Methane budget of a Black Forest spruce ecosystem considering soil pattern

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Abstract. Study included seven soils, an adjacent spring and brook and was conducted to estimate CH_4 source and sink strengths of forest soils along a wetness gradient, i.e. their exchange with atmosphere (*direct* emission), and hydrosphere (*indirect* emission). Soils are represented by anaerobic Histosol, oxic Cambisols, Histosol with degraded peatlayers and Gleysols having intermediate redox state. They could be separated into three emission groups: CH_4 emitting (248–318 kg C ha^{-1} a^{-1}), CH_4 uptake (−0.1 to −5 kg C ha^{-1} a^{-1}), and soils on the edge of CH_4 uptake and release (−0.2–20 kg C ha^{-1} a^{-1}). Although soils with CH_4 uptake were dominant (75%), the soil specific CH_4 budget identified the study field (6.53 ha) as CH_4 source (40.9 kg C ha^{-1} a^{-1}). Not only CH_4 emissions, but also dissolved CH_4 in soil solution varied regularly with soil type. Individual soil solutions contained 0.008–151 μmol CH_4 l^{-1}. CH_4 vanished to negligible loads, when dissolved CH_4 passed an oxidative downslope soil zone, but promoted CH_4 uptake was measured at this soil. In turn, CH_4 was discharged to the atmosphere, when the soil solution left the pedosphere across an anaerobic soil zone. These measured indirect emissions were low (34 g C a^{-1}), but the values of individual soil solution indicate possible higher discharges (3.9 kg a^{-1}) at a different soil pattern. The results suggest that CH_4 uptake rates of temperate forests are overestimated.

Introduction

Methane (CH_4) is contributing about 20% to global warming (IPCC 2001). It is an important product of anoxic degradation of organic matter typical for wetland soils. Thus, wetland soils are the largest natural source of atmospheric CH_4 between 92 and 225 Tg CH_4 a^{-1} (equal 15–37% of the total CH_4 source) (IPCC 2001). In the following, only transmissions to the atmosphere are called emissions. Contradictory, well-aerated soils are sinks for atmospheric methane, estimated with 10–44 Tg CH_4 a^{-1} (equal 2–7.8% of the total CH_4 sink). However, these estimates are rather uncertain (summarised in Bodegom et al. 2002; Christensen et al. 2003).

Methane emissions have been investigated fairly numerously from rice and natural wetland soils (Matthews and Fung 1987; Aselman and Crutzen 1989; Bartlett and Harriss 1993; Hou et al. 2000; Huttunen et al. 2002a, b). CH_4-uptake by soils was reported first by Harris and Sebacher (1981) followed by

other studies of well-aerated soils, especially under forests (Steudler et al. 1989; Castro et al. 1995; Kähkönen et al. 2002). Missing are publications about CH_4 cycling of hydric mineral soils. These tend to cover relevant proportions within humid climates. If methane cycling is to be understood, the CH_4 budgets of these soils have to be understood.

Methane from soils interacts with the hydrosphere as well, since it is dissolvable in water according to Henry's law. Therefore, it can be transported via internal water flow within the pedosphere and eventually be emitted to the atmosphere after the soil solution is discharged to the surface (Sawamoto et al. 2002). Such emissions occurring at site remote to the production are defined as *indirect* emissions. As for nitrous oxide (N_2O), the IPCC Guidelines for National Greenhouse Gas Inventories (1996) state the possibility of *indirect* CH_4 emissions, but in contrast to N_2O, it does not take them into account. This was probably due to limited studies. However, presently some reports about dissolved methane concentrations from peatlands (Brown et al. 1989; Huttunen et al. 2002a, b; Eilrich and Steinmann 2003) and flooded rice soils (Lu et al. 2000) are available. All highlight super-saturated CH_4 solutions up to 93,000 times the atmospheric equilibrium concentration (Huttunen et al. 2002b). More studies should be conducted to reveal the relevance of dissolved methane, explicitly as possible *indirect* emission path.

The objective of this study was to estimate CH_4 source and sink strengths of forest soils at the hierarchical level of soil subtype, according to the German soil classification (DBG 1998). It could be demonstrated that these reflect satisfyingly prevailing environmental conditions (Fiedler and Sommer 2000). In other taxonomic systems this name does not exist for a certain level. Therefore, the rather neutral word soil type is used in the following, as a synonym for available soil mapping unit. The emphasis was on hydric mineral soil types which are rather common in humid climates. Until now, well-aerated soils are known to uptake atmospheric methane and anaerobic soils emit it. Little is known about the methane budget of intermediately aerated soil types (e.g., Gleysols, Fluvisols, Planosols). This study intends to help bridge this gap of knowledge, i.e. to evaluate the potential risk of methane emissions by intermediately aerated soils. For more detailed estimates it is wise to combine proxy information, e.g., vegetation mirroring well the biotic and soil types as indicators for the abiotic environment. The investigated soil types were differentiated by distinct water and redox regime along a topo sequence. Additionally, to the exchange with the atmosphere (*direct* emission), their interactions with the hydrosphere (including *indirect* emission) were investigated.

Hypothesised was, (i) spatial net CH_4 emissions and concentrations of dissolved CH_4 are linked to soil type being proxies of the prevailing environmental conditions. (ii) The aquatic system adjacent to the investigated pedosphere is characterised by CH_4 enrichment compared to the atmospheric equilibrium (ambient), whereas autochtonic CH_4 formation must be negligible. (iii) Since the system has to move towards ambient, CH_4 is discharged to the

atmosphere (as *indirect* emissions) during transport via liquid phase in two phases: spontaneously and gradually.

Materials and methods

Environmental setting

The study site 'Wildmosswald' has been presented previously in other studies (Fiedler et al. 2002; Jungkunst et al. 2004). Briefly, the catchment (6.53 ha) is located in the cool-humid (MAT 6 °C, MAP 1600 mm) Central Black Forest (Southwest Germany) on a north exposed slope between 1090 and 1099 m a.s.l. The site is covered by a 100-year-old uniform Norway spruce (*Picea abies* [L.] Karst.) forest, upon soils from well-aerated Cambisols to completely water-logged Histosols and different types of Gleysols (ISSS-ISRIC-FAO 1998).

Seven soils (Table 1) and an adjacent spring-brook system were selected, representing two different alignments (from up-hill to toe-hill) of pedo-elements (catena) typical for the Central Black Forest. According to the downward lateral water flow, these pedo-elements (soil types) are arranged as follows:

Catena (1): Endoskeletic Cambisol (BBl) – Humic Gleysol (SGn) – Histic Gleysols (SGo 1 + 2) – Fibric Histosol (HNu) – Sapric Histosol (HNuv) – spring–brook
Catena (2): Endoskeletic Cambisol (BBl) – Humic Gleysol (SGn) – Histic Gleysols (SGo 1 + 2) – Chromic Cambisol (GGx)

The major difference between those catenae is the terminal element. Catena (1) discharges the water into the aquatic system across an anaerobic carbon accumulation zone (Histosols), while catena (2) discharges into a well-aerated zone (Cambisol). The greatest distance between the soil sites was 200 m. The distance between sampling points of spring and appending brook was 17 m.

Indirect emissions

According to IPCC (1997), direct emissions are *in situ* emissions, i.e. the emissions occur directly at the place of production, whereas *indirect* emissions include an identifiable transportation away from the production zone. In this study case, the pedosphere is regarded as the production zone either emitting directly to the atmosphere or indirectly via hydrosphere. These indirect emission via water transport reach the atmosphere in two pathways: (i) by spontaneous degassing at the site where the soil solution discharges, i.e. in this study case a small spring and (ii) by gradual degassing until ambient (0.087 $\mu l \, l^{-1}$ at 5 °C water temperature). Evidences for autochtonic methane formation at the spring itself were not found (fast moving water, high redox values, few organic

Table 1. Selected static and dynamic properties of soils of the study field 'Wildmooswald'.

Soil	Texture (%) Sand	Silt	Clay	BD (g cm^{-3})	pH (CaCl$_2$)	C_{org} (g kg^{-1})	Peat degrad[#]	Thickness of O/H horizon (cm)	C stock (kg m^{-2})	GWL Range (a+b)	GWL Median (a/b)	Eh (mV) (≤10 cm) $Q1/Q2/Q3$ (a+b)	Eh (mV) (20 ± 5 cm) $Q1/Q2/Q3$ (a+b)	Eh (mV) (30 ± 5 cm) $Q1/Q2/Q3$ (a+b)
BB1* Endoskeletic Cambisol** Andic Dystrudept***	51–54	26–32	17–21	0.1–1.2	2.8–4.3	22–319	–	7/none	16.2	–	>100/>100	618/657/705	599/645/685	568/618/665
SGn* Humic Gley-sol** Humic Epiaquept***	50–58	24–28	17–22	0.1–1.0	2.8–3.7	23–425		10/none	21.1	–100 to –3	–26/–25	355/425/561	250/279/351	252/274/321
SGol* Histic Gley-soll** Histic Humaquept1***	44–47	30–32	23–24	0.1–1.2	3.1–3.8	25–430	H3–H8	7/26	25.1	–42 to –6	–14/–12	262/314/386	23/57/203	73/133/188
SGo2* Histic Gley-sol2** Histic Humaquept2***	50	30–32	18–20	0.1–0.7	3.0–3.7	54–415	H3–H6	6/30	28.6	–38 to –4	–13/–18	270/526/591	–62/2/61	–89/–30/37
HNu* Fibric Histo-sol** Fibric Haplohemist***	None	None	None	0.1–0.2	3.3–3.6	439–540	H4–H7	none/>100	75.5	–27 to –3	–8/8	265/485/600	–92/–18/58	–121/–43/42
HNuv* Sapric His-tosol** Sapric Haplohemist***	None	None	None	0.1–0.2	3.4–3.6	450–500	H7–H10	5/97	42.9	–40 to –10	–18/–20	13/77/188	2/12/23	–54/–10/12
GGx* Chromic Cambisol** Andic Dystrudept***	50–63	24–28	12–22	0.1–1.0	3.1–3.9	11–360	–	7/none	15.6	–100 to –14	–69/–69	531/540/553	540/553/567	544/555/569

(a) 01.01.2001–31.12.2001/(b) 01.01.2002–31.12.2002.
BD, bulk density; [#]Peat degradation was classified according to von Post (DBG 1998); C stock, values were calculated according to Sommer et al. (1997); C stock was calculated without O-horizons; GWL, ground water level; Eh, redox potential; $Q1$, 25% of all Eh values are $< Q1$; $Q2$, 50% of all values are $< Q2$ (median); $Q1$, 75% of all Eh values are $< Q3$; C_{org}, was calculated without buried wood; Soil classification according to *DBG (1998) official abbreviation, **ISSS-ISRIC-FAO (1998) and ***Soil Survey Staff (1999). The range of the soil properties is presented until the depth of 60 cm to keep them comparable. Below 60 cm the C-Horizon began at the Endoskeletic Cambisol (BB1).

sediments). According to Reddy et al. (2000) methane formation is strictly bound to anaerobic metabolism debaring presence of nitrate, which was constantly found in elevated values compared to soil solutions (data not shown). However, it could be of importance further down the brook. Therefore, it is not certain, that the measured differences of CH_4 concentrations between brook (at a certain distance away from the spring) and spring resulted solely of gradual degassing without autochtonic methane formation within the brook. Therefore, it was presumed that the dissolved methane of the spring water would eventually reach the atmosphere until the ambient equilibrium. Consequently, the complete indirect methane emissions are the sums of spontaneous degassing at the spring and dissolved loads of methane of the spring water.

Sampling

Methane exchanges between pedo- and atmosphere were monitored over 132 weeks (August 2000–January 2003) in weekly intervals at 12:00 h Central European Standard Time. A closed chamber technique (2×1 m^2) described in detail by Fiedler and Sommer (2000) was used. Gas samples were taken from the chamber headspace 0, 20, 40 and 60 min after closing by vacutainers (22.5 ml). Sampling times were extended during winter (October–April) to 30 min intervals.

Measurements of dissolved CH_4 and gas exchange across the water–air interface at the spring were done weekly from August 2002 to July 2003 (53 weeks). A series of slotted (1 mm wide and 35 mm length) PVC wells (3 per site, 1 m, i-diameter of 6 cm, Stockmann, Warendorf, Germany) were installed for soil water sampling. Before sampling, all wells were completely pumped out. After reaching the original water level (15–60 min), soil solution was collected with a pump-tube-system. A small Teflon-tube (i.d. 5 mm) was inserted 20 cm into the water, while the other end was connected to a weakly evacuated glass bottle ($\sim$700 hPa). As water was flowing into the bottle, the tube was closed by a clamp and the glass bottle was replaced by a needle (0.55×25 mm; Braun, Melsungen, Germany). Following pressure equalisation, a vacutainer ($\sim$20 hPa) filled itself with soil solution after the needle was inserted and the clamp opened. The process was interrupted, as the vacutainer was filled half. Triplicates were collected at each well. Samples from the spring and brook (5 replicates) were collected with the same principle by vacutainer and multi-sampling needle (0.7×40 mm; Terumo, Eschborn, Germany). Aluminium cap and butyl rubber septum fitted vacutainers were flushed (N_2) and evacuated 5 times before collecting. Samples were stabilised against microbial reactions using aqueous $HgCl_2$ (0.1%, 0.5 ml).

Gas exchanges across water–air interface at the spring was measured using a closed chamber (volume 25 l). The spring surface was completely covered by the chamber (1244 cm^2) standing in the water ($\sim$5 mm) upon four permanently installed stakes adjustable to height. Gas samples were taken as described above.

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Analysis and calculations

Atmospheric and dissolved CH_4 were analysed using a Flame Ionisation Detector (PE Autosystem XL Gas Chromatograph, Perkin Elmer, Wellesley, MA, USA). For calibration three external standards were used. All single values were corrected for air pressure and temperature. Methane emissions (μg C m^{-2} h^{-1}) were calculated using a linear regression (Lessard et al. 1994). All annual flux rates (Table 2) are expressed as interpolated cumulative values (Jungkunst et al. 2004).

CH_4 (μg C) in the water samples was calculated as follows (Tiedje 1982):

$$M = C_g(V_g + V_l\alpha) \tag{1}$$

where C_g is the gas concentration of vacutainer headspace (μg C l^{-1}), V_g is the gas volume (l), V_l is the solution volume (l) and α is the Bunsen solubility coefficient (0.03 at 25 °C) (Clever and Young 1986). Results were converted to μg C l^{-1}. The equilibrium CH_4 concentration in water at the given temperature ($\alpha = 0.0497$ at 5 °C) was calculated using the average atmospheric concentration of 1.745 μl l^{-1} ($= 0.817$ μg C l^{-1}) (IPCC 2001).

CH_4 exchange between hydro- and atmosphere (g C) at the spring was estimated by the following equation:

$$M_{CH_4} = V_H \sum_{i=1}^{n} \frac{1}{q_i}\left(\frac{\Delta C}{\Delta t}\right)_i Q_i \tag{2}$$

where V_H is the volume of the chamber (m^3), q_i is the water flow rate (m^3 h^{-1}), $(\Delta c/\Delta t)_i$ is the change of CH_4 gas concentration within fixed time intervals at sampling day i (g m^{-3} h^{-1}) and Q_i is the interpolated water flow of the i to $i+1$ sampling day (m^3).

The brook water could be captured placing the beaker below a brook cascade. Water flow rate was calculated by the time when a 2 l beaker was filled. Discharges of dissolved methane (g C) were calculated as follows:

$$M_{CH_4} = \sum_{i=1}^{n} C_i Q_i \tag{3}$$

where c_i is the dissolved CH_4 (g m^{-3}) and Q_i is the interpolated water flow of the i to $i+1$ sampling day (m^3).

Additional characterisation of water samples and soils

Water level was measured at each well using a flashlight attached to the end of a retractable tape. Separate samples were collected for measuring immediately water temperature and pH in the field (pH 191, WTW, Frankfurt, Germany). For DOC determination samples were filtered (0.45 μm pore size, PET45/25;

Table 2. Descriptive statistics of net-CH$_4$-emission and groundwater level of the soils of the study field "Wildmooswald".

	Net-CH$_4$-emission (μg C m^{-2} h^{-1})			Annual (a/b) (kg C ha^{-1} a^{-1})	Area (ha)	SWF (a/b) (kg C a^{-1})
	Range ($a + b$)	Mean (a/b)	Median (a/b)			
BB1	−64 to −10	−32/−37	−31/−38	−2.8/−3.3	3.96	−11.09/−13.07
SGn	−28 to 49	−2/−9	−2/−10	−0.1/−0.7	0.74	−0.07/−0.52
SGo1	−19 to 298	−3/25	−4/0	−0.2/2.6	0.81	6.72/11.45
SGo2	−15 to 1784	191/219	69/69	16.8/20.3		
HNu	110 to 31193	3593/3193	1859/2138	318.4/248.1	0.15	47.76/37.21
HNuv	−30 to 244	16/32	0/19	1.4/3.0	0.69	0.97/2.07
GGx	−120 to 11	−46/−60	−42/−64	−4.0/−5.0	0.18	−0.72/−0.90
Total net-CH$_4$-emission from the study field ' Wildmooswald' (a/b)						43.57/35.64

(a) 01.01.2001–31.12.2001/(b) 01.01.2002–31.12.2002; **BB1**, Endoskeletic Cambisol; **SGn**, Humic Gleysol; **SGo1**, Histic Gleysol 1; **SGo2**, Histic Gleysol 2; **HNu**, Fibric Histosol; **HNuv**, Sapric Histosol; **GGx**, Chromic Cambisol.
SWF (Soil Weighted Flux), annual soil specific net–CH$_4$-emission weighted by area. Total net-CH$_4$-emission from the study field "Wildmooswald" (6.53 ha) is presented in kg C a^{-1}.

Macherey-Nagel, Düren, Germany) and analysed by DIMA-TOC 100 (Dimatec, Essen Germany).

Platinum electrodes (2–5 replicates per horizon) and Ag/AgCl reference electrode were used to measure the reduction–oxidation potential (Eh) (Fiedler et al. 2003). Data of the Gleysols (SGn, SGo1) and Endoskeletic Cambisol (GGx) were recorded hourly (Delta-T-Devices LTD, Burwell, Cambridge, UK), those of the others soils manually on a weekly basis (WTW, Weinheim, Germany). The soil temperature of the litter (−3 cm), and the depths −10, −20, and −30 cm were recorded hourly (Jungkunst et al. 2004).

Statistical analysis

Non-parametric analyses were used, since data were not normally distributed (Sharpo–Wilks' W test) and not transformable. The Mann–Whitney U-Test was taken to prove significant differences between the individual soil types, spring and brook regarding environmental parameters. Spearman rank correlation analyses were calculated to identify relationships between two parameters of one sampling site. Analyses were done using Statistica 5.0 (StatSoft Inc., Tulsa, USA).

Results and discussion

Water and redox regime

As previously reported (Fiedler et al. 2002) soil types represent well water and redox regimes. Although precipitation varied from 1840 mm in 2001 to 1604 mm in 2002 (Jungkunst et al. 2004), only marginal differences between annual water levels were observed (Table 1). Water levels exhibited higher spatial than temporal variability. Whereas the wettest soils (Fibric and Sapric Histosol, Histic Gleysol 1 and 2) were characterised by nearly static water levels, Chromic Cambisol and Humic Gleysol showed high amplitudes (Figure 1, Tables 1 and 3).

A decrease in Eh-levels and amplitudes with depth, and an Eh-gradient among soils were detected. The driest soils (Endoskeletic and Chromic Cambisol) represented the highest Eh levels with small range (Tables 1 and 3). The most reductive milieu existed in the Fibric Histosol (HNu) followed by the Histic Gleysols (SGo1 + 2) and Sapric Histosol (HNuv). Low, but compared to the presented soils, medium Eh conditions with a wide range existed inside the Humic Gleysol (SGn).

Water and redox regime of the individual soils showed the identical ranking from driest/well-aerated to wettest/reducing type (BBl – GGx – SGn – HNuv – SGo – HNu). Scattering redox levels suggest the dominance of different electron acceptors. All hydric soils, in particular SGo1 + 2 and HNu, exhibited

the existence of sharply separated oxic (topsoil) and anoxic zones, (Tables 1 and 3). Redox conditions indicated both O_2 consumption over the entire depth of the Cambisols (BBl, GGx), and in contrast CO_2 consumption in the range > 15–20 cm below surface inside the Histic Gleysols (SGo1 + 2) and Histosols (HNu, HNuv).

CH$_4$ exchange between pedo- and atmosphere

Cumulative annual emissions differed from −5 to 318 kg C ha^{-1} a^{-1} (Table 2). Generally, a higher inter-site than inter-annual scattering of emission data was observed. Based on net CH_4 emissions, soils can be separated into three emission groups: (i) CH_4 emitting (HNu), (ii) CH_4 uptake (GGx, BBl, SGn), and (iii) soils on the edge of net CH_4 uptake and release (SGo1 + 2, HNuv). Hypothesis one is fulfilled, if this grouping and not the individual soil types are considered.

Net CH_4 emissions and soil temperatures of all depths correlated significantly ($p < 0.001$) and comparatively, for example (−10 cm): (i) positively at the SGO2 ($r = 0.68$), HNu ($r = 0.79$), HNuv ($r = 0.35$), and (ii) negatively at the CH_4 uptake sites (BBl $r = -0.56$; GGx −0.76).

In agreement with Fechner and Hemond (1992) and Whalen et al. (1996), CH_4 emissions were triggered mainly by the thickness of the oxidative zone above the water level. According to Nykänen et al. (1998), high flux occurred when water levels were situated 10 cm below surface. Thus, only the wettest soil (Fibric Histosol) with non-degraded peatlayer exhibited continuously high direct emissions (mean 3593/3193 μg C m^{-2} h^{-1} 2001/2002). At this site CH_4 emission and water level correlated ($r = -0.49$, $p < 0.001$) indicating, that emission peaks occurred simultaneously to slightly falling water levels. This finding is consistent with results from studies of Windsor et al. (1992); Moore and Dalva (1993); Shurpali et al. 1993; Kettunen et al. (1996), where lowering of water table enhanced the methane fluxes. Obviously, at sites having favourable conditions for continuous methane emissions, this contrasting behaviour was the rule (see SGo2 below).

Both Cambisols showed expected uptake, varying from 10 to 120 μg C m^{-2} h^{-1} (Table 2). Data fit the values of well-drained temperate and boreal forest soils (Crill 1991; Bowden et al. 1993; Dörr et al. 1993; Priemé and Christensen 1997; Butterbach-Bahl et al. 1998), where the average of CH_4 consumption rates varied between 41 and 60 μg C m^{-2} h^{-1}. Higher uptake rates of forest soils between 120 and 361 μg C m^{-1} h^{-1} were published by Castro et al. (1995), Dobbie and Smith (1996), and Tamai et al. (2003). All studies highlighted forest soils to be more effective sinks than arable soils, reaching only 20–50% of the oxidation rate of forest soils (Moiser et al. 1991; Dobbie et al. 1996; Flessa et al. 1998).

Remarkably, the Cambisol (GGx) with episodic waterlogging had higher uptake rates than Cambisol (BBl), where meteoric water percolated freely

Table 3. Dissolved methane (exchange between soils and hydrosphere) and CH₄ exchange across air–water interface at the spring during the measurement period, 1 August 2002–31 July 2003 ('Wildmooswald').

Site	Dissolved CH₄ (μmol CH₄ l⁻¹)			CH₄ FA ×10²	GWL ± SD (WFR ± SD) (cm below surface, 1 d⁻¹)	Eh (≤ 10 cm) (mV)	Eh (20 ± 5 cm) (mV)	Eh (30 ± 5 cm) (mV)	Eh (60 ± 10 cm) (mV)	DOC ± SD (mg C l⁻¹)	pH ± SD	T ± SD (°C)
	Range	Median	Mean	Mean		*Q1/Q2/Q3*	*Q1/Q2/Q3*	*Q1/Q2/Q3*	*Q1/Q2/Q3*			
SGn	0.008 to 15.6	0.22	1.29	3.8	33.2 ± 19.7	320/410/565	242/265/299	249/267/300	167/207/246	14.7 ± 7.8	5.8 ± 0.7	6.7 ± 3.3
SGo2	0.09 to 53.5	1.80	6.02	17.6	20.1 ± 14.1	325/562/607	61/76/164	24/45/96	−115/−93/−51	17.1 ± 4.7	5.8 ± 0.8	6.9 ± 3.6
HNu	0.56 to 118.1	31.13	35.65	104.3	10.5 ± 10.0	332/409/697	−23/7/63	−51/−32/81	−117/−75/−7	17.4 ± 10.3	5.9 ± 0.6	8.0 ± 4.4
HNuv	0.48 to 151.3	6.10	24.13	70.6	23.8 ± 10.8	15/54/150	4/14/25	−43/−13/10	−76/−3/256	27.7 ± 13.3	5.1 ± 0.9	7.0 ± 2.8
GGx	0.017 to 0.3	0.05	0.07	0.2	77.7 ± 24.1	569/594/613	548/585/610	550/580/606	539/564/591	3.1 ± 3.3	5.4 ± 0.8	5.4 ± 2.6
Spring	0.10 to 0.8	0.31	0.30	0.9	(23509 ± 19251)					6.6 ± 5.5	5.2 ± 0.4	6.8 ± 3.0
Brook	0.07 to 0.8	0.24	0.27	0.8								
CH₄ exchange across air–water interface (μmol CH₄ m⁻² h⁻¹)												
Spring	0.11 to 19.3	3.8	3.8	5.42								
(nmol CH₄ l⁻¹)												
Spring	0 to 5.0	0.7	0.8									

SGn, Humic Gleysol; SGo2, Histic Gleysol 2; HNu, Fibric Histosol; HNuv, Sapric Histosol GGx, Chromic Cambisol; FA, factor to ambient (with atmosphere, 0.003 μmol CH₄ at 5 °C); SD, standard deviation; GWL, mean of ground water level; WFR, mean of water flow rate; DOC, mean of dissolved or anic carbon; T, mean of water temperature.

(2001/2002, 4.0/5 vs. 2.8/3.3 kg C ha^{-1} a^{-1}). There was no moisture limitation for the methanotrophs due to high and evenly distributed precipitation and free drainage at the Endoskeletic Cambisol (BBl) at all times. Additionally, the oxidation rates of Endoskeletic Cambisol are already comparatively high particularly for acidic soils (Smith et al. 2000). Therefore, the even higher oxidation rates of Chromic Cambisol have to be considered as elevated. Bender and Conrad (1992) demonstrated the existence of two types of methanotrophs oxidising CH$_4$ with a high and a low affinity, which could be the reason of the different behaviour of both Cambisols. For Endoskeletic Cambisol no additional methane source other than the atmosphere is supposable. Whereas for Chromic Cambisol the soil water was supersaturated exhibited an additional CH$_4$ source (Table 3). Additionally, the frequently changing water level in Chromic Cambisol is acting as an 'air pump' promoting diffusion into the highly porous soil. According to Del Grosso et al. (2000) diffusion is the key variable of CH$_4$ uptake. Other factors of CH$_4$ oxidation, such as temperature, pH (Dunfield et al. 1993), vegetation (Menyailo and Hungate 2002), texture (Boeckx et al. 1997), mineral N stock (Crill et al. 1994), and thickness of O-horizons (Brumme and Borken 1999) were comparable.

Although both Histic Gleysols (SGo1 + 2) have a comparable water and redox regime, annual emission differed between $-0.2/16.8$ and 2.6/20.3 kg C ha^{-1} a^{-1} (2001/2002). However, for SGo1, a slightly degraded peat layer was observed contrasting SGo2, which has been the reason for selecting two plots of this soil type. Remarkably, this field observation reflects the difference in their *direct* methane emission, as do the Histosols. The Histosols are differentiated by the degradation of the peat as well (Table 1). Comparable to Fibric Histosol, the methane emissions and water levels correlated negatively ($r = -0.29$, $p < 0.001$) at SGo2, whereas at SGo1, the correlation was positive ($r = 0.28$). At Sapric Histosol the correlation was not significant.

Noticeable, the water levels of the soils at the edge of CH$_4$ uptake and release fluctuated between 12 and 20 cm below surface. Fiedler and Sommer (2000) defined a critical threshold of water level at $\sim$15 cm below surface, which adjudicate on CH$_4$ uptake or release. Based on their redox status, Fiedler et al. (2002) assumed that the two Histic Gleysols are situated between methane and nitrous oxide production, having a minimum of both (Yu et al. 2001). The wide range of emission rates proved the fragility of this status. Thus, the conditions within the Histic Gleysols can be defined as turning points between CH$_4$ uptake and release.

CH$_4$ exchange between pedo- and hydrosphere

Dissolved CH$_4$ concentration of soil solution ranged from 0.008 to 151 μmol CH$_4$ l^{-1} ($= 0.1$ to 1815 μg C l^{-1}) (Figure 1, Table 3). Results were comparable to published data from natural peat soils (56–243 μmol CH$_4$ l^{-1}, Waddington and Roulet 1997). All samples were supersaturated, being 20–11,000 times the
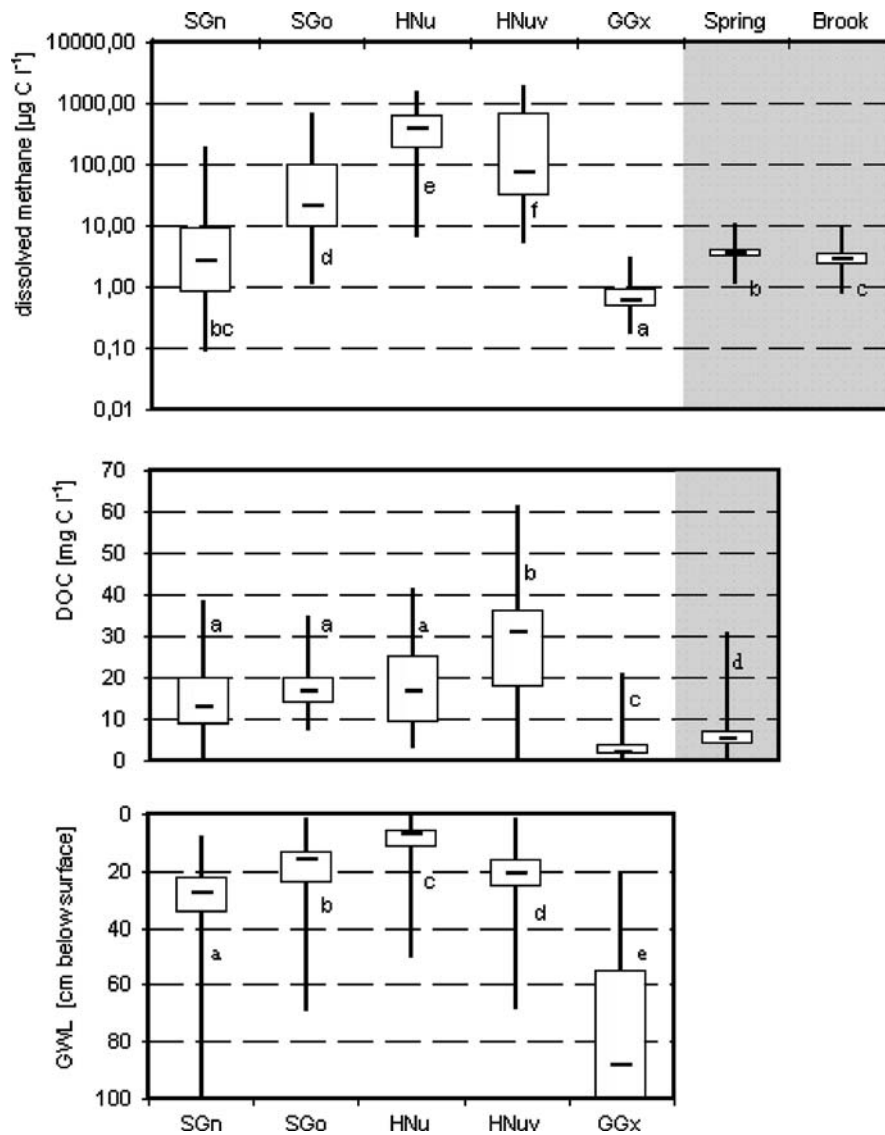
Figure 1. Dissolved methane, dissolved organic carbon and groundwater level (GWL) of studied objects. Box plots with minimum, maximum, 25, 50 (median), 75 percentiles. Significant differences ($p < 0.001$) are expressed by different letters. SGn, SGo, HNu, HNuv, and GGx are abbreviations of the soil types (see Table 1). The aquatic system is grey shaded.

equilibrium concentration with the atmosphere (3.36 nmol CH_4 l^{-1} at 5 °C, Table 3).

Concentrations varied regularly with soil types: GGx < SGn < SGo(1 + 2) < HNuv < < HNu. All differences were significant ($p < 0.001$, Figure 1) confirming hypothesis one. Ranking fits the distinct water and redox regime of soil

types (Table 3). In agreement with Alberto et al. (2000) and Wassmann et al. (2002), significant correlation between CH_4 emission and dissolved methane was found if all sites were combined based on the overlapping data in the period from August 2002 to January 2003 ($n = 25$, $r = 0.77$, $p < 0.001$). However, no correlation was found at any individual sites. This finding indicated that dissolved methane could not be taken as an indicator for methane emission for natural ecosystems, such as forwarded by Alberto et al. (2000) for rice field plots. For example, both Fibric (HNu) and Sapric Histosol (HNuv) are characterised by high concentrations of dissolved CH_4, suggesting high *direct* CH_4 emissions. Compared to Fibric Histosol, Sapric Histosol usually emitted truly less CH_4 where even episodic uptakes were observed. It seemed that the thicker oxidative zone above the water level in the latter soil must reduce the *direct* emission efficiently. Many studies have indicated that vascular plants play an important role in determining net CH_4 exchange between pedo- and atmosphere (Whiting et al. 1991; Christensen et al. 1999; Joabsson and Christensen 2001). Wetland vegetation may influence fluxes (summarised by Joabsson et al. 1999). However, wetland vegetation was found only at the Fibric Histosol (Eriphoro-Trichophoretum). Therefore, it was probable that CH_4 in the Fibric Histosol by-passed mainly the consumption zone via plant vascular transport. While the main plant association on the Sapric Histosol as well as all other sites was identified as Vaccino-Picetea due to significant lower water table. Consequently, site-specific vegetation was solely an efficient indicator for high CH_4 effluxes, whereas the greatest differences in flux are brought about by depth of water table suiting well to the review results of Smith et al. (2000).

DOC may serve as a C source for CH_4 production. Thus, significant correlation was found between dissolved CH_4 and DOC ($r = 0.44$, $p < 0.001$). Comparison of concentrations between dissolved CH_4 and DOC showed that the dissolved C–CH_4 represented only a small proportion of the DOC pool (varied between 0.01 (SGn) and 2.5% (HNu)).

CH_4 exchange between hydro- and atmosphere

As hypothesised the aquatic system adjacent to the investigated pedosphere is characterised by CH_4 enrichment. CH_4 concentrations inside the spring-brook system varied within a relatively small range between 70 and 800 nmol CH_4 l^{-1} ($= 0.8$–9.9 μg C l^{-1}) (Table 3). The aquatic system was approximately 9000% supersaturated with CH_4. Generally, lower values were reported for oceanic (4 nmol CH_4 l^{-1}, Kelley and Jeffrey 2002) or estuarine systems (670 nmol CH_4 l^{-1}, Upstill-Goddard et al. 2000) and for fresh water rivers (3–152 nmol, Upstill-Goddard et al. 2000).

CH_4 emission across water–air interface at the spring varied from 0.11 to 19.3 μmol CH_4 m^{-2} h^{-1} ($= 1.3$ to 232 μg C m^{-2} h^{-1}). The third hypothesis is confirmed, but in comparison to other aquatic systems, the CH_4 emissions were disproportional low. For example, Smith and Lewis (1992) who investigated

temperate and alpine lakes reported CH_4 exchange rates between hydro- and atmosphere ranging from 2.9 to 122.5 μmol CH_4 m^{-2} h^{-1}. Even higher flux rates (2.4 mmol m^{-2} h^{-1}) were documented for ponds of boreal zones (Bubier et al. 1993 quoted by Huttunen et al. 2003). A significant correlation was found between the amount of spontaneously emitted and dissolved CH_4 (g C h^{-1}) ($r = 0.51$, $p < 0.001$).

CH_4 budget in relation to soil pattern

CH_4 budgeting of temperate forests bases on measurements of well-drained soils. Uptake rates between 0.4 and 6.7 kg C ha^{-1} a^{-1} were reported (Lessard et al. 1994; Kasimir-Klemedtsson and Klemedtsson 1997; Dobbie et al. 1996; Dobbie and Smith 1996; Brumme and Borken 1999, Smith et al. 2000). In agreement to these CH_4 uptake up to 5 kg C ha^{-1} a^{-1} of the Chromic Cambisol (GGx) and $\sim$3 kg C ha^{-1} a^{-1} CH_4 of the Endoskeletic Cambisol (BBl) supported that temperate forests are considered as methane sinks. Therefore, if calculated with the dominant soil type (BBl 60.6% of the total area) as usually done, the *direct* CH_4 emissions of total catchment yielded -18.3 and -21.6 kg C a^{-1} for 2001 and 2002, respectively. Nevertheless, their sink strength is overpowered by soils, which may be left out of account due to low area proportion. CH_4 budgeting based on soil specific emission weighted by their area, resulted in 36 and 44 kg C a^{-1} (2002, 2001), respectively (Table 2). The 'hot spot' Fibric Histosol (2.3% of total area) is responsible for switching the landscape from a sink into a source of atmospheric methane. Therefore, area proportion is not a criterion on whether to consider a pedo-element or not.

In relation to the *direct* emissions of the 'Wildmooswald' having an annual mean of 40 kg C a^{-1}, the *indirect* emissions of 0.034 kg C a^{-1} are subordinate. This is true even if the catchment has additional outlets, which cannot be ruled out. A CH_4 exchange between (semi-)terrestrial and appending aquatic system was only observed when dissolved CH_4 passed an anaerobic soil zone (Histosols) entering the spring and brook represented by catena (1). Referring to the water flow of 9232 m^3 a^{-1}, 34.3 g C–CH_4 was discharged by the pedosphere and/or *in situ* production into the aquatic system. Anoxic sediments responsible for *in situ* production were not found. After passing pedosphere, CH_4 emission from water phase into the atmosphere became a function of the CH_4 concentration gradient between water and air (Conrad 1996). The spontaneous degassing directly at the spring was 0.1 g C a^{-1} (see equation 2).

The transfer velocity was mainly a function of water agitation, which can be determined by turbulence (Middelburg et al. 2002). This fact explained the temporal variability of CH_4 emissions at the spring by simultaneously steady concentrations of dissolved CH_4. It underlines the necessity of seizing gaseous emission directly at the spring. Flow rates were significantly correlated to CH_4 exchanges ($r = 0.50$, $p < 0.01$). During transit from the spring to the brook

(gradually emission), 3.8 g C a^{-1} were lost. This could be proven by multiplying emission per square meter ($= 0.6$ g C m^{-2}) and estimated water surface area of 5.1 m^2 (17 m length $\times \sim$0.3 m width), a C loss was 3.1 g C a^{-1}. The missing 0.7 g C a^{-1} is explainable by the uncertain estimation of the temporal variable area and further water surface agitation resulting from additional cascades. On the base of equilibrium concentration (0.041 μg C l^{-1} = 0.003 μmol CH l^{-1}) it is calculable, that 0.378 g C a^{-1} can be transported via the aquatic system without CH_4 degassing, i.e. yet another 30.12 g C a^{-1} were emitted during transit in the aquatic system. Assuming uniform conditions, a water surface area of 56 m^2 is needed – equal to 187 m length of the investigated brook – for the total degassing of the dissolved methane until equilibrium.

The differences in the CH_4 concentrations of the soil solutions (explicitly Histosols) and the aquatic system indicate that a high proportion is either emitted and/or oxidised during the transit through the pedosphere. The lateral water flow within the catchment results from periglacial cover sediments, which developed a low permeable subsoil layer (Fiedler et al. 2002). It can be assumed that these layers cross out upstream at the spring. Probably, this zone acts as a sink for dissolved CH_4 and/or a source of atmospheric CH_4.

The absence of an anaerobic zone at the end of catena (2) resulted in marginal CH_4 discharges via soil solution. CH_4 leaching is an irrelevant pathway, if dissolved methane passes an oxidative downslope zone such as the Chromic Cambisol. However, the measured uptake rates of the Chromic Cambisol are very high, especially if related to other investigated sinks. Giving the reason to speculate, that slightly CH_4-enriched soil solution turns this particular terminal catena element into such an efficient methane sink.

Conclusion

The results support previous findings that soil types are proxies of the prevailing environmental conditions and consequently of their CH_4 source and sink strengths (Fiedler and Sommer 2000; Fiedler et al. 2002; Sommer and Fiedler 2002). In this context, Jungkunst et al. (2004) state that especially if used in combination with data pools of other important proxies, such as maps of vegetation (Bartlett et al. 1992) and wetland types (Roulet et al. 1994), detailed soil maps are valuable tools for up-scales of trace gas emissions.

The results clearly indicate that the methane uptake rates of temperate forests are overrated. Conventional CH_4 budgeting based on well-aerated soils and the budget considering soil specific emissions weighted by their area vary in > 300%. The non-degraded Histosol was detected as 'hot spot' of CH_4 emission responsible for switching the landscape from a sink into a source for CH_4 to the atmosphere (mean annual value -20 vs. 40 kg C). Since *direct* CH_4 fluxes of temperate forest have solely been measured for well-aerated soils, their estimation is highly uncertain. Referring to the stated importance of forest soils within the global CH_4 budget, more information about their 'true'

strength is needed. The study suggests a gap of knowledge about forest soils situated at the edge of CH_4 uptake and release. For example, even if the Histosols are excluded (not common in temperate forest) these mineral hydric soils have dramatic impact on the total CH_4 balance. This was emphasised by the results of 2002, where the sink strength of 3.96 ha of Endoskeletic Cambisol were nearly nullified by 0.81 ha of Histic Gleysols (-13.1 vs. 11.5 kg C). Furthermore, hydric mineral soils can be very efficient sinks, as was indicated by Chromic Cambisol (GGx).

Our results support other ecosystem studies on the influence of soil pattern and water chemistry of adjacent aquatic systems (Harris and Sebacher 1981; De Angelis and Scranton 1993). It is demonstrated that the relevance of dissolved methane leaching is controlled by soils surrounding the inlets to aquatic systems. CH_4 transfer from (semi-)terrestrial to aquatic systems is occurring when the pedosphere is discharged into aquatic system across an anaerobic soil zone (Histosols), as demonstrated by catena (1). The results indicate, if CH_4 enriched soil solution gets in contact with the atmosphere it will spontaneously or gradually release its loads. Therefore, despite the low amount of this study case (34.3 g a^{-1}), in other ecosystems not having a CH_4 reduction zone up-stream to springs, it could bear a potential risk. Assuming that soil solution of the Fibric Histosol is directly discharged to the surface it would result in a value of 3.9 kg a^{-1}, taking the mean concentration and the same water flow rate. Referring to the transfer velocity, in such a case it would be indispensable to obtain the spontaneous degassing directly at springs. Otherwise a major fraction of the *indirect* emission would not be acquired. In contrast, CH_4 leaching is negligible when downslope aerobic zone, like catena (2), exist.

The results shall not be taken to justify, that the IPCC Guidelines are not considering *indirect* CH_4 emission, since individual soil solutions were extremely CH_4-enriched. However, in order to incorporate the factor of *indirect* emission into regional models, it will be necessary to validate our results. Therefore, it is important to extend the investigations into other regions, ecosystems and land uses.

Acknowledgements

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