

A peat core based estimate of Late-glacial and Holocene methane emissions from northern peatlands

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Abstract

We estimate the intensity of Late-glacial and Holocene methane emissions from peatlands based on their paleo net primary production (PNPP). The PNPP is derived from the carbon accumulation rates of the studied bog profile (Etang de la Gruère, Switzerland), which are corrected for the degree of peat degradation. The obtained PNPP curve is taken as a proxy for methane emissions. It shows relatively high values ($90 \text{ g C m}^{-2} \text{ yr}^{-1}$) early in the Bolling/Allerod and drops to low values ($40 \text{ g C m}^{-2} \text{ yr}^{-1}$) during the Younger Dryas cold period. With the onset of the Holocene the PNPP increases strongly up to $150 \text{ g C m}^{-2} \text{ yr}^{-1}$ around ca. 10,000 Cal. yr BP. This is followed by a decline to minimum values (30 to $40 \text{ g C m}^{-2} \text{ yr}^{-1}$) between 6500 and 4000 Cal. yr BP. Thereafter, the PNPP starts to increase again to reach its highest value ($175 \text{ g C m}^{-2} \text{ yr}^{-1}$) around 1000 Cal. yr BP.

The PNPP curve correlates well with the evolution of the atmospheric methane concentrations as derived from Greenland ice-cores. For example, minima in atmospheric methane reported during the Younger Dryas and around 5200 Cal. yr BP are coinciding with the lowest values of PNPP and the negative atmospheric methane peak at 8200 Cal. yr BP corresponds to a marked decrease in PNPP.

Our PNPP curve suggests that the methane emissions from northern peatlands evolved similar to those of low latitude wetlands and together they largely determined the evolution of atmospheric methane throughout the Late-glacial and the Holocene. The abruptness of the rise of atmospheric methane at the end of the Younger Dryas probably points to an additional source (e.g. marine gas hydrates), but very early in the Holocene the peatlands have likely become the dominant source of atmospheric methane.

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1. Introduction

Many of the rapid climate oscillations observed during the last 400 kyr coincide with huge and abrupt

changes in atmospheric methane (Petit et al., 1999) — the Younger Dryas (YD) being the most recent episode (Chappellaz et al., 1993). Methane is a potent greenhouse gas and wetlands account for approximately 25% of the total present day methane emissions and represent the most important (ca. 80%) natural source of atmospheric methane (Lelieveld et al., 1998).

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Therefore, wetlands have been considered as the dominant source of atmospheric methane during the Late-glacial and the Holocene. This wetland source hypothesis is, however, contested by Kennett et al. (2000, 2003) who argue that the sudden increase of methane at the beginning of the Bolling/Allerod (B/A) and at the end of the YD were not due to wetlands, which were not wide-spread enough at that time and which were unlikely to respond rapidly enough. Instead Kennett and co-workers put forward the release of methane from marine gas hydrates.

Recent research on the relationship between wetlands and atmospheric CH₄ concentrations over the Holocene focuses on the areal extent of peatlands. Smith et al. (2004) present a comprehensive data set on age dating of basal peat layers documenting the spreading of peatlands in Western Siberia, which is thought to be proportional to methane emissions.

Although the extension of peatlands is an eminent factor, the intensity of methane emission per area must not be neglected. For the Oxygen Isotope Stage 3, for example, van Huissteden (2004) highlighted the site conditions as a very important factor. We argue that the same is true for the Late-glacial and the Holocene. For a reconstruction of methane emission intensities over this time period we investigated the changes in the rate of peat formation at a well-dated, ideal site of peat accumulation (Etang de la Gruère, Switzerland). From the observed carbon accumulation rate we calculate a paleo net primary production (PNPP) and relate this to methane emissions. We are aware of the limitations of our approach using a single site and a very simple geochemical proxy. However, the studied bog has been shown to be very undisturbed and to reflect global signals in many respects (see below) and is certainly among the best-suited sites for this kind of study. We, therefore, think that it is justified and instructive to discuss the obtained results assuming that the observed tendencies are characteristic for larger parts of the northern (>30° N) hemisphere. Our main goal is to show the potential of achieving a more quantitative understanding of the role of peatlands as a source of methane by confronting detailed peat core data with paleoconcentrations of methane in the atmosphere.

2. Methods

2.1. Study site: Etang de la Gruère (Switzerland)

The Etang de la Gruère peat bog (EGR) lies in the Jura Mountains (Switzerland) at an elevation of 1000 m

a.s.l. with an annual precipitation of 1.5 m and a mean annual temperature close to 5 °C. Due to the high elevation of the area its climate is not fundamentally different from climates of the typical regions of northern peatlands (<60° N). The EGR bog is a particularly well-developed domed ombrotrophic bog that covers a total area of 22.5 ha. Numerous studies on the EGR bog (pore water geochemistry: Steinmann and Shoty, 1997a; peat chemistry: Steinmann and Shoty, 1997b; atmospheric deposition of trace metals: Shoty et al., 1998; Shoty et al., 2002; methanogenesis: Eilrich and Steinmann, 2003; peat humification: Roos-Barraclough et al., 2004) have shown that the bog is very undisturbed and has stored global environmental signals for the Late-glacial and the Holocene with many respects.

The sampling site lies in an open tree-less part in the centre of the bog, where 6.5 m of peat have accumulated more or less continuously over the last approximately 14,500 Cal. yr BP (Shoty et al., 1998). The peat at the sampling site is dominated by *Sphagnum* in the uppermost part (0 to 60 cm depth), *Sphagnum–Eriophorum* from 60 to 250 cm, *Sphagnum* from 250 to 420 cm and by *Carex* below (Steinmann and Shoty, 1997a). The transition from a fen to a bog is, therefore, located at ca. 4.2 m.

The data used for the reconstruction of the carbon accumulation rates and the paleo net primary production (PNPP) are (1) a high resolution (2 cm, core EGR 2A) density curve from Roos-Barraclough et al. (2004); (2) a detailed age model for the same core based on 31 conventional ¹⁴C age determinations (Roos-Barraclough et al., 2004); and (3) the measurements of organic carbon and C/N ratios of the bulk peat (at 25 cm resolution, core EGR 1069). Total organic carbon and total nitrogen were measured using standard elemental analyser techniques.

The two cores (EGR 2A and EGR 1069) were taken within a distance of a few meters and can be correlated based on the depth. A comparison of ash profiles of three different peat cores from the centre of the EGR bog shows good agreement, indicating that the peat accumulation rate and compaction are homogeneous. For calculating carbon accumulation rates (CAR, in g C m⁻² yr⁻¹) we averaged the density data from the EGR 2A core to match the resolution of the second core.

The age model from Roos-Barraclough et al. (2004) gives unrealistic high peat accumulation (nearly 800 g C m⁻² yr⁻¹) between 465 and 499 cm depth. Because the age date at 499 cm depth falls out of a linear regression line we modified the original age model by ignoring this age date.

2.2. Paleo net primary production (PNPP)

In order to assess the paleo methane emissions from peatlands we propose to use the paleo net primary production (PNPP) – i.e. the observed carbon accumulation rate (CAR) corrected for secondary peat decay – as a proxy. Our reasoning is that the PNPP is to a great extent controlled by temperature and water saturation of a bog, two parameters that are also key factors for CH₄ emissions (Bartlett and Harriss, 1993). The observed CAR alone is not a good measure for the PNPP, because the initial plant litter resulting from the primary production undergoes varying degrees of degradation in the acrotelm (Malmer and Holm, 1984). For example, a wet ombrotrophic bog may have high net primary production (and high CH₄ emissions) with little degradation of the peat; that is, high CAR. On the other hand, a minerotrophic mire may have equally high net primary production (and high CH₄ emissions) with relatively low CAR due to the abundance of nutrients that leads to thriving microbial C-mineralisation. In order to compensate for such differences in mineralisation we correct the CAR for secondary peat decay following the approach of Malmer and Holm (1984) and Malmer and Wallén (2004). Malmer and co-workers use the carbon to nitrogen ratio of bulk peat. They argue that the changes in C/N result from the loss of carbon while nitrogen is essentially retained and that higher values of C/N found in deeper parts of a profile indicate interruption of the decay process in an early stage. Accordingly we obtain:

$$\text{PNPP} = \text{CAR} \times 100 / (\text{C/N})$$

In the above equation the factor of 100 represents the assumed original C/N ratio of plant litter at the beginning of the decay process. Malmer and Wallén (2004) state that the initial C/N ratio of plant litter can be considered constant — at least for *Sphagnum* dominated peat (they use C₀/N₀=120). Perhaps this is not strictly valid for fen peat litter, which may have a lower initial C/N ratio. If this was the case at the EGR profile our PNPP estimates older than ca. 10,000 Cal. yr BP (see Fig. 2) were overestimated, but the shape of the curve would still be largely retained. However, the fact that at the EGR site the C/N profile correlates well with other indicators of peat decomposition at all depths (see below) suggests that the initial C/N ratio was reasonably constant and justifies the use of the PNPP as obtained from the above equation — at least for a first order estimate of paleo methane emissions.

2.3. Rock-Eval analyses

For an independent check of the validity of the C/N ratios as an indicator of degradation, the peat samples' oxygen indices (OI), and R400 ratios were analysed using Rock-Eval 6 pyrolysis (Disnar et al., 2003). With this method the sample is pyrolysed by applying a temperature gradient from 200 °C to 650 °C. The volatilised hydrocarbons and CO₂ are analysed using FID and IR detection, respectively. The R400 ratio corresponds to the fraction of hydrocarbons pyrolysing below 400 °C. The material pyrolysing below 400 °C typically includes little degraded biopolymers, while the more degraded and refractory geopolymers (e.g. humic substances) pyrolyse at temperatures above 400 °C. The R400 ratio can therefore be interpreted in terms of degree of degradation of the organic matter: lower R400 values are found in more decomposed peat. The oxygen index (OI) corresponds to the amount of CO₂ emanating during pyrolysis below 400 °C divided by the total organic carbon content. The OI is proportional to the oxygen content of the organic matter and decreases with increasing degree of decomposition of the peat.

3. Results

3.1. Degree of peat decomposition

The measured organic carbon contents range from 430 to 540 mg C/g and the C/N ratios vary between 25 and 70 (Fig. 1). These values are in the expected range for both parameters (see e.g. Malmer and Holm's, 1984, data on Swedish mires). Broadly, the C/N ratios are >40 in the middle part of the bog (between 2 and 4 m) and are <40 below and above this zone, except for the near surface sample. For the EGR bog profile the C/N ratios thus indicate a less decomposed layer in the middle part. The Rock-Eval parameters reveal the same degradation pattern and thus confirm that the C/N ratio depends mainly on decomposition and not on variations in the initial C/N ratio of plant litter. The oxygen index (OI) and the R400 ratio show the same trends as the C/N ratio (Fig. 1). In other words the samples with low C/N ratio contain less oxygen and less readily pyrolysable moieties, which is consistent with a more degraded character of this material. A peak in the pyrolysis FID signal around 355–360 °C is found for all samples with high C/N ratio. This peak originates most probably from cellulose (Disnar et al., 2003) and corroborates the interpretation of a lesser degree of decomposition for samples with high C/N ratio. A change in the initial C/N

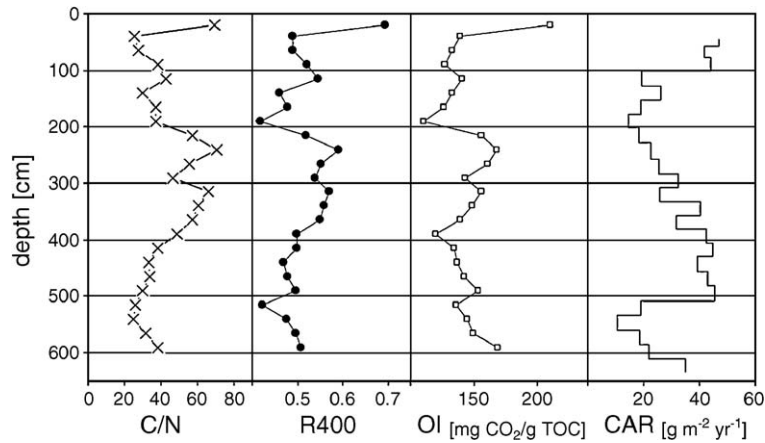


Fig. 1. Geochemical parameters (C/N ratio, Rock-Eval R400 ratio, and Rock-Eval oxygen index OI) and the calculated carbon accumulation rate (CAR) of the EGR peat profile.

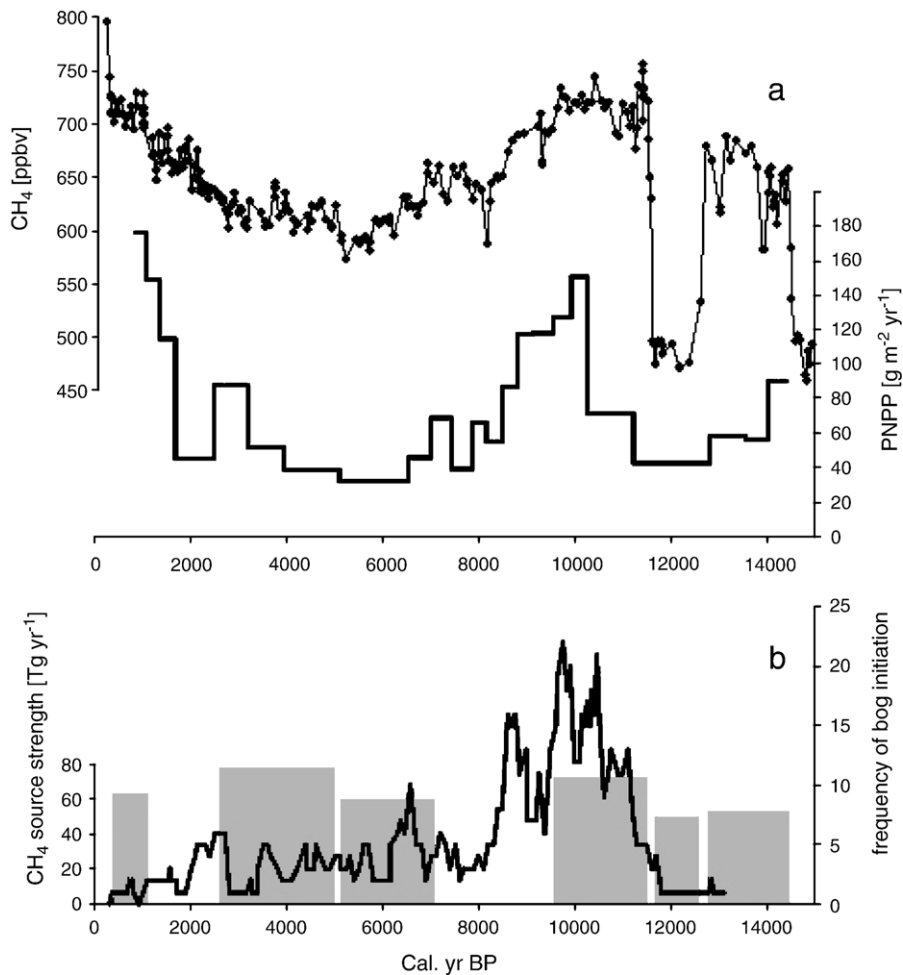


Fig. 2. (a) Atmospheric methane concentrations as reconstructed from Greenland ice cores (filled diamonds; GRIP; Chappellaz et al., 1993; Blunier et al., 1995) and estimated paleo net primary production (PNPP) at the EGR bog (full line). (b) Estimated source strength of northern peatlands (grey bars; Chappellaz et al., 1997; Dällenbach et al., 2000) and frequency of peatland initiation in Western Siberia (full line; Smith et al., 2004).

ratio of peat litter at the transition of fen to bog peat would result in an offset of the curve at the corresponding age. However, the potential over-correction of the fen peat values may compensate the generally higher methane emission of fens compared to bogs (Bartlett and Harriss, 1993); that is, the corresponding shift in the PNPP values would be in the “right” direction.

3.2. PNPP

Fig. 2a shows the curve obtained for the paleo net primary production (PNPP). The values are comparable with measurements of net annual production of northern fens and bogs (200–400 g C m⁻² yr⁻¹, cited in Malmer and Holm, 1984). The PNPP curve shows elevated values (up to 90 g C m⁻² yr⁻¹) during the B/A, which then decline and reach a minimum (ca. 40 g C m⁻² yr⁻¹) during the YD cold period. With the onset of the Holocene the PNPP values increase, although the increase is less sharp than for the atmospheric methane concentration. A high PNPP (150 g C m⁻² yr⁻¹) is reached around 10,000 Cal. yr BP. After that time PNPP declines to reach 40 g C m⁻² yr⁻¹ around 8000 Cal. yr BP. Around 7000 kyr the PNPP slightly increases, and then decreases again. From ca. 6500 to 4000 Cal. yr BP it remains low (30 to 40 g C m⁻² yr⁻¹) and after that starts to increase towards the maximum value in the youngest sample analysed (175 g C m⁻² yr⁻¹ around 1000 Cal. yr BP). A further feature of the curve is the minimum around 2000 Cal. yr BP.

The PNPP variations result mainly from the variations of the linear accumulation rate (r.s.d. 38%), the C/N ratio (r.s.d. 32%), and the variability of the bulk density (r.s.d. 15%). All of the PNPP curve's features are already visible in the organic C-accumulation curve (Fig. 1). Again note, that the PNPP values may be slightly offset at the fen to bog transition (see above).

4. Discussion

4.1. Comparison of PNPP, W-Siberian peatland initiation and atmospheric methane

Based on the reasonings presented above we assume that there is a positive correlation between a peatland's high net primary production and its methane emissions, and that the EGR site is representative for the evolution of northern peatlands on a larger scale. We shall below attempt a more global interpretation of our results.

We observe that the paleo net primary production (PNPP) obtained for the EGR peat bog and used as a

proxy for methane emission intensity shows similar trends as the atmospheric methane concentrations inferred from the CH₄ mixing ratio in gas bubbles from the Greenland ice cores (Fig. 2a; GRIP; Chappellaz et al., 1993; Blunier et al., 1995). Furthermore, the PNPP curve shares many features with the evolution of the peatland initiation frequency in Western Siberia (Smith et al., 2004; Fig. 2b). In the following these three curves – the PNPP from EGR, atmospheric methane, and W-Siberian peatland initiation – will be compared in more detail.

During the YD low PNPP and a low rate of peatland spreading in W-Siberia both point to minimal CH₄ emissions in agreement with low concentration of atmospheric methane. During the B/A atmospheric methane concentrations are high and the concomitant high PNPP values prove good conditions for peatland growth and thus a potential for methane emissions from northern peatlands already at that time. In contrast Smith et al. (2004) observed no Late-glacial peat formation in W-Siberia. In fact, based on the available evidence it is unlikely that the total peatland area at high latitudes was large enough for a significant contribution during the B/A. After the YD the PNPP increases by a factor of 4 between 11,500 and 10,000 Cal. yr BP, coinciding with the most vigorous spread of W-Siberian peatlands. Thus, the methane emissions from the northern peatlands have certainly boosted at that time and significantly contributed to atmospheric methane.

However, the observed rate of PNPP increase (and W-Siberian peatland spreading) appears to be too slow to fully explain the sudden rise of atmospheric methane by some 50% within ca. 100 years at ca. 11,700 Cal. yr BP. Kenneth et al. (2000, 2003) suggest that these rapid changes are caused by the release of methane from gas hydrates stored in marine sediments. These authors argue that terrestrial peatlands would not adapt fast enough to explain the observed rapidity of the increase in atmospheric methane. They use the same argument to interpret the rapid increase of methane at the beginning of the B/A (ca. 14,700 Cal. yr BP).

At the beginning of the Holocene the atmospheric methane concentrations are high and decline to a minimum around 8200 Cal. yr BP (Fig. 2). The PNPP and the W-Siberian peatland spreading also diminish over that same time interval. The most pronounced decrease of atmospheric methane is observed between 9000 and 8200 Cal. yr BP and corresponds to a similar decrease in PNPP. Around 7200 Cal. yr BP the atmospheric methane concentrations and the PNPP are again slightly higher. This is noteworthy, because the

atmospheric CO₂ concentrations start to increase at that time (Raynaud et al., 2000) and a terrestrial source had been invoked (Indermuehle et al., 1999). However, the concomitant increase in PNPP indicates good conditions for peat accumulation at that time and therefore makes enhanced release of CO₂ from these terrestrial environments little plausible.

Between ca. 6000 and 4000 Cal. yr BP the atmospheric methane concentrations are low. The fact that the PNPP and the spreading of W-Siberian peatlands are also low points to a decreased intensity of CH₄ release from northern peatlands. After ca. 4000 Cal. yr BP atmospheric methane and PNPP start to rise again, while the rate of peatland initiation in W-Siberia remains low. This latter observation could be simply due to the fact that by this time all suitable land was covered by peatlands. The increasing values of PNPP indicates that the contribution of northern hemisphere peatlands to atmospheric methane after 4000 Cal. yr BP was more via increased intensity of emission than via increased total area of peatlands. The drop of PNPP around 2000 Cal. yr BP is not seen in the atmospheric methane record.

In many studies the emissions from low latitude wetlands and their variations are considered as the main cause for changes in atmospheric methane during the Late-glacial and the Holocene (Petit-Maire et al., 1991; Chappellaz et al., 1993). Accordingly, the reduced methane emissions from tropical wetlands were put forward to be responsible for the low atmospheric CH₄ concentrations during the YD, the marked CH₄ drop at 8200 Cal. yr BP and the minimum value at 5200 Cal. yr BP. All of these periods coincide with lake level low stands in many of Africa's lakes (Roberts, 1998). However, the fact that these three features also clearly appear in the PNPP curve of the EGR bog, suggests that methane emissions from northern peatlands varied in a similar way as the tropical sources and significantly have contributed to the development of the Late-glacial and Holocene climate.

The high values of PNPP and W-Siberian peatland initiation very early in the Holocene together with the good agreement of these two parameters with the atmospheric methane concentrations throughout the Holocene, corroborates the importance of the wetland source of methane for the Holocene. It appears that the turning from a probable marine gas hydrate source at the end of the YD towards a dominant wetland source has occurred very soon after the onset of the Holocene — earlier than suggested by Kennett et al. (2003) who placed this change around 5000 Cal. yr BP.

4.2. Comparing PNPP and modelled source strengths

In Fig. 2b the PNPP-estimate of methane emissions from northern peatlands is also compared to the model-derived estimates of total methane sources north of 30° N published by Chappellaz et al. (1997) and Dällenbach et al. (2000). Their 3 box model (3 latitude bands) is based on inter-polar CH₄ concentration gradients as obtained from the ice-core records. A surprising result of the model is that the methane emissions north of 30° N are relatively high during the YD (Fig. 2b). Moreover, the increase of modelled source strength after the YD is much lower than the one inferred from PNPP (Fig. 2a) and Siberian wetlands (Fig. 2b). Considering gas hydrates as an additional source of methane at the end of the YD (Kennett et al., 2003), the modelled source strength appears to be too high during the YD and/or too low in the early Holocene. The diminution of modelled source strength around 6000 Cal. yr BP and the higher values around 4000 Cal. yr BP correspond well to the here-inferred emissions from peatlands. However, the subsequent decrease of the modelled source strength around 1000 Cal. yr BP is opposite to the expected peatland emissions based on PNPP (Fig. 2a).

5. Conclusions

Based on our data we suggest that the main features of the curve of atmospheric methane are in phase with CH₄ emission intensity for northern wetlands during the Late-glacial and the Holocene until at least 1000 Cal. yr BP. Therefore, similar variations in methane emissions from both, tropical and northern wetlands have shaped the evolution of atmospheric methane. Although the EGR bog shows a high PNPP and thus high methane emissions during the B/A warm period, the missing evidence for widespread northern peatlands does not allow the generalization of an important northern peatland source of methane at that time. With respect to the fluctuations of atmospheric methane levels during the Holocene the northern peatland source was of importance, since the high early Holocene PNPP, the low PNPP from 6000 to 4000 Cal. yr BP, and the again high PNPP in the late Holocene are all reflected by the concentrations of atmospheric methane. With the exception of the steep rise of atmospheric methane concentrations at the end of the YD and at the beginning of the B/A our results corroborate the view of a dominant wetland source of atmospheric methane with an important contribution from the northern hemisphere.

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