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Decadal variability of soil CO_2 NO, N_2O, and CH_4 fluxes at the Höglwald Forest, Germany

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Abstract

Besides agricultural soils, temperate forest soils have been identified as significant sources of or sinks for important atmospheric trace gases (N_2O, NO, CH_4, and CO_2). Although the number of studies for this ecosystem type increased more than tenfold during the last decade, studies covering an entire year and spanning more than 1–2 yr remained scarce. This study reports the results of continuous measurements of soil-atmosphere C- and N-gas exchange with high temporal resolution carried out since 1994 at the Höglwald Forest spruce site, an experimental field station in Southern Germany. Annual soil N_2O emission, NO emission, CH_4 uptake, and CO_2 emission (1994–2010) varied in a range of 0.2–3.2 kg N_2O-N ha^{-1} yr^{-1}, 6.4–11.4 kg NO-N ha^{-1} yr^{-1}, 0.9–3.5 kg CH_4-C ha^{-1} yr^{-1}, and 7.0–9.2 t CO_2-C ha^{-1} yr^{-1}, respectively. The observed high fluxes of N-trace gases are most likely a consequence of high rates of atmospheric nitrogen deposition (> 20 kg N ha^{-1} yr^{-1}) of NH_3 and NO_x to our site. For N_2O cumulative annual emissions were > 0.8 kg N_2O-N ha^{-1} yr^{-1} high in years with freeze-thaw events (5 out 14 yr). This shows that long-term, multi-year measurements are needed to obtain reliable estimates of N_2O fluxes for a given ecosystem. Cumulative values of soil respiratory CO_2 fluxes were highest in years with prolonged freezing periods e.g. the years 1996 and 2006, i.e. years with below average annual mean soil temperatures and high N_2O emissions. The results indicate that long freezing periods may even drive increased CO_2 fluxes not only during soil thawing but also throughout the following growing season.

Furthermore, based on our unique database on GHGs we analyzed if soil temperature, soil moisture, or precipitation measurements can be used to approximate GHGs at weekly, monthly, or annual scale. Our analysis shows that simple-to-measure environmental drivers such as soil temperature or soil moisture are suitable to approximate fluxes of NO and CO_2 in weekly and monthly scales with a reasonable uncertainty (accounting for up to 80 % of the variance). However, for N_2O and CH_4 we so far failed to find meaningful correlations and, thus, to provide simple regression models to estimate

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fluxes. This is most likely due to the complexity of involved processes and counteracting effects of soil moisture and temperature, specifically with regard to N_2O production and consumption by denitrification and microbial community dynamics.

1 Introduction

Temperate forest soils are significant sources of atmospheric greenhouse gases (GHG), namely CO_2, N_2O and NO (Brumme and Beese, 1992; Castro et al., 1993; Butterbach-Bahl et al., 1998; van Dijk and Duyzer, 1999; Pilegaard et al., 2006; Phillips et al., 2010), and significant sinks for atmospheric CH_4 (Borken and Brumme, 1997; Henkel, 2000; Smith et al., 2000; Brumme and Borken, 1999; Butterbach-Bahl and Papen, 2002; Borken and Beese, 2006). Based on an ISI search, studies on trace gas exchange between temperate forest soils and the atmosphere have increased by a factor of 12 from the decade 1990–2000 to the decade 2001–2010. Nevertheless, continuous field measurements over long time periods (> 1–2 yr) at high temporal resolution are still required to improve our understanding of the biogeochemical N and C turnover processes and thereby temporal variability of GHG fluxes on daily to multi-year scales.

N-trace gases in forest soil are produced (and consumed) mainly by the microbiological processes nitrification and denitrification (Firestone and Davidson, 1989; Conrad, 1996). Soil microorganisms, for instance chemolithotrophic CH_4 oxidizers, catalyze the uptake of atmospheric CH_4 by forest soils as well (Roslev et al., 1997; Schimel and Gulledge, 1998; Henckel et al., 2000). Like all other biogenic processes, the soil microbiological processes involved in soil-atmosphere GHG exchange are strongly affected by a number of soil environmental factors and ecological drivers such as temperature, moisture, precipitation, soil aeration, pH or texture. Among these parameters, soil moisture and temperature are identified as key drivers for soil-atmosphere exchange in many field investigations (e.g. Gasche and Papen, 1999; Papen and Butterbach-Bahl, 1999; Borken et al., 2002; Butterbach-Bahl and Papen, 2002; Wu et al., 2010)

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and process studies (Schindlbacher et al., 2004). The effects of soil temperature on soil-atmosphere exchange of N_2O, NO, CH_4 and CO_2 are mostly direct, and increases in temperature result in increasing emissions as long as other factors are not limiting. In contrast, the effect of soil moisture is more complex. In addition to its function as a transport medium for nutrients such as NO_3^- and NH_4^+, soil water influences the rate of O_2 supply and thereby determines whether aerobic processes such as nitrification or anaerobic processes such as denitrification prevail within the soil (Schindlbacher et al., 2004; Pilegaard et al., 2006). However, the relative importance of a specific parameter is variable, and interactive effects of environmental drivers on soil microbial processes are highly complex, specifically if competitions of microbes with plants for nutrients, water, and nutrient leaching processes are considered. Furthermore, many of these relationships remain unexplored due to the lack of sufficiently detailed observational data.

Interannual variability of soil trace gas fluxes has hardly been explored. Specifically with regard to soil N_2O fluxes recent reports about the importance of freeze-thaw N_2O pulse emissions for cumulative annual emissions from natural and semi-natural ecosystems such as grasslands (Wolf et al., 2010) or forests (e.g. Papen and Butterbach-Bahl, 1999; Teepe et al., 2001) imply that fluxes may vary significantly. Significant interannual variations in soil CO_2 fluxes have been reported as well (Phillips et al., 2010). Therefore, soil flux datasets comprising only sporadic measurements or not covering complete seasons and/or years may not be representative for a site. Long-term datasets are rare, but important to better understand environmental controls of ecosystem C and N turnover and associated exchange of C and N and compounds between the biosphere and atmosphere. For example, more than ten years (1992–2004) of eddy covariance (EC) measurements at Harvard Forest demonstrated that interannual variability of CO_2 ecosystem fluxes are controlled by climate variability and ecosystem factors (Urbanski et al., 2007; Phillips et al., 2010). Long-term, multi-year measurements of soil CH_4 and N_2O fluxes are even scarcer than measurement of soil and ecosystem CO_2 fluxes. For temperate forest ecosystems the time series obtained

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at the Solling, Central Germany (Borken and Brumme, 1997; Brumme and Borken, 1999; Borken et al., 2002) started in form of measuring campaigns in 1990. For the spruce site at the Höglwald Forest continuous soil trace gas flux measurements started in November 1993. Though part of the dataset has been published earlier (e.g., Papen and Butterbach-Bahl, 1999; Butterbach-Bahl et al., 2002; Wu et al., 2010), the entire dataset – covering the period from 1994–2010 (incl. a two-year break in 1998/1999) or meanwhile 15 yr of observation – remains unpublished so far. Moreover, this dataset has never been evaluated with regard to multi-year relationships between soil environmental parameters such as soil moisture, temperature or precipitation and soil trace gas fluxes. Also inter-relationships between individual C- and N-trace gases have hardly been evaluated so far, except for the study of Wu et al. (2010), with the latter study only using less than one-third of the full dataset. Therefore the main objectives of this study are,

a) to summarize 15 yr of continuous trace gas measurements at the Höglwald site and to evaluate seasonal and interannual variability of fluxes,

b) to use the multi-year dataset to elucidate relationships between environmental parameters and soil trace gas fluxes,

c) to test if easy-to-measure environmental parameters such as soil moisture and soil temperature can be used to approximate trace gas fluxes at weekly, monthly or annual time scales.

2 Material and methods

2.1 Experimental site

The Höglwald Forest is situated in the temperate suboceanic broadleaf zone in the south of Germany. The region is characterized by interspersed forest in an agricultural area used for maize and cereal production and livestock breeding agriculture. Chronic

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atmospheric nitrogen (N) deposition at a rate of 20–30 kg N ha^{-1} yr^{-1}, due to emissions from livestock farming, N fertilizer use, and NO_x emissions from traffics and industries, resulted in N saturation of the forests in this region (Butterbach-Bahl et al., 1997, 2002). Field measurements of soil CH_4, CO_2, N_2O and NO fluxes and simultaneous monitoring of climate and soil environmental parameters were performed in an old spruce plantation (48.50° N, 11.17° E), established around 1904. The site is 540 m a.s.l. and the mean annual precipitation is approx. 932 mm, while the mean annual temperature is 8.6 °C (values for the period 2004–2010). The soil at the experimental site is a Typic Hapludalf (FAO: dystric cambisol), strongly acidified in the top soil and weakly aquic in the argillic horizon (Kreutzer, 1995). The soil pH value (measured in 0.1 M $CaCl_2$) is 2.9–3.2 in the organic layer and 3.6–4.0 in the uppermost mineral soil layer (Kreutzer, 1995). Further information about the Höglwald Forest site can be found in Kreutzer (1995), Kreutzer and Weiss (1998), Butterbach-Bahl et al. (2002) or Wu et al. (2010).

2.2 Measurements of soil CH_4, CO_2, N_2O, and NO fluxes

Continuous measurements of complete annual cycles of soil-atmosphere trace gas fluxes started in late 1993 at the spruce site. The automated measuring systems at the Höglwald sites have been described previously by (Butterbach-Bahl et al., 1997, 1998; Papen and Butterbach-Bahl, 1999; Gasche and Papen, 1999).

In brief: five chambers of the closed type were used for N_2O and CH_4 flux determinations, and five dynamic measurement chambers plus one reference chamber were used for NO and CO_2 flux measurements. The chambers (dimensions: 0.5 m × 0.5 m × 0.15 m, length × width × height) consisted of aluminum frames in which perspex panes were fixed. Only a small stainless steel frame of 2.0 cm, which was fixed at the frame of the chambers, was sunk into the organic layer of the soil with care in order to avoid cutting of the fine root mat. For measurements of N_2O and CH_4 fluxes the covers of the chambers were opened and closed automatically in an angle of 90° by pneumatic actuators every 60 min. Gas samples were withdrawn four times every

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15 min within the 60 min closure time. The temporal resolution of flux measurements was 2 h for N_2O and CH_4 fluxes. N_2O and CH_4 concentrations in the sample air were determined by gas chromatography using a gas chromatograph (Shimadzu GC 14, Duisburg, Germany) equipped with a ^{63}Ni electron capture detector (ECD). Water vapor and CO_2 in sample air were removed by a permapure dryer and a pre-column filled with Ascarite (sodium hydroxide-coated silica), respectively. The GC was equipped with a stainless steel column packed with Hayesep N (3 m, 1/8 inch, 60/80 mesh). The oven and detector temperature was 60 and 340 °C. The carrier gas flux (N_2) amounted to of 20 ml min^{-1}. Automatic calibration of the N_2O/CH_4 measuring system was performed every 2 h using standard gas (0.4 ppmv N_2O and 4000 ppmv CH_4 in 79 % N_2 and 21 % O_2, Messer Griesheim, Germany). Fluxes were calculated on basis of the linear/non-linear increase/decrease of gas concentrations with time, thereby using the r^2 value to judge which type of curve fitting was finally used for flux calculation. For CH_4 we predominantly observed a decrease of CH_4 concentrations with time, which in most cases could be best described with an exponential decay curve. Changes of N_2O concentrations in the closed chambers could mostly be best described by a linear regression.

For measurements of soil NO and CO_2 fluxes, the dynamic chambers were closed for 6 min and re-opened again for 6 min. After re-opening of the measuring chambers, gas samples were drawn from the reference chamber that was sealed towards the soil. Since during a 6-min period gas samples could only be taken from one out of five chambers, the respective 12 min cycle (measuring chamber + reference chamber) was repeated five times to sample all chamber plots. Thus, the temporal resolution was 1 h. During sampling, ambient air was sucked at a constant rate (50 l min^{-1}) through the chambers by means of a sampling pump and transferred via PTFE tubing (inner diameter: 10 mm; length 20 m, internal volume: 1.6 l) to the analyzers, i.e. a chemoluminescence detector for NO/NO_2 (CLD 770 AL ppt and photolysis converter PLC 760, Eco Physics AG, Switzerland) and an infrared gas analyzer (BINOS 100, Rosemount, Hanau, Germany) for CO_2. Calibration of the NO_x analyzer was performed weekly with

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a multigas calibrator (Eco Physics AG, Switzerland) using standard gas (1 ppm NO in synthetic air, Messer Griesheim, Germany), which was diluted with synthetic air to a final NO concentration of 10 ppb. Determination of NO, NO_2 and O_3 concentrations in ambient air and at the outlet of the chambers, calculation of NO fluxes and efficiency of photolytic cleavage of NO_2 into NO were described in detail by Butterbach-Bahl et al. (1997). The calculation of CO_2 fluxes are in principle similar to the calculation scheme of NO fluxes, with the difference that the CO_2 analyzer detected the difference between reference and measuring chambers directly. The CO_2 analyzer was calibrated regularly with two reference gases (400 and 450 ppm CO_2 in synthetic air, Messer Griesheim, Germany) by applying one gas simultaneously to both cuvettes of the instrument for setting the zero point, and the two gases for setting the span. All fluxes were corrected for temperature and air pressure. Detailed descriptions of the automated measuring systems including design of chambers, gas chromatographic conditions and modes of calculation of flux rates can be found in previous publications (Butterbach-Bahl et al., 1997; Gasche and Papen, 1999; Rosenkranz et al., 2006; Wu et al., 2010). Gaps originating from instrumental failure were filled by linear interpolation between measured fluxes for calculation of cumulative annual emissions.

2.3 Soil environmental and climate measurements

Daily precipitation and air temperature at 2 m a.g.l. from 1994 to 2010 were obtained from the German Weather Service station Augsburg-Mühlhausen, which is about 20 km northwest from the Höglwald Forest site. Soil temperatures at various depths (organic layer, 5, 10, 15 and 20 cm) were measured every minute by PT100 probes (IMKO GmbH, Germany) in close vicinity to the chambers. Hourly soil moisture measurements were carried out with horizontally installed TDR probes (IMKO GmbH, Germany, or UMS, Germany) at 10 cm soil depth from 1994 to 2010.

Due to instrumental failure and removal of the soil moisture sensors, in situ soil moisture measurements from July 1996 to August 1999 and from September 2004 to December 2006 were not available. To fill these gaps, a machine-learning technique

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– support vector machine (SVM) – was employed. The SVM method was based on a statistical learning algorithm and had been successfully applied to bioinformatics, data mining, surface temperature prediction, and hydrology. The fundamental principle of SVM and its formulation were described in detail by Kecman (2001). Daily meteorological input data, required as model drivers, i.e. minimum and maximum temperature, mean relative humidity, total precipitation, sunshine duration, mean degree of cloud cover, mean wind force from 1994 to 2010, were either obtained from continuous measurements at the Höglwald Forest site or from the German Weather Service station Augsburg-Mühlhausen. Since soil moisture was not only determined by observations of the very day, meteorological variables were aggregated to different additional cumulative sums (i.e., 1, 2, 5, 10, 15, and 30 days previously) for creating a training data set. The best 13 variables, which could explained more than 93 % of the variance in the data set, were used to predict soil water content for the years when soil moisture was missing. To train the support vector machines, the R-package e1071 was used (Dimitriadou et al., 2011; R Development Core Team, 2011).

2.4 Regression models for trace gas flux calculation

Long-term observations of soil trace gas fluxes are extremely costly, therefore, to estimate annual fluxes, simple though site specific empirical model based on easy to measure soil environmental or meteorological parameters is an appealing approach. To develop and assess empirical models, weekly aggregated data, monthly aggregated data and data aggregated within comparatively larger temporal resolutions were all split into two subsets. One of them with about 50 % data of the entire dataset was used to determine model parameters using multivariate linear regression (first order), while the other half of the dataset was used to validate the obtained empirical model. Different models were compared according to their explanatory power and the explanatory variables (soil temperature, soil volumetric water content, precipitation, or air temperature) were stepwise selected according to their importance. In addition, the under- or overestimation of the mean flux was compared to the measured mean flux. To avoid

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non-linearity and non-normality of the residuals and to reinforce the prerequisites for multivariate linear regression, the logarithm-transformed fluxes were used in the regression models.

2.5 Statistical analysis

Linear and nonlinear regression analysis and Pearson Correlation were used to identify significant positive or negative relations between trace gas fluxes and environmental drivers. Significances of differences were either tested by using F-statistics in ANOVA (analysis of variance) or by using a parametric T-test (SPSS 10, SPSS Inc.). In multivariate linear regression analysis, the co-linearity diagnostics, homoscedasticity, normality of residuals, and the Durbin-Watson test for autocorrelation were included.

3 Results

3.1 Soil moisture modeling

Measured and simulated soil volumetric water contents were compared from 2000 to 2003 in order to validate the performance of SVM regression modeling. Figure 1 showed that the SVM approach was able to capture the seasonal dynamics of changes precisely ($R^2 = 0.91$, $n = 1406$). The magnitudes of simulated soil volumetric water contents were in good agreement (RMSE = 1.06) with measured values in 10 cm soil depth at the spruce site, though simulated values generally tended to underestimate measured soil moisture values by < 1 % (Fig. 1).

3.2 Variability of environmental drivers

Following gap filling and harmonization for soil moisture measured by different sensors in different periods we calculated annual mean temperature, annual mean moisture, and annual cumulative precipitation (Table 1). As shown in Table 1, soil temperature,

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soil moisture, and precipitation had a pronounced interannual variability. For instance, annual precipitation in the relatively dry years 1997 and 2003 was much lower than in the relatively wet years 2000 and 2002, leading to a large range of annual precipitation (627–1265 mm). The mean value of 932 mm for the whole observation period 1994–2010 was approx. 40 mm higher than the measured (892 mm) value by Rothe et al. (2002) for the period 1994 to 1997. Maximum soil moisture values were observed in early spring, due to snow melt, soil thawing, and spring rains. 2003 was an exceptionally dry year with only 633 mm of rainfall. In this year mean annual soil moisture in 10 cm soil depth was 26.1 %, i.e. 4 % lower than the mean for the entire observation period. The mean air temperature was 8.6 °C in our study period (1994–2010), which was 1 °C higher as compared to observations by Rothe et al. (2002).

3.3 Seasonal and interannual dynamics of trace gas fluxes

Subdaily measured fluxes were stepwise aggregated to daily, weekly, monthly, and annual average values. The annual mean soil-atmosphere trace gas exchange was calculated based on the subdaily measurements. Our analysis revealed substantial seasonal and interannual variation (Figs. 2 and 3). Over the entire observation period the soil of Höglwald spruce forest functioned as a sink for atmospheric CH_4. Highest mean monthly uptake rates of 20–30 µg CH_4-C m^{-2} h^{-1} were usually observed at the end of summer or in autumn (Fig. 3). Seasonal patterns of soil N_2O fluxes were characterized by pulse emission events, which were mostly associated with spring soil thawing (2–10 weeks) following long soil freezing periods. Therefore, highest mean monthly N_2O fluxes were observed in February and March with average monthly mean values being in the range of 25–35 µg N_2O-N m^{-2} h^{-1} (Fig. 3). A seasonal, temperature-driven variation in the magnitude of N_2O fluxes was also evident, but less pronounced. In contrast to N_2O emissions with late winter maximum values, the seasonal patterns of NO and CO_2 soil-atmosphere exchange followed the seasonal course of soil temperature, with the maximum of mean NO and CO_2 emission rates in July and August, respectively. A notable finding was that monthly mean CO_2 emissions were also

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significantly increased in February as compared to mean fluxes in January and March, possibly due to an increased soil microbial activity during the period of soil thawing (Fig. 3). NO fluxes were on average approximately one order of magnitude higher than N_2O fluxes (Figs. 2 and 3; Table 2) during most of the observation period.

The pronounced interannual variability in meteorological parameters was also mirrored by an evident interannual variability in soil trace gas fluxes (Table 2). Annual soil emission of N_2O, NO, and CO_2 fluxes varied between 1994 and 2010 in a range of 0.2–3.24 kg N_2O-N ha^{-1} yr^{-1}, 6.38–11.44 kg NO-N ha^{-1} yr^{-1}, and 6.99–9.24 t CO_2-C ha^{-1} yr^{-1}, respectively. The mean annual emissions of N_2O, NO, and CO_2 from the Högwald soil for the years 1994–2010 were 0.80 ± 0.20 kg N_2O-N ha^{-1} yr^{-1} (±SE), 8.4 ± 0.65 kg NO-N ha^{-1} yr^{-1}, and 7.91 ± 0.34 t CO_2-C ha^{-1} yr^{-1}, respectively. Compared to NO and CO_2 fluxes, large interannual fluctuations of N_2O were observed due to peak emissions during spring thawing after long frost periods in 1996, 1997, 2005, 2006, and 2009. This meant that out of 15 observational years significant freeze-thaw pulses of N_2O emissions were observed only in five years. We also found a strong tendency that the length of the frost period is positively correlated to the magnitude of soil N_2O emissions (Fig. 4). A quadratic fit between the duration of frost and the cumulative emission was found. Annual atmospheric uptake of CH_4 ranged from 0.94 to 3.45 kg CH_4-C ha^{-1} yr^{-1}. The mean annual uptake rate of atmospheric CH_4 was 1.82 ± 0.22 kg CH_4-C ha^{-1} yr^{-1}. Highest CH_4 uptake was observed in 1997 (3.45 kg CH_4-C ha^{-1} yr^{-1}), whereas in 2002 the rate of atmospheric CH_4 uptake was only 0.94 kg CH_4-C ha^{-1} yr^{-1}.

3.4 Environmental controls over trace gas fluxes

Soil CO_2 emissions were significantly positively correlated (Figs. 5 and 6) with soil temperature (5 cm), whereas they were only weakly negatively correlated with soil moisture (10 cm). Figure 7a showed that highest fluxes were observed during warm and wet periods.

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The individual effects of soil temperature and soil moisture on CH_4 uptake were generally weak ($r^2 < 0.1$) though significant. The relationship between soil temperature and CH_4 uptake could be best described by a quadratic regression (Figs. 5 and 6). Figure 7b showed that highest rates of CH_4 uptake were observed under warm and dry conditions.

NO emission was positively correlated with soil temperature, with soil temperature being the better predictor as compared to soil moisture. Lorentzian function and polynomial fitting were used here to describe the relationship between soil moistures and NO fluxes, while between temperature and NO fluxes the relationship was best described by an exponential function. Interactive effects of soil temperature and soil moisture on the fluxes showed that NO fluxes were highest when the temperature was high (> 15 °C) but the soil moisture was still less than 24 vol % (Fig. 7d).

Similar to CH_4, the correlations between N_2O emissions and both drivers were weak but significant (r^2 was not more than 0.1). Generally, increased soil moisture led to an increase in N_2O emission, while increased soil temperature led to an increase in N_2O emission as well, though both effects were clearly biased due to high N_2O emissions during freeze-thaw events. However, after excluding the freeze-thaw periods for data analysis, the r^2 value of the soil moisture-N_2O relationship increased to more than 0.1, and the r^2 value of the soil temperature-N_2O relationship increased to more than 0.2. The dominant environmental factor affecting the magnitude of N_2O fluxes was soil moisture for soil temperatures < 3 °C. The highest fluxes were observed for cold/moist or warm/moist environmental conditions (Fig. 7c).

Figure 8 demonstrated how monthly NO : N_2O ratios depended on soil moisture and soil temperature. The dominant environmental factor affecting the ratio was soil moisture rather than soil temperature, especially for periods with soil temperatures > 10 °C and soil moisture < 26 vol %. Higher ratios of NO fluxes to N_2O fluxes were found for drier and warmer environmental conditions. In contrast, the smallest ratio was found for cool and wet conditions.

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The $CO_2 : N_2O$ ratio was highest for warm/dry conditions. For cool/wet conditions low soil CO_2 fluxes but high N_2O emissions resulted in the lowest $CO_2 : N_2O$ ratio. $CO_2 : NO$ ratios were highest when soil temperature was > 12 °C and soil moisture was > 34 vol %. The graph showed that at soil temperatures < 10 °C or if soil temperature was > 10 °C and soil moisture was < 32 vol %, the $CO_2 : NO$ ratio was close to 1, which means that under these conditions CO_2-C emissions were approx. 1000 times higher than NO-N emissions or that per 1000 mol CO_2-C per 1 mol of NO-N was emitted.

3.5 Regression models for approximating trace gas fluxes

Variables tested included soil temperature (organic layer, 5, 10, 15, and 20 cm soil depth), soil moisture (volumetric water content in 10 cm soil depth), air temperature at 2 m a.g.l. (average, maximum, and minimum air temperature), and precipitation. The results of the multiple linear regression analyses for predicting soil-atmosphere fluxes of N_2O, NO, CO_2, and CH_4 due to changes in environmental drivers were given in Table 3.

All soil trace gas fluxes correlated strongly (NO and CO_2) or weakly (CH_4 and N_2O) with soil temperature, though best fits for individual trace gases differed with regard to the measuring depth of soil temperature. For example, soil CO_2 and NO emissions were positively correlated with surface layer temperatures (either measured in 2 cm (organic layer) or 5 cm soil depth). In contrast, for soil N_2O emission and atmospheric CH_4 uptake, soil temperatures measured in deeper soil depths (20 and 15 cm, Table 3) were best to explain temporal variations in fluxes. For the monthly aggregated dataset only the soil temperature in the organic layer was significantly correlated with soil NO emission, while soil moisture was the only predictor of monthly mean fluxes of atmospheric CH_4 uptake. For monthly mean N_2O fluxes a correlation to soil temperature became significant if spring freeze-thaw periods were excluded (Table 3).

For both datasets the models had high explanatory power for NO and CO_2 fluxes (accounting for up to 80 % of the variance; Table 3). The best regression results were obtained from empirical regression models for CO_2, which in some cases had

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an explanatory power for the temporal variability in soil CO_2 fluxes as high as 88.5 % by considering soil moisture as well as soil temperature in the regression analysis. This value decreased to 76.8 % when using soil temperature as predictor only. However, for N_2O and CH_4 we failed to find meaningful correlations and, thus, to provide simple regression models to estimate fluxes from weekly to annual scales.

The performance of the obtained simple empirical models was validated by using these models to predict GHG fluxes based on the remaining observational data. The last two columns summarized the predicted and observed mean value of all fluxes. Monthly (weekly) soil fluxes were on average overestimated by 19 % (23 %) with regard to CO_2, and 21 % (13 %) with regard to NO if empirical relationships were used to approximate fluxes (Fig. 9). For longer time periods, such as monthly, 3- or 6-months periods or entire years, correlations weakened or even disappeared.

4 Discussion

4.1 Comparison with other studies

4.1.1 CO_2

Soil CO_2 flux measurements started in May 1995 and were performed continuously except for the period January 1998 to June 1999 and the years 2002 and 2003 in subdaily resolution. The obtained multi-year dataset on CO_2 fluxes and fluxes of N_2O, CH_4 and NO – for which even more observation years are available – is to our knowledge unique. Only a few studies covered so many trace gas species, and none of the published datasets lasted such a long period of time. For instance, continuous automatic chamber measurements of soil CO_2 fluxes (Griffis et al., 2004), covering a 7-yr period (1994 and 1996–2001), were made at an old aspen forest site in Saskatchewan, Canada, resulting in an overall mean value of 13.15 t C ha^{-1} yr^{-1}. For the Harvard Forest, USA, Phillips et al. (2010) published a 4-yr dataset for the period 2003–2007, using eight automated chambers. Average soil respiration was 8.19 t C ha^{-1} yr^{-1} at the upland and

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6.27 t C ha^{-1} yr^{-1} at wetland margin. Wang et al. (2010) reported on soil respiration and its relationship to soil carbon content, forest floor mass, root biomass, soil temperature, and soil moisture at three different temperate forest sites in the Changbai Mountains, Northeastern China. Average annual soil CO_2 efflux over a measuring period of four years (2003–2005) at a site with middle-aged, broad-leaved secondary forest was 14.8 ± 0.6 t CO_2-C ha^{-1} yr^{-1} and, thus, significantly higher as compared to a young coniferous plantation site (8.3 ± 0.5 t CO_2-C ha^{-1} yr^{-1}) or an old-growth, mixed coniferous and broad-leaved primary forest (9.4 ± 0.5 t CO_2-C ha^{-1} yr^{-1}). These long-term measurements of soil respiration as well as observational data from other temperate forest sites worldwide (Raich and Schlesinger, 1992; Raich and Tufekcioglu, 2000; Savage and Davidson, 2001; Rosenkranz et al., 2006) show that the observed soil respiration fluxes at the Höglwald site (6.99–9.24 t C ha^{-1} yr^{-1}; mean: 7.91 t C ha^{-1} yr^{-1}) are well within the reported ranges for soil respiration.

Our long-term measurements of soil respiration also showed that soil respiration rates varied largely from year to year by > 30 %. Highest annual soil respiration (> 9 t CO_2-C ha^{-1} yr^{-1}) was found for the year 1996, which was the year with the coldest mean annual soil temperature (5.7 °C), longest continuous soil freezing period (approx. 2 months), and annual rainfall (778 mm) which was approx. 20 % below the average of the entire observation period. Lowest annual soil respiration rates (approx. 7 t CO_2-C ha^{-1} yr^{-1}) was observed for the year 2004, the year with the highest mean annual soil temperature (11.9 °C), but also approx. 20 % lower annual rainfall (754 mm) as compared to the entire observation period (932 mm). These patterns suggest, that in cold years freeze-thaw events seem to stimulate soil carbon mineralization, whereas in warm and dry years soil respiration is hampered due to soil moisture deficits, which might impede not only heterotrophic, but also root respiration. However, even though soil thawing led to small peak emissions of soil CO_2 in the early spring not only in those years when pronounced freeze-thaw effects were observed for N_2O as well (1996, 1997, 2005, 2006, 2009), but also in other years (e.g. 2004, 2007), the contribution of spring CO_2 fluxes for cumulative annual soil CO_2 fluxes was of little importance.

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Higher CO_2 fluxes were observed in years with below average mean soil temperature (e.g. in 1996, 2006), i.e. years with rather cold winters and springs. This indicates that extended freezing periods are increasing the pool of easy degradable organic matter, e.g. due to the dieback of part of the microbial biomass during frost (Papen and Butterbach-Bahl, 1999). This increased availability of substrate at the end of the freezing period may finally prime also the decomposition of organic matter in the following growing season (Kuzyakov et al., 2000). Based on four years (2003–2006) of sub-daily measurements of soil respiration at adjacent upland and wetland forest sites at Harvard Forest, Phillips et al. (2010) found that annual soil respiration decreased, although air temperature increased during this period. Instead, mean spring soil temperatures decreased over the same period. Thus, they concluded that annual soil respiration rates might be positively correlated with mean spring soil temperature. This, as well as our finding that years with strong freezing periods showed highest annual CO_2 respiration rates, indicated that climate conditions during the dormant or early growing season might determine annual soil respiration rates in temperate forest ecosystems.

Years with summer droughts, as e.g. the years 1997 or 2004 showed reduced annual soil respiration rates. This observation is in line with experiments at a spruce site at Solling, Germany, where artificially prolonged drought of 172 days during the summer period resulted in a reduction of soil respiration while during the following rewetting period soil CO_2 emissions in the first 30 d significantly increased by 48 % in 1993 and 144 % in 1994 (Borken et al., 1999). Strong interannual variations up to 2.3 t C ha^{-1} yr^{-1} due to extended summer droughts were observed for the Harvard Forest, Northeastern USA (Savage and Davidson, 2001). Re-wetting of soil following a drought period was often associated with a period of pulse soil CO_2 emissions. The intensity of these pulses may depend strongly on soil temperature (Borken et al., 1999, 2002). Our results together with observations from Borken et al. (2002) for soil CO_2 flux measurements in the year 1998 and 1999 at forest sites at Unterlüss, Germany, further revealed that higher soil respiration rates due to soil re-wetting after the prolonged drought period did not compensate the previous decrease in soil respiration.

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Besides, the observed reduction of soil respiration in years with summer droughts at our site are supported by observations from several forest sites across Europe during the extremely dry and hot year 2003 (Yuste et al., 2005; Nikolova et al., 2009). In this respective year, for which soil respiration measurements at Höglwald were missing, Europe experienced a particularly extreme climate anomaly with July temperatures up to 6 °C above long-term means, and annual precipitation deficits up to 300 mm yr^{-1}, or 50 % below the average (Ciais et al., 2005).

4.1.2 NO and N_2O

Cumulative annual soil emissions for N_2O and NO varied in a range of 0.2–3.24 kg N_2O-N ha^{-1} yr^{-1} and 6.38–11.44 kg NO-N ha^{-1} yr^{-1} for the observation period 1994–2010, respectively. Datasets spanning entire years and providing estimates of annual fluxes of NO and N_2O on the basis of continuous measurements are scarce. The most relevant dataset is the one of Pilegaard et al. (2006), as obtained within the EU-funded NOFRETETE project. These authors reported on annual NO and N_2O fluxes at various forest sites across Europe, also including data for the Höglwald site for the years 2002–2004. Comparably high annual fluxes (6.59 kg NO-N ha^{-1} yr^{-1}) of NO as observed for the Höglwald in this study were only documented for the Speulderbos Douglas fir forest site in the Netherlands, a site also receiving high loads of atmospheric N inputs of approx. 40 kg N ha^{-1} yr^{-1}.

Together with other studies carried out in N-affected forests in Central (Brumme and Beese, 1992; van Dijk and Duyzer, 1999; Butterbach-Bahl et al., 2002; Jacinthe and Lal, 2004; Jungkunst et al., 2004) and Northern Europe (Pilegaard et al., 1999; Skiba et al., 1998) our dataset shows that atmospheric N deposition has obviously changed the emission strength of forest soils as compared to non-N-affected temperate forest elsewhere (Williams et al., 1992; Castro et al., 1993). For example, Bowden et al. (1991) as well as Castro et al. (1993) reported mean N_2O fluxes of less than 2.5 µg N_2O-N m^{-2} h^{-1} (or approx. 0.2 kg N ha^{-1} yr^{-1}) for both a pine and a spruce

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fir forest in the US, with both sites receiving low atmospheric N-input of less than 10 kg N ha^{-1} yr^{-1}.

The high fluxes of both N_2O and NO at our site are a consequence of high nitrogen deposition at the Höglwald Forest in a range of 20–30 kg N ha^{-1} yr^{-1} since more than three decades. This high N deposition has led to elevated N trace gas emissions, a narrowing of needle C : N ratios (Kreutzer, 1995), accelerated forest growth (Rothe et al., 2002) and N-cycling (Kreutzer et al., 2009; Rosenkranz et al., 2010), and finally high nitrate leaching rates of more than 20 kg N ha^{-1} yr^{-1} (Rothe et al., 2002; Weis et al., 2006; Huber et al., 2004), which all together are signs of ecosystem N-saturation (Aber, 1992).

Our multi-year dataset shows that occasionally occurring freeze-thaw pulse emissions are dominating annual N_2O fluxes in certain years. Out of 15 observation years, the annual N_2O budget was significantly affected by freeze-thaw N_2O emissions in five years. Linked to the meteorological conditions among the five years, we found that in these years average annual soil temperatures were significantly lower, and the period of soil frost lasted at least 3–4 weeks. This is in accordance with earlier publications stating that severity and duration of frost determined the strength of freeze-thaw pulse N_2O emissions (Papen and Butterbach-Bahl, 1999; Wu et al., 2010). Teepe et al. (2004) found that the duration of the frost period determined the overall effect on freeze-thaw pulse N_2O emissions, which may be related to the release of nutrients due to the dieback of soil microorganisms as well as due to the physical cracking of soil aggregates and associated nutrient release with increasing time of freezing. Our long-term measurements confirm that evidently the duration of freezing has a remarkable influence on the amount of N_2O emitted during the following thawing period.

In our study the years with highest annual N_2O fluxes, i.e. 1996 and 2006, with annual emissions of approx. 3 kg N ha^{-1} yr^{-1}, pulse emissions during freeze-thaw periods were contributing 88 % (1996) or 87 % (2006) to total annual emissions. This reflects the necessity of performing continuous, all-season measurements of N_2O fluxes over multiple years in order to obtain a more realistic estimation of monthly and annual

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fluxes. The data base obtained by short-term continuous measurements – even if performed at different season – may lead to a significant under- or overestimation of the trace gas source strength of soils. Therefore, there is a need for a new type of monitoring network which aims at the measurement of biosphere-atmosphere exchange over multiple years in order to get more reliable estimates of trace gas exchange for a larger number of sites across Europe and elsewhere.

The importance of pulse emission during freeze-thaw periods as major determinant of the annual exchange of N_2O has also been demonstrated for other ecosystems types such as temperate grasslands (e.g., Wolf et al., 2010) or arable systems (Teepe et al., 2001; Koponen et al., 2004; Kurganova et al., 2004; Matzner and Borken, 2008). The most likely explanation of freeze-thaw pulse emissions, which were largely driving inter-annual variability of N_2O fluxes at Höglwald, is increased microbial activities in water-saturated soils with microbes being supplied with sufficient easily degradable C and N substrates due to the dieback of the microbial community during the preceding freeze period (Wolf et al., 2010; De Bruijn et al., 2009). Our observation that N_2O but not NO emissions (which are mainly originating from nitrification (Conrad, 1996)) are elevated certifies that denitrification is the main driver of elevated N_2O emissions during freeze-thaw periods rather than nitrification. This conclusion is further supported in the modeling study of De Bruijn et al. (2009). Soil CO_2 emissions during such periods also slightly increased (Fig. 3) confirms measurements of Wolf et al. (2010) in steppe ecosystems that indeed not only denitrification but also microbial activity increased in general.

4.1.3 CH_4

In the year 2000, Smith et al. (2000) summarized results of an EU project on measurements of soil methane oxidation rates in Denmark, Germany, Norway, Poland, Sweden, and the UK, including not only agricultural land, peat bogs, and moorland but also forest and woodland soils. Compared to other land uses, temperate forest soils showed the highest CH_4 uptake rates (up to 150 $\mu g\, CH_4\text{-}C\, m^{-2}\, h^{-1}$). Nevertheless,

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rates of atmospheric CH_4 oxidation for European forest soils were varying widely in a range of 1–165 µg CH_4-C m^{-2} h^{-1} (Ambus and Christensen, 1995; Borken and Brumme, 1997; Butterbach-Bahl et al., 1998; Brumme and Borken, 1999; Borken and Beese, 2006). Some rather acidic forest soils in Germany with pH values of the organic layer below 4.0, as found at the Solling site in Central Germany (Borken and Brumme, 1997; Brumme and Borken, 1999), showed rather low oxidation rates of approx. 10–20 µg CH_4-C m^{-2} h^{-1}, which is in line with the low CH_4 oxidation rates found for the acidic and N deposition-affected soils at our site (18.7 µg CH_4-C m^{-2} h^{-1}). Brumme and Borken (1999) hypothesized that the reduction of CH_4 oxidation rates in highly acidic soils was partly due to a reduction in bio-turbation by soil fauna. Consequently organic material, inactive with regard to CH_4 oxidation (Butterbach-Bahl and Papen, 2002) may accumulate at the soil surface and a more compact mineral soil may develop, hampering CH_4 diffusion to the sites of microbial CH_4 oxidation.

Another reason for reduced rates of CH_4 uptake by forest soils is that many forest ecosystems in Europe have experienced increased atmospheric nitrogen input for several decades. Nitrogen deposition has resulted in the acidification and eutrophication of many forest soils and triggered changes in plant and soil microbial community composition as well as in soil chemistry (Butterbach-Bahl et al., 2011). Chan et al. (2005) performed 8-yr-long measurement of soil CH_4 exchange in a temperate deciduous forest in Northwestern Pennsylvania and found that in situ atmospheric CH_4 uptake rates had been reduced by 35 % after 8 yr of N amendments (100 kg N ha^{-1} yr^{-1}). The result confirmed the suggestion made by Castro et al. (1993) that soils in ecosystems receiving high N-deposition were likely to exhibit higher N_2O emission and lower CH_4 uptake compared to soils in ecosystems receiving lower N-deposition. Comparable results were also obtained by the metadata analysis by Liu and Greaver (2009), who estimated the detrimental effects of N_r addition to forest soils on CH_4 uptake as 0.016 ± 0.004 kg CH_4-C ha^{-1} yr^{-1} for non-agricultural ecosystems, per 1 kg N_r ha^{-1} yr^{-1} being added to the ecosystem. The Höglwald Forest soil received annually approx. 20–30 kg atmospheric N deposition and had a mean annual CH_4 uptake rate of 1.82 kg

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CH_4-C ha^{-1} yr^{-1}. This suggested reduction of the annual uptake rate of 0.3–0.5 kg CH_4-C per year or a reduction of more than 20 % as compared to a situation assuming zero atmospheric N input. This value is close to the N assessment study on forest soil CH_4 uptake by Bowden et al. (1991) and Steudler et al. (1989), who found that fertilization of a pine forest soil with 37 kg N ha^{-1} yr^{-1} as NH_4NO_3 resulted in a 24 % reduction of CH_4 uptake rates as compared to untreated plots. The effects of N inputs on the CH_4 oxidation capacity of a soil are complex. The inhibiting effect of ammonium has been ascribed to a stimulation of ammonia-oxidizing bacteria, allegedly at the expense of CH_4-oxidizing bacteria, although the mechanisms involved in this competition are unclear. An alternative explanation for persistent effects of ammonia could be that the competitive inhibition of methane monooxygenase by ammonia is sufficient to kill a substantial proportion of the CH_4-oxidizing bacteria (Smith et al., 2000).

4.2 Environmental control on flux rates

4.2.1 CO_2

Our observations spanning several years showed significant positive correlations between monthly mean fluxes of CO_2 and soil temperature, whereas changes in soil moisture were of minor importance. The strong positive relationships between temperature and soil CO_2 fluxes were in agreement with numerous field studies that had documented strong relationship between them for different temperate forest sites (Saiz et al., 2007; Graf et al., 2008; Wu et al., 2010; Wang et al., 2010) and could be explained by stimulation of the biological activity of autotrophic (roots; Bouma et al., 1997) and heterotrophic organisms (microbial communities and soil fauna) by temperature.

In the frame of a 15-months study at a Norway spruce forest in the north of Zealand, Denmark (Elberling et al., 2005), CO_2 efflux correlated well with near-surface soil temperature. This was in line with our finding that soil respiration was more closely correlated to temperature measurements in the organic layer than to temperatures measured in deeper soil layers. Comparable results were also found by Borken

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et al. (2002) for mature beech, spruce and pine stands at both Solling and Unterlüss, Germany. Exponential functions, as also used in our study, were employed to describe the relationship between soil respiration and soil temperature in many studies before (Wang et al., 2006; Jacinthe and Lal, 2004; Borken et al., 2002; Bagherzadeh et al., 2008; Pilegaard et al., 2006).

The influence of soil moisture on soil respiration was more variable. In general, gas transport within the soil cannot be an important constraint for soil CO_2 flux, since soil fluxes are mostly the result of production processes in the highly porous litter humus and uppermost mineral soil (Borken et al., 2002; Subke et al., 2003; Elberling et al., 2005). Soil water limitation of the CO_2 production could be best explained by a reduction in the temperature-insensitive basal respiration rate, with no discernible effect on the temperature sensitivity. However, a notable finding for our site is that maximum soil respiration occurred under wet and warm environmental conditions. This was specifically remarkable if monthly soil temperatures increased to values > 8 °C, which explains why more than a half of the annual soil CO_2 emission occurred from June to September, in line with observations at other temperate forest sites in Europe (Pilegaard et al., 2006; Saiz et al., 2007; Graf et al., 2008).

4.2.2 CH_4

Monthly mean CH_4 fluxes at our site correlated only weakly with soil moisture (negative) and soil temperature (positive). Also in other studies, such as the work of Borken et al. (2006), only weak correlations were found between temperatures and forest soil CH_4 uptakes, as long as temperature were from 5 to 10 °C (Steinkamp et al., 2001; Castro et al., 1995). However, the missing correlation of CH_4 uptake rates at the Höglwald forest sites to changes in soil moisture is somewhat surprising, especially since it is widely accepted that the diffusivity of soils is a primary controller of CH_4 uptake rates. For example, Borken et al. (2006) showed that soil moisture strongly controlled the uptake of atmospheric methane, since at higher soil moisture values diffusion of methane into the soil was limited. Castro et al. (1994) even used soil moisture

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alone as a predictor of methane uptake in temperate forest soil at Harvard Forest. Our failure to demonstrate such a relationship between soil moisture and CH_4 uptake rates is likely a result of the weekly and monthly aggregation of measurement data.

4.2.3 NO and N_2O

For the spruce forest site at the Höglwald Forest, NO emission increased exponentially with soil temperature. This is in line with results of others who found exponential relationships between soil NO fluxes and soil temperatures for agricultural (Williams et al., 1998; Roelle et al., 2001) as well as for forest soils (Van Dijk and Meixner, 2001; Schindlbacher et al., 2004). The strong temperature response of soil NO fluxes at our site may not only be due to the stimulation of nitrification as the assumed main process of NO production at our site (Gasche and Papen, 1999), but may also be explained by increasing contributions of NO production by chemo-denitrification in the acidic organic layer (pH of forest floor ≤ 3.2) at increasing temperatures (Kesik et al., 2006). In contrast to several field and laboratory studies (Smith et al., 1998; Dobbie and Smith, 2001; Schindlbacher et al., 2004), which reported that not only nitric oxide but also nitrous oxide emissions increased exponentially with soil temperature, obviously in our long-term dataset N_2O emissions did not exponentially increase with temperature in most cases with soil moisture limiting microbial activity and N_2O production in soils during summer time.

Due to the hypothesized main production process for soil NO emissions at our site, i.e. nitrification, soil moisture may hamper as well as stimulate emissions. Soil moisture limitations for NO production can be expected if soils are too dry, thereby restricting substrate (NH_4^+) diffusion to micro-sites with microbial activity and exposing soil microbes to water stress. At the other hand, if soils are too wet, which results in increased anaerobiosis, NO produced by microbes may already further reduces in the soil profile to N_2O by denitrifying microorganisms (Skopp et al., 1990; Cardenas et al., 1993; Ormeci et al., 1999; Gasche and Papen, 1999; Roelle et al., 2001). Maximum soil NO fluxes were often observed at low to medium water content (Pilegaard et al.,

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2006; Wu et al., 2010). Ludwig et al. (2001) suggested an optimum at approximately 20 % WFPS. In contrast, maximum NO emissions were reported at WFPS between 43–85 % by other studies (Gasche and Papen, 1999; van Dijk and Duyzer, 1999). In our study the soil moisture optima for NO emissions ranged from 20–24 vol % or 33–39 % WFPS. Schindlbacher et al. (2004) compared the optimum soil moisture for NO production at different forest sites across Europe and found a wide range from 15 % WFPS for sandy textured soils of the Po floodplain, Italy, to 65 % WFPS for a clay dominated soil texture at a beech forest site in Austria. In this respect the value for our site, with loamy clay textured soil is well in the range of reported values.

4.2.4 C : N trace gas ratios

Figure 8a showed that the dominant environmental factor affecting the ratio of NO to N_2O emissions was soil moisture rather than soil temperature, especially for conditions with soil temperatures > 10 °C and soil moisture values < 26 vol %. For such conditions NO emissions were typically high, since soil aeration and, thus, oxidative microbial processes such as nitrification were favored. On the other hand, the NO : N_2O ratio shifted toward N_2O at high soil water as well as high or low temperature conditions, without revealing a distinct pattern. However, annual NO emissions at our sites were always approx. one order of magnitude higher than N_2O emissions (Fig. 2), indicating that N trace gas emissions at our site were primarily driven by nitrification rather than by denitrification as already pointed out earlier by Gasche and Papen (1999) and Papen and Butterbach-Bahl (1999).

The limited contour plot showing the joint effect of soil temperature and moisture on the emission ratios of CO_2 : NO indicated that both gases were controlled in the same way by changes in temperature and moisture. Even though magnitudes of both fluxes were different by a factor of 1000, which showed that NO production and emission at our site was closely coupled to the microbial mineralization of organic matter and subsequent nitrification of mineralized N.

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4.3 Empirical models to describe soil GHG fluxes

4.3.1 CO_2

For the Höglwald Forest site soil respiration rates at weekly or monthly scale could be successfully approximated from prevailing soil moisture and temperature values. Using volumetric soil water content and soil temperature as parameters, we were able to explain 84.9 % (weekly) or 88.5 % (monthly) of variations in soil respiration rates. This result is consistent with findings for other forests. For example, based on two years of measurements of soil respiration at six temperate forest stands (mature beech, spruce and pine stands) in Germany, Borken et al. (2002) found that soil temperatures at 5 and 10 cm depth were able to explain 83 % of the temporal variation in soil respirations. Similar results were also reported by Subke et al. (2003). In their open dynamic chamber system measuring the soil CO_2 flux intensively and continuously throughout a growing season in a mature spruce forest in Southern Germany, soil temperature alone explained 72 % of the variation in the flux rate, and including soil water content as an additional variable increased the explained variance to about 83 %.

Mariko et al. (2000) and Davidson et al. (2000) pointed out the limitation of using a simple temperature function from one soil depth (5 cm in the present work) to describe CO_2 production by microbial mineralization activity and root respiration throughout the profile due to the heterogeneity of substrate availability as well as temperature and moisture gradients. Splitting the temperature response into several components to represent the flux contribution from different soil layers was one step towards a better understanding of the origin of CO_2 within the soil. However, this would increase the number of parameters in a regression model, thus requiring more data points to yield a significant regression result (Draper and Smith, 1981). Despite sufficient data obtained in our study, it was not possible to further improve simulation results by including soil temperature measurements from different soil depths, since the temperature measured at a depth of 5 cm alone was adequate to describe observed variations of CO_2 fluxes at the soil surface, as reported by Subke et al. (2003).

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4.3.2 NO, N_2O and CH_4

With regard to NO a multiple linear regression including soil moisture and soil temperature as parameters explained almost 60 % of the observed variation of weekly aggregated NO emission rates. However, if monthly mean data were used, the correlation between soil moisture and NO flux was not significant anymore. Including this parameter in the regression with weekly aggregated dataset increased the explanatory power of the relationship only from 58.1 % (temperature alone) to 59.2 %. This showed that at our site soil temperature was the main driver of temporal variations in soil NO emissions and soil moisture had only a little effect on NO production and consumption at weekly to monthly scale. This may be due to the fact that NO is mainly produced in the approx. 7 cm thick acid organic layer (Butterbach-Bahl, 1997; Gasche and Papen, 1999), which hardly becomes water-saturated – conditions at which NO production and emission are limited – and seldom dries out during summer. In contrast to NO, the only controlling factor for CH_4 fluxes at monthly time scales was soil moisture. This result was most likely closely linked to the observation that at our site (Butterbach-Bahl and Papen, 2002), but also at other temperate forest sites (Smith et al., 2000). The main active zone for CH_4 oxidation is located in the mineral soil (approx. 10–20 cm soil depth). These soil layers may get water-logged following rainfall events or snow melt at various times throughout the year, which limits gas diffusion and thus reduces CH_4 uptake activity in the respective layer.

Due to freeze-thaw effects on N_2O fluxes, regressions based on the entire dataset of the present work yielded no significant correlations. After excluding the freeze-thaw periods for the calculation of regression equations, the empirical relations of N_2O fluxes with soil moisture and soil temperature were able to explain 30.6 and 37.8 % of the observed temporal variation of N_2O fluxes at weekly and monthly time scales, respectively. This rather low predictive power showed that simple regression models using measured soil environmental parameters hardly work to simulate soil N_2O fluxes. This was clearly due to the complexity of processes involved in the soil surface emission

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of N_2O, which included not only aerobic (autotrophic and heterotrophic nitrification, nitrifier denitrification) and anaerobic (denitrification, dissimilatory nitrate reduction) microbial production processes but also possible N_2O consumption (Baggs, 2008; Conen and Neftel, 2007).

4.3.3 Comparison between temporal scales, trace gas fluxes, samplings

In our study we evaluated the performance of regression models from weekly to annual time scales. However, for longer time periods, such as three months, six months or entire years, correlations deteriorated or even disappeared. Only monthly or weakly regression models were meaningful, at least for NO and CO_2. This is in line with results from the study by Pilegaard et al. (2006), who failed to unravel any significant relationship between soil temperature and N_2O emission at annual scale for a series of investigated forest sites across Europe. The question, whether accuracy of flux prediction (for example N_2O) could be increased by examining relationships between fluxes and environmental parameters at larger spatial and temporal scales, was also assessed by Groffman et al. (2000). They compared relationships between annual rather than hourly or daily fluxes and ecosystem-scale variables such as soil types and annual climate rather than field-scaled variables such as soil moisture and temperature. They found that there were coherent patterns in annual N_2O flux at the ecosystem scale for forest, cropland and rangeland ecosystems, but that ecosystem-scale controls of N_2O fluxes varied within and between regions and only emerge with continuous – at least daily – flux measurements over multiple years.

5 Conclusions

Fluxes of trace gases were measured with automated static or dynamic chamber systems at an approx. 100 yr old spruce forest site in subdaily resolution (hourly/2-hourly) between 1994 and 2010. Our dataset represented the most complete and long-lasting

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dataset on trace gas exchange between forest soils and the atmosphere worldwide. Measured soil trace gas fluxes encompassed CO_2, CH_4, N_2O, and NO. Overall conclusions based on the entire dataset and on subsets of the data are as follows:

1. The soil of the Höglwald spruce forest functioned as a sink for atmospheric CH_4 and sources of CO_2, N_2O, and NO. NO fluxes were in average approximately one order of magnitude higher than N_2O fluxes. The high fluxes of N-trace gases and reduced rates of CH_4 uptake at our site are a consequence of high nitrogen deposition at the Höglwald Forest in a range of 20–30 kg N ha^{-1} yr^{-1} since more than three decades.

2. Distinct seasonal patterns and interannual variations of CO_2, CH_4, N_2O, and NO were found for Höglwald. The highest variability in annual trace gas fluxes was observed for N_2O, due to freeze-thaw pulse emissions in some years. Furthermore, soil respiration rates varied largely from year to year by > 30 %. These results show that long-term, multi-year measurements are needed to obtain reliable estimates of GHG fluxes for a given ecosystem.

3. Using field data for the first time we were able to show that with an increasing length of soil freezing period N_2O emissions during the following thawing period were increasing as well.

4. Higher annual cumulative CO_2 fluxes were found in years with relatively lower mean soil temperature. This indicated that increased release of easily degradable substrate during the freezing period might prime the increased decomposition of organic matter throughout the following growing season

5. Environmental drivers such as soil temperature and moisture could be used to approximate NO and CO_2 fluxes at weekly and monthly scales. However, no suitable empirical models were found for N_2O and CH_4 fluxes, most likely due to the complexity of underlying oxidative and reductive microbial production and consumption processes.

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Table 1. Annual means (±SE) of soil temperature (5 cm depth), air temperature, soil moisture (10 cm depth), and cumulative precipitation.

Year	Soil temperature (°C)	Air temperature (°C)	Soil moisture (vol %)	Precipitation (mm)
1994	9.1 ± 0.4	10.1 ± 0.4	33.0 ± 0.2	1006
1995	7.2 ± 0.3	7.9 ± 0.4	33.0 ± 0.2	997
1996	5.7 ± 0.3	6.1 ± 0.4	32.3 ± 0.1	778
1997	6.9 ± 0.2	9.4 ± 0.4	29.1 ± 0.2	627
1998	n.a.	8.9 ± 0.4	30.2 ± 0.2	952
1999	6.6 ± 0.4	8.8 ± 0.4	29.0 ± 0.2	1052
2000	6.9 ± 0.2	9.4 ± 0.4	30.0 ± 0.1	1135
2001	5.9 ± 0.2	8.6 ± 0.4	29.6 ± 0.2	1047
2002	8.7 ± 0.2	9.1 ± 0.4	30.4 ± 0.1	1265
2003	8.6 ± 0.3	8.9 ± 0.5	26.1 ± 0.2	633
2004	11.9 ± 0.4	8.4 ± 0.4	29.3 ± 0.2	754
2005	11.9 ± 0.4	8.0 ± 0.4	30.5 ± 0.1	1067
2006	7.3 ± 0.3	8.7 ± 0.4	29.4 ± 0.2	908
2007	7.9 ± 0.2	9.4 ± 0.4	30.5 ± 0.1	986
2008	8.0 ± 0.3	9.1 ± 0.4	29.6 ± 0.1	816
2009	7.4 ± 0.3	8.6 ± 0.4	28.0 ± 0.1	834
2010	7.2 ± 0.3	7.5 ± 0.4	29.5 ± 0.1	984
Mean	7.9 ± 0.5	8.6 ± 0.2	30.0 ± 0.4	932 ± 3

n.a.: not available due to the removal of the sensors.

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Table 2. Annual means of soil trace gas fluxes of CO_2 ($t\,C\,ha^{-1}\,yr^{-1}$), CH_4 ($kg\,C\,ha^{-1}\,yr^{-1}$), N_2O ($kg\,N\,ha^{-1}\,yr^{-1}$), and NO ($kg\,N\,ha^{-1}\,yr^{-1}$) for the individual observation years. N: number of days per year with valid observations.

Year	CO_2	N	CH_4	N	N_2O	N	NO	N
1994	n.a.		–1.57	352	0.41	345	6.38	357
1995	n.a.	287	–2.78	360	0.81	358	8.52	342
1996	9.24	355	–1.81	340	2.95	343	9.01	350
1997	7.81	362	–3.45	341	0.67	345	7.59	359
2000	n.a.	165	–1.40	297	0.53	304	n.a.	285
2001	n.a.	228	–1.53	333	0.42	329	n.a.	270
2002	n.a.		–0.94	335	0.68	343	n.a.	277
2003	n.a		–1.90	309	0.37	339	n.a.	277
2004	6.99	299	–1.89	299	0.20	295	9.13	314
2005	7.90	334	–1.46	345	1.02	343	6.69	322
2006	8.37	331	n.a.	267	3.24	264	n.a.	263
2007	n.a.	268	n.a.	253	0.60	295	n.a.	263
2008	n.a.	262	–1.26	304	0.76	338	n.a.	253
2009	7.15	297	n.a.	288	0.97	320	n.a.	245
2010	n.a.	285	n.a.	260	n.a.	267	11.44	295
Mean (±SE)	7.91 ± 0.34		–1.82 ± 0.22		0.80 ± 0.20		8.40 ± 0.65	

n.a.: not available either due to lack of measurements or since number of valid flux observation days (N) was < 292 (80 % of a year (365 days)).

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Table 3. Results from first order linear regression analysis of log-transformed soil N_2O, NO, CO_2 and CH_4 fluxes versus soil temperature and moisture using weekly or monthly aggregated data. T_depth gives the depth of the temperature measurement selected by models. Measured and modeled values were transformed back to units: CO_2 (mg C h^{-1} m^{-2}), NO (µg N h^{-2} m^{-2}), CH_4 (µg C h^{-2} m^{-2}), and N_2O (µg N h^{-2} m^{-2}).

	Weekly mean fluxes				
	CO_2 emission	CH_4 uptake	NO emission	N_2O emission	N_2O emission[a]
Intercept	0.669	7.344	2.767	–1.721	–1.430
T	0.072	0.057	0.121	0.052	0.077
M	0.025	–0.133	0.025	0.105	0.084
T_depth	5 cm	15 cm	organic	20 cm	15 cm
R^2	0.849 0.740[c]	0.357	0.581	0.141	0.306
Measured	77.5 ± 1.93	16.3 ± 1.93	73.7 ± 2.31	5.4 ± 2.59	5.3 ± 2.18
Modeled	95.6 ± 2.27	29.7 ± 1.60	83.1 ± 1.86	6.1 ± 1.40	5.9 ± 1.39
	Monthly mean fluxes				
	CO_2 emission	CH_4 uptake	NO emission	N_2O emission	N_2O emission[a]
Intercept	1.477	7.300	3.742	1.418	–1.675
T	0.160	[b]	0.101	–0.032	0.079
M	0.062	–0.130	[b]	0.023	0.094
T_depth	5 cm	[b]	organic	20 cm	20 cm
R^2	0.885 0.768[c]	0.372	0.592	0.037	0.378
Measured	76.7 ± 1.65	13.5 ± 1.8	80.6 ± 1.97	[b]	5.5 ± 2.36
Modeled	90.9 ± 2.08	33.1 ± 1.45	97.5 ± 1.72	[b]	6.1 ± 1.45

T: Soil temperature, *M*: volumetric soil water content.
[a] Measured data during spring freeze-thaw periods was excluded.
[b] Not calculated, since no significant relationship could be found.
[c] r^2 when using soil temperature alone as predictor. Measured and modeled: measured and modeled mean fluxes.

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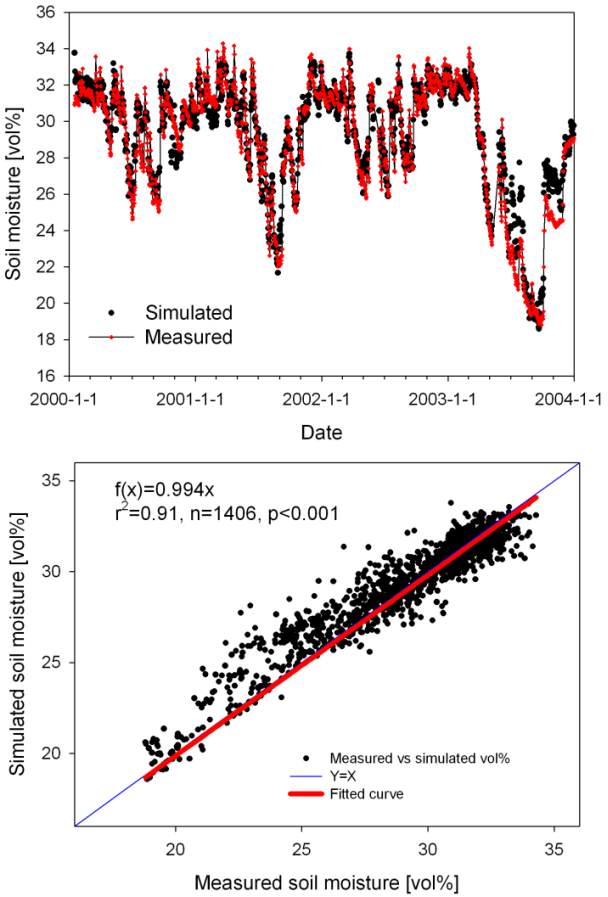

Fig. 1. Comparison of measured and modeled values of volumetric water content in 10 cm depth from 2000 to 2003. Simulation of soil volumetric water content was done using a support vector machine modeling approach.

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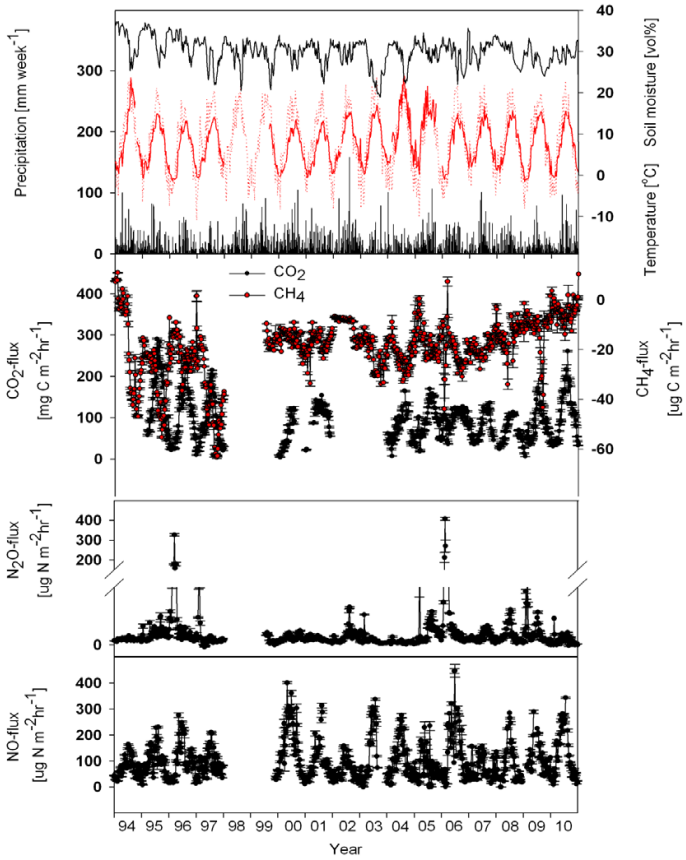

Fig. 2. Weekly aggregated values of environmental parameters (upper panel: precipitation (black bars), temperature (red line: soil temperature, red dashed line: air temperature), soil moisture (black line)) and trace gas fluxes (second panel to lowest panel: CO_2, CH_4, NO, N_2O) at the Höglwald Forest spruce site for the years 1994 to 2010. Error bars for fluxes are representing the SE of hourly data.

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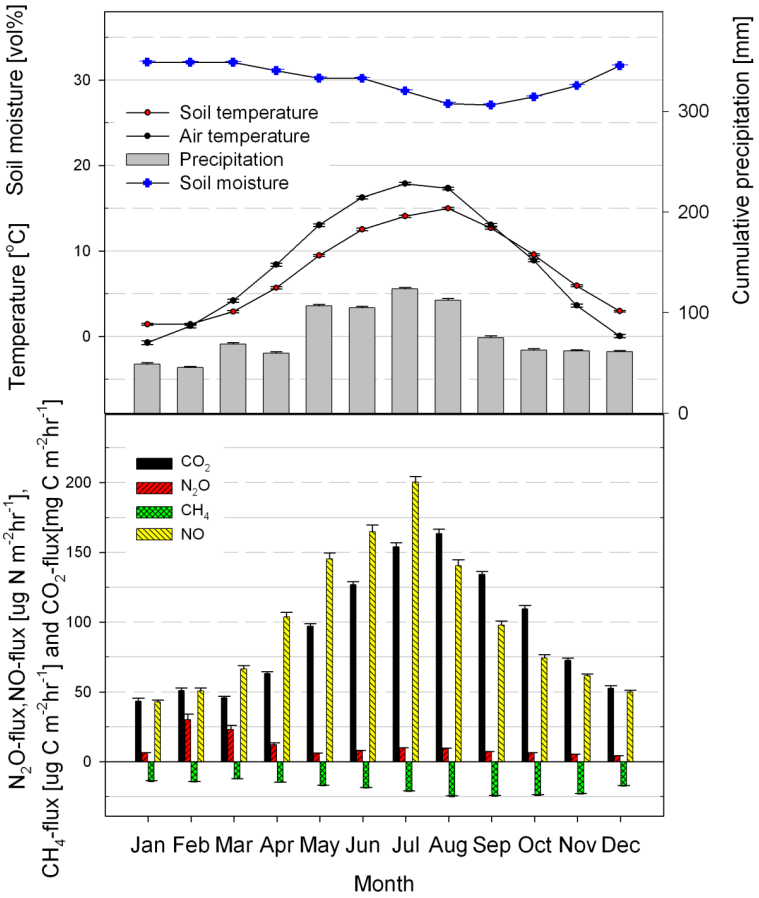

Fig. 3. Average seasonal variability of both, environmental drivers and trace gas fluxes for the observation period 1994–2010. Top panel: monthly means (±SE) of air- and soil-temperature (5 cm), soil moisture (10 cm) and the average sum of monthly precipitation. Lower panel: Monthly means of trace gas fluxes (±SE).

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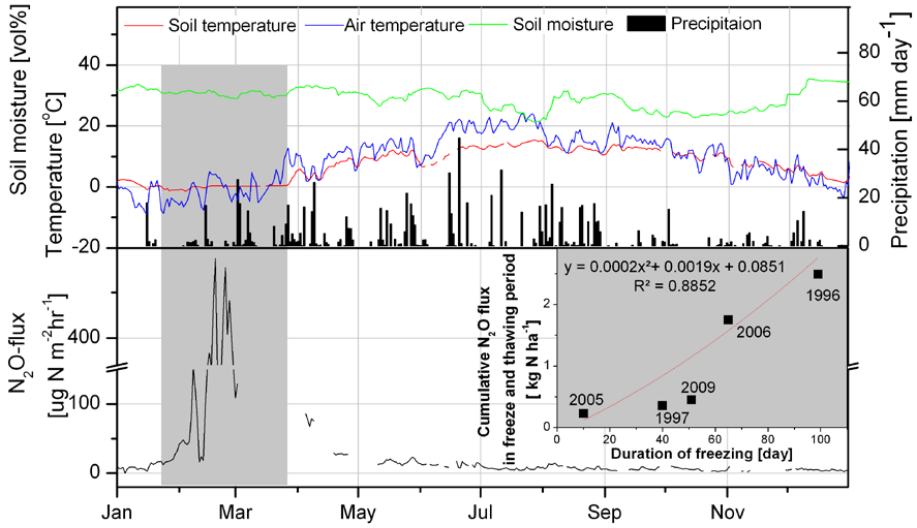

Fig. 4. Example for the temporal dynamics of daily N_2O emissions in a year with freeze-thaw pulse N_2O emissions (year 2006). The gray bar indicates the frost period (soil temperature in 5 cm < 0 °C). Daily air-temperature (2 m) and soil-temperature (5 cm), soil moisture (10 cm) and the sum of precipitation are shown. The insert shows the cumulative N_2O fluxes during and immediately following the freeze-thaw period in years with significant freeze-thaw N_2O emission pulses.

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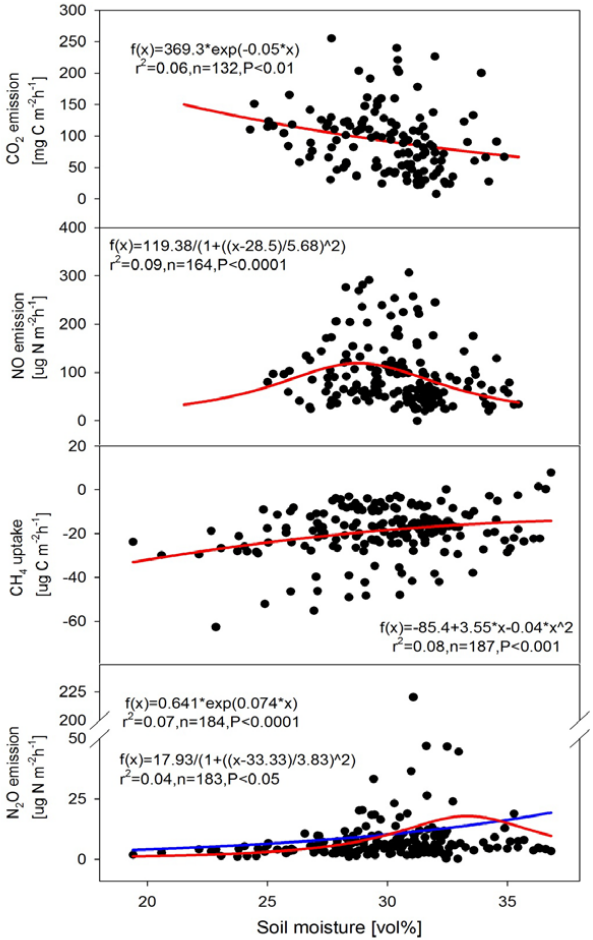

Fig. 5. Dependencies of soil trace gas emissions on soil moisture (in 10 cm soil depth). For this analysis monthly mean values as obtained for the period 1994–2010 were used.

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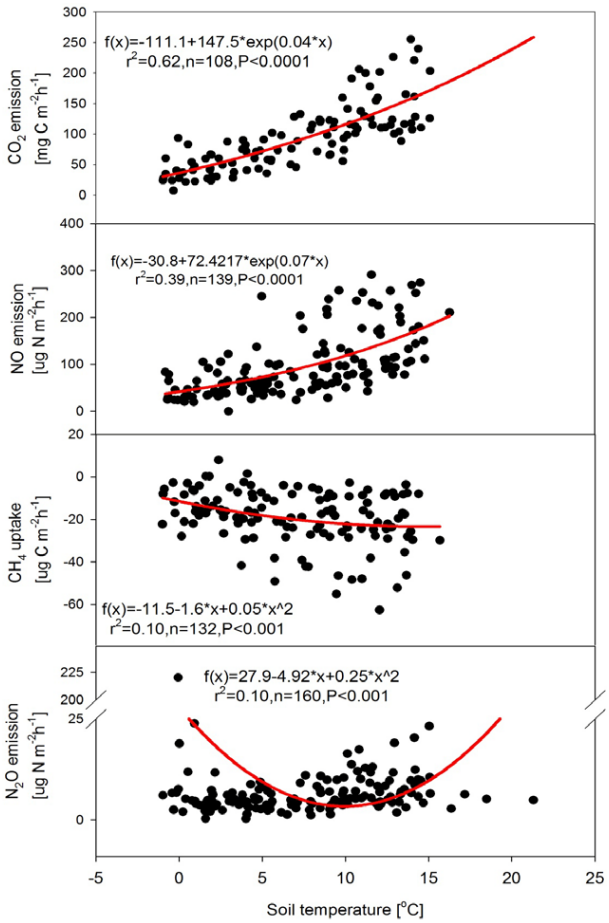

Fig. 6. Dependency of soil trace gas emissions on soil temperature (in 5 cm soil depth). For this analysis monthly mean values as obtained for the period 1994–2010 were used.

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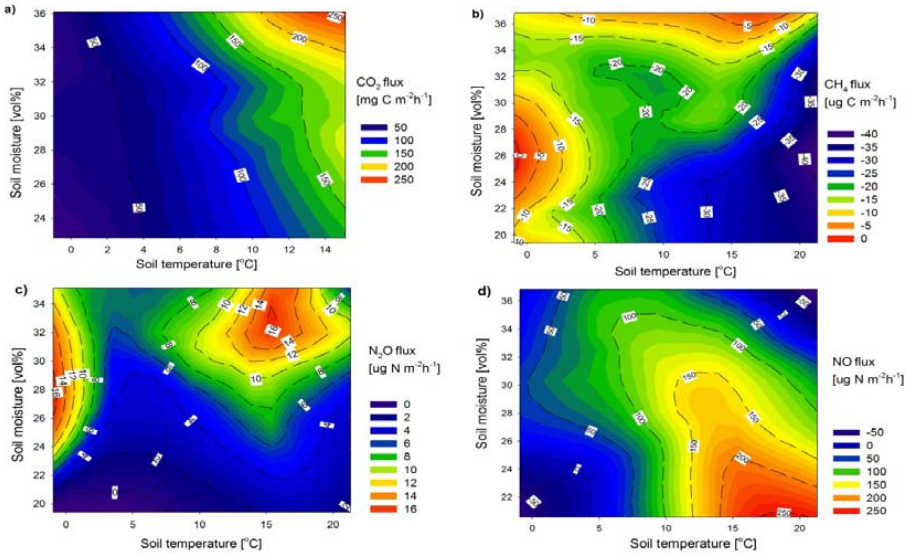

Fig. 7. Conjunct effects of soil moisture and temperature on monthly means of soil trace gases fluxes **(a)** CO_2 **(b)** CH_4 **(c)** N_2O. Note that with regard to N_2O the freeze and thaw periods were excluded. **(d)** NO.

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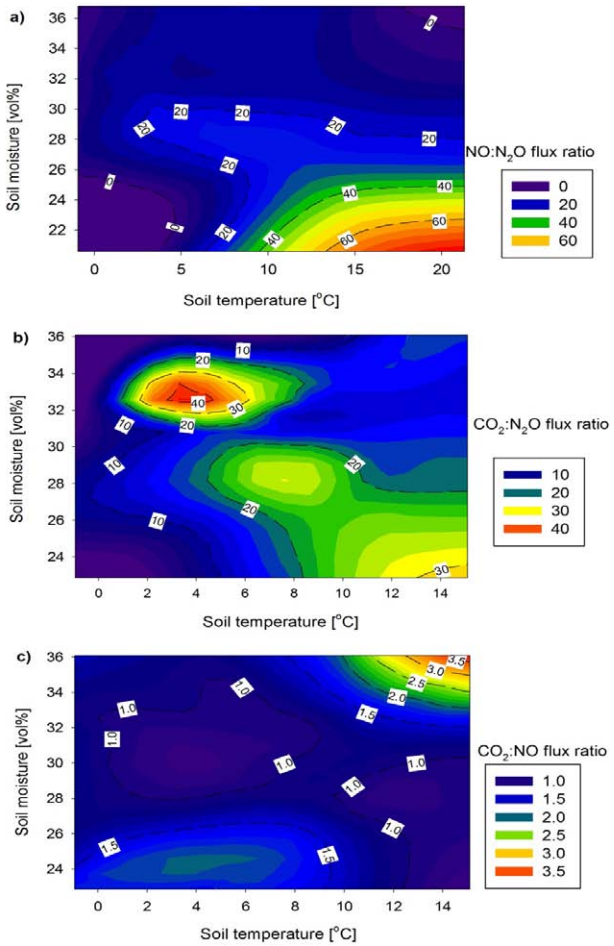

Fig. 8. Conjunct affects of soil moisture and temperature on monthly flux ratios **(a)** $NO:N_2O$ **(b)** $CO_2:N_2O$ **(c)** $CO_2:NO$. Note that CO_2 fluxes were divided by 1000 for this analysis.

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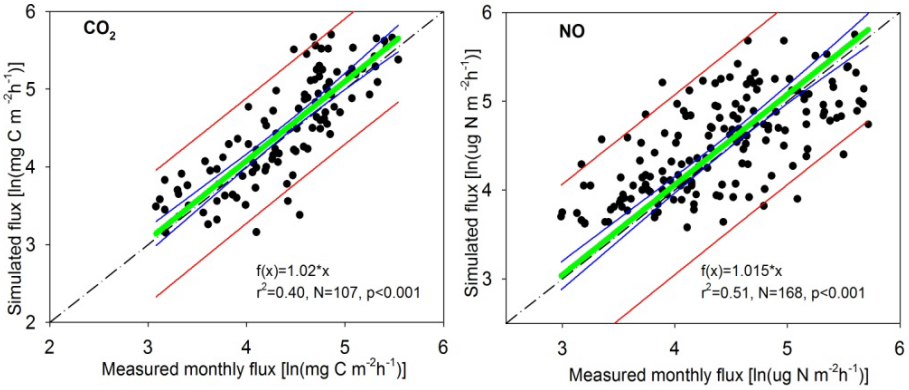

Fig. 9. Measured versus simulated soil CO_2 and NO fluxes. There presents the empirical relationship for monthly time steps as presented in Table 3. The green line shows the linear regression of simulated monthly vs. measured monthly flux. Note that the blue and red lines represent the 95 % confidence limits for slope (blue line) and expected data point distribution (red line), respectively.

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