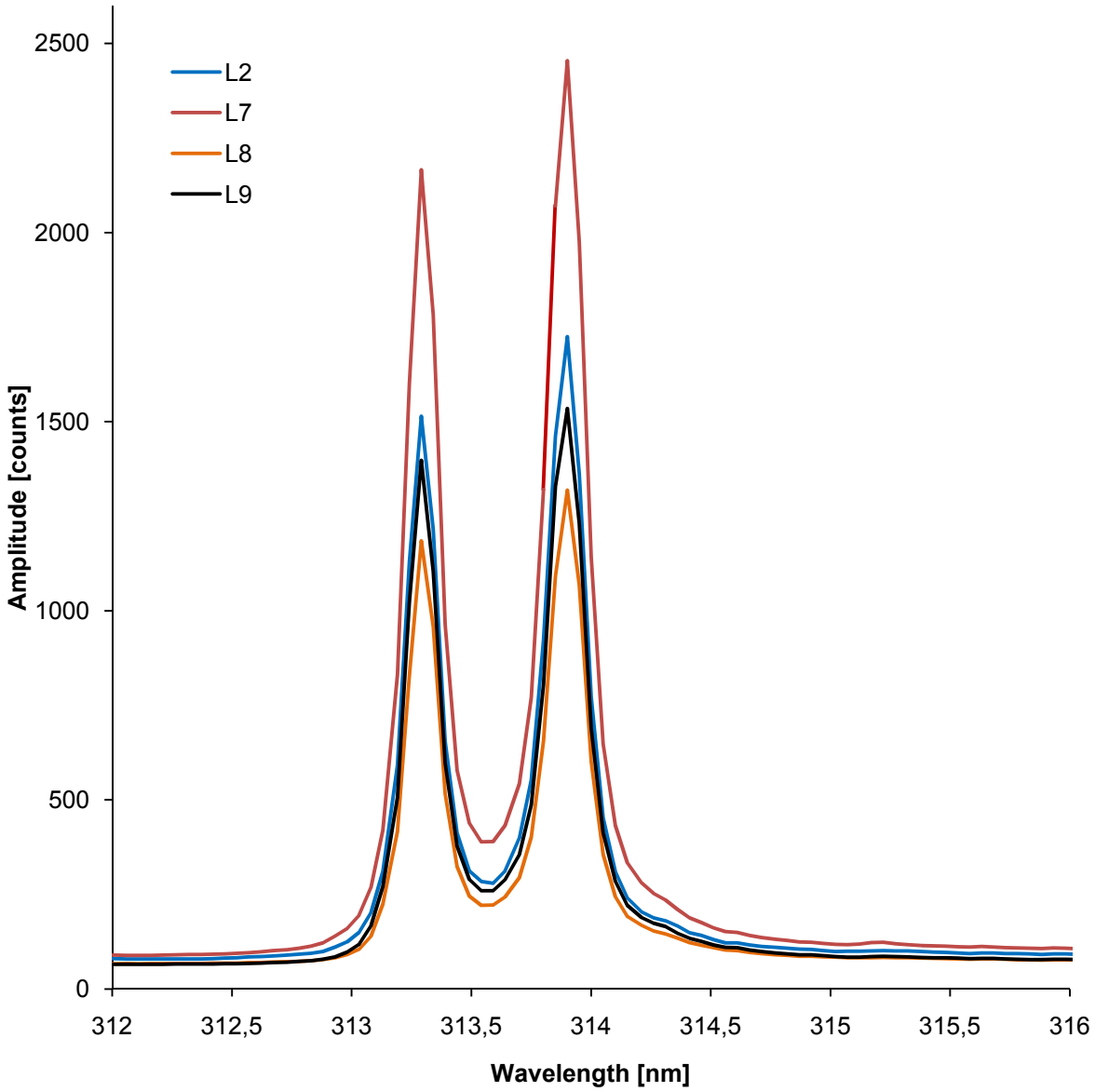


***Fig. A-2**: Excerpt from Fig. A-1: detailed diagram for maxima at wavelengths between 312 and 316 nm. The sources show maxima at the same wavelength but in different intensities.*

A.2 Overview on all drying rewetting cycles

	dry	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7	Cycle 8	Cycle 9	Cycle 10
Peat PH 30 °C	0.05 ± 0.02	0.19 ± 0.01	0.18 ± 0.04	0.11 ± 0.03	0.22 ± 0.07	0.26 ± 0.03	0.26 ± 0.03	0.27 ± 0.02	-	-	-
Peat PH 40 °C	0.05 ± 0.01	0.41 ± 0.01	0.23 ± 0.02	0.45 ± 0.09	0.37 ± 0.08	0.46 ± 0.03	0.18 ± 0.01	0.59 ± 0.04	0.24 ± 0.04	0.34 ± 0.05	0.39 ± 0.11
Peat PH 50 °C	0.10 ± 0.01	0.10 ± 0.01	0.54 ± 0.10	0.62 ± 0.07	0.69 ± 0.08	0.63 ± 0.14	0.53 ± 0.05	0.53 ± 0.05	-	-	-
Lignin 30 °C	0.09 ± 0.03	0.78 ± 0.11	0.34 ± 0.12	0.43 ± 0.04	0.29 ± 0.03	0.45 ± 0.1	0.30 ± 0.07	-	-	-	-
Soil Häver 30° C	0.01 ± 0.02	0.03 ± 0.01	0.23 ± 0.02	0.26 ± 0.05	0.29 ± 0.03	0.29 ± 0.02	-	-	-	-	-
Soil Häver 40° C	0.01 ± 0.01	0.24 ± 0.06	0.21 ± 0.08	-	-	-	-	-	-	-	-

Table A-1: *Overview on all drying rewetting cycles*

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