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## Response of terrestrial N<sub>2</sub>O and NO<sub>x</sub> emissions to abrupt climate change

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**Abstract.** Being a potent greenhouse gas, N<sub>2</sub>O emitted by the terrestrial biosphere during abrupt climate change events could have amplified externally forced warming. To investigate this possibility, we tested the sensitivity of terrestrial N<sub>2</sub>O emissions to an abrupt warming event by applying the ARVE-DGVM in combination with a novel scheme for process-based simulation of terrestrial N<sub>2</sub>O and NO<sub>x</sub> emissions at the Gerzensee site in Switzerland. In this study, we aim to quantify the magnitude of change in emissions for the abrupt climate change event that occurred at the transition from Oldest Dryas to Bølling during the last deglaciation. Using high-resolution multiproxy records obtained from the Gerzensee that cover the Late Glacial, we apply a prescribed vegetation change derived from the pollen record and temperature and precipitation reconstructions derived from δ<sup>18</sup>O in lake sediments. Changes in soil temperature and moisture are simulated by the ARVE-DGVM using the reconstructed paleoclimate as a driver. Our results show a pronounced increase in mean annual N<sub>2</sub>O and NO<sub>x</sub> emissions for the transition (by factor 2.55 and 1.97, respectively), with highest amounts generally being emitted during summer. Our findings suggest that summertime emissions are limited by soil moisture, while temperature controls emissions during winter. For the time between 14670 and 14620 cal. years BP, our simulated N<sub>2</sub>O emissions show increase rates as high as 1% per year, indicating that local reactions of emissions to changing climate could have been considerably faster than the atmospheric concentration changes observed in polar ice.

### 1. Introduction

To understand the role of the terrestrial biosphere in influencing climate change and air quality, it has become increasingly important to quantify the magnitude and variability of trace gas emissions from the earth’s land surface to the atmosphere, e.g., [1]. The ice core record of atmospheric N<sub>2</sub>O concentrations shows considerable temporal variability that closely parallels polar temperature records [2], [3], [4], [5], indicating that nitrogen trace gas emissions may be very sensitive to climate change. Variability in atmospheric N<sub>2</sub>O and NO<sub>x</sub> concentrations is linked to nitrogen cycling in the oceans, e.g., [6] and

the terrestrial biosphere [1]. Given the high greenhouse warming potential of N<sub>2</sub>O [7] it is conceivable that increases in its atmospheric concentration could have amplified ongoing climate change during periods of rapid warming [8].

Over the last decade, a number of studies have attempted to quantify N<sub>2</sub>O emissions both for the present-day and the past based on measurement-based inventories of N<sub>2</sub>O concentrations in ice cores [2], [3], [4], [5]. In addition, several research groups have attempted to model regional and global source emissions of N<sub>2</sub>O and NO<sub>x</sub>, e.g [9], [10], [11]. However, process-based, mechanistic modeling of nitrogen trace gas emissions using Dynamic Global Vegetation Models (DGVMs) is still at an early stage, and only a few attempts have been made so far to successfully apply a process-oriented nitrogen cycle model in a DGVM [12], [13], [14], [15]. The implementation of a novel scheme for simulating emissions of N<sub>2</sub>O and NO<sub>x</sub> into the ARVE-DGVM - part of the current study - will allow us to explicitly simulate the emissions of different nitrogen trace gas species (e.g., N<sub>2</sub>O, NO<sub>x</sub>) on regional to global scales.

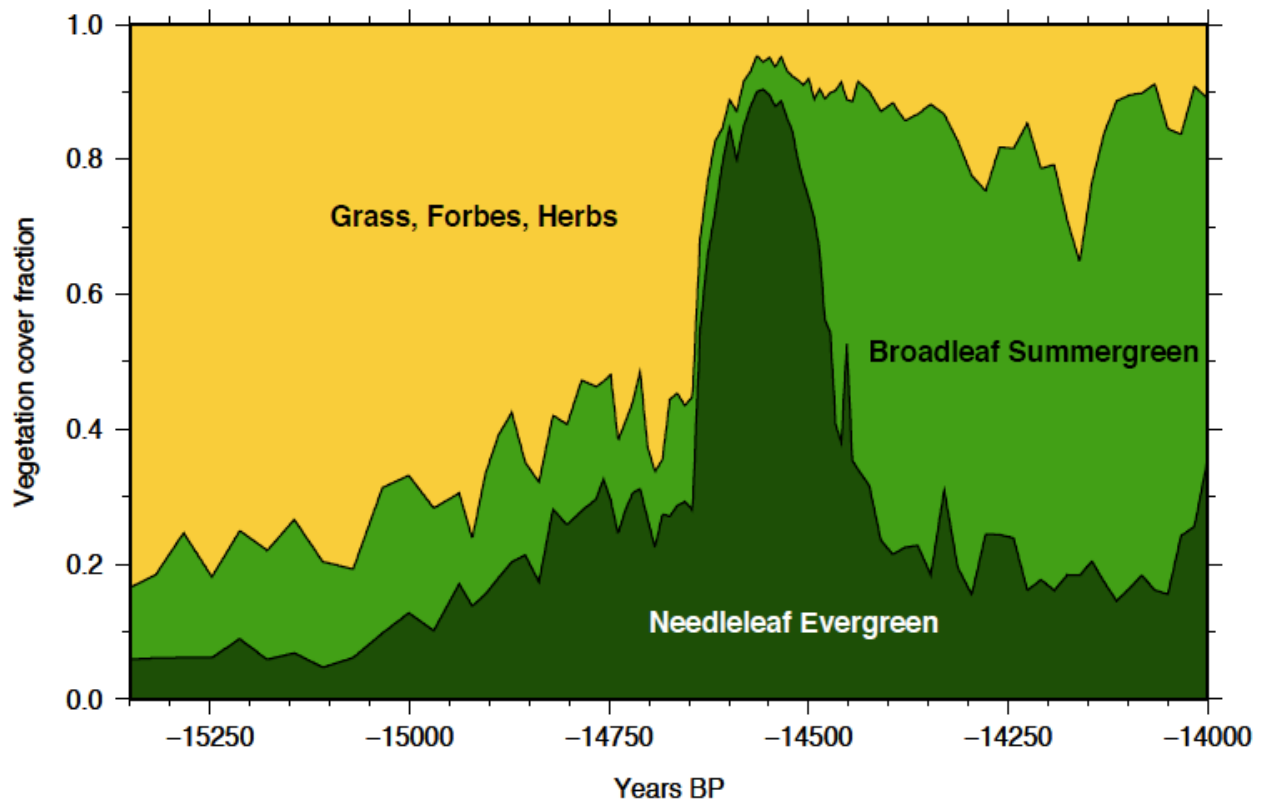
From Greenland ice cores it is known that the transition from Oldest Dryas (~18000 - 14650 cal. yrs. BP) to Bølling (14650 - 14000 cal. yrs. BP). was linked to a significant increase in atmospheric N<sub>2</sub>O concentration from approx. 210 ppbv to 260 ppbv [2]. Analyses of lake sediment and pollen records at the Gerzensee site in Switzerland have provided reconstructions of both mean annual air temperature based on δ<sup>18</sup>O of lake carbonates and other proxies, e.g., [16], [17], and changes in vegetation cover from pollen records, e.g. [18]. The very similar oxygen isotope records from Greenland ice cores and European lake sediments during the Glacial Termination [19] suggest that drastic climatic changes occurred quasi-simultaneously on hemispheric scale [16]. Greenland summit is reported to have warmed 9 ±3 °C [20], while the temperature of the warmest month in Western central Europe increased between 3 °C [21] and 5.5 °C [22] within approx. one century. We hypothesize that the pronounced and abrupt change in climate conditions caused an increase in N<sub>2</sub>O and NO<sub>x</sub> emissions at the Gerzensee site. Our aim for the study presented here is to quantify the proportional difference of N<sub>2</sub>O and NO<sub>x</sub> emissions before and after the abrupt climate warming at the Gerzensee site in Switzerland that occurred at the end of the last glacial.

## 2. Materials and methods

Gerzensee (46.830 °N, 7.547 °E) is located on the Swiss Plateau approx. 15 km southeast of Bern, at 602 m above sea level. The lake was formed as a kettle-hole after the last glaciation, and has a surface area of 0.27 km<sup>2</sup>, a catchment area of 2.6 km<sup>2</sup>, and a maximum depth of 10 m. A number of studies performed at the Gerzensee in recent years investigate how abrupt climate change effects ecosystem behavior on a local to regional scale using different proxies such as pollen, plant macrofossils, δ<sup>18</sup>O, chironomids and charcoal, e.g., [23], [24], [25], [26], [27], [28], [29].

For the time of Termination 1, quantitative July temperature reconstructions using fossil chironomid and pollen assemblages, as well as bulk sediment oxygen isotopes from Gerzensee have been carried out for the period between 15000 and 13000 cal. years BP [17]. The excellent correlation between the Gerzensee bulk sediment δ<sup>18</sup>O and the layer-counted North GRIP ice core provides a precise, high-resolution chronology for the record.

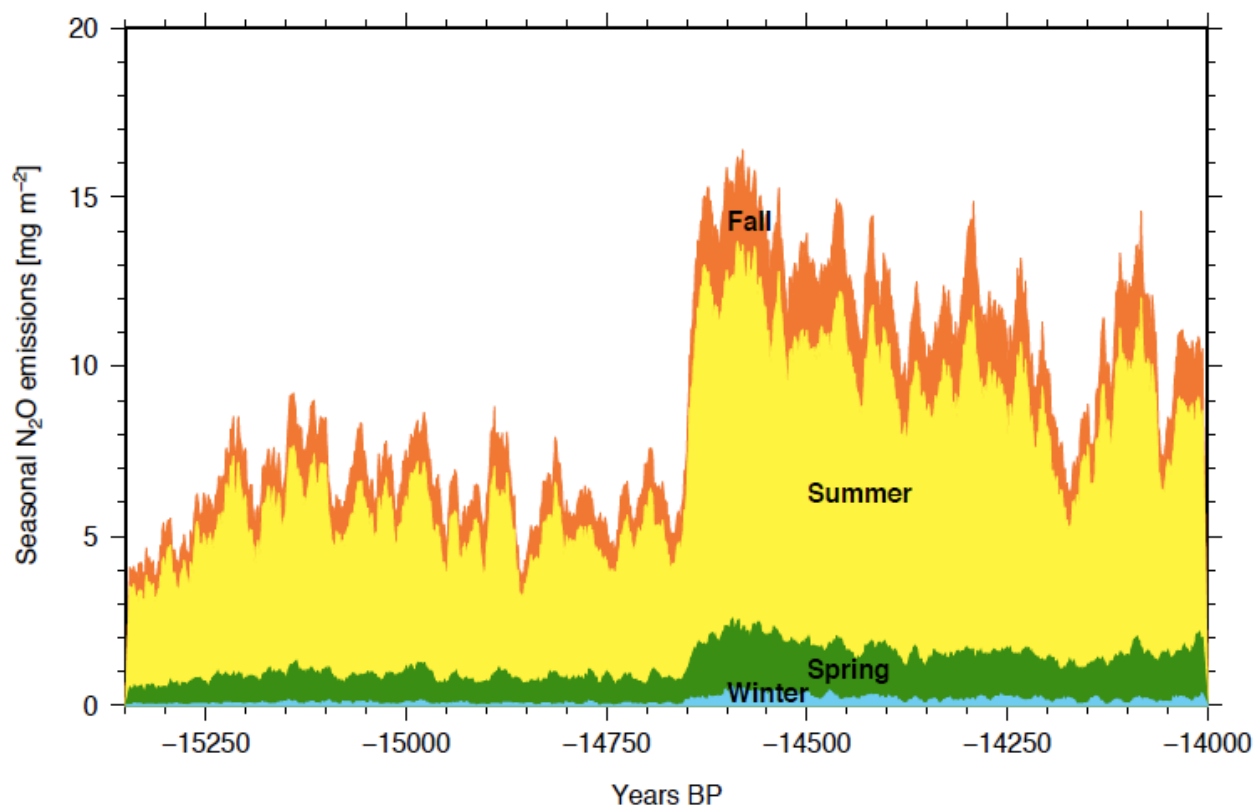
To simulate the impact of the rapid warming on emissions of N<sub>2</sub>O and NO<sub>x</sub>, we used the δ<sup>18</sup>O derived July temperature anomaly reconstruction based on isotopic analysis of shell carbonate picked from the lake sediments (*U. von Grafenstein et al.* pers. comm.) to infer monthly mean temperatures during the deglaciation from current monthly mean temperatures at Gerzensee. The original δ<sup>18</sup>O derived temperature anomalies for the period 15350 cal. years BP to 14000 cal. years BP have roughly decadal resolution, and we used linear interpolation in order to obtain annual temperature anomaly



**Figure 1:** Vegetation cover at Gerzensee during the transition from Oldest Dryas to Bølling, reconstructed from pollen accumulation rates [29].

values between years. We used the WGEN-based weather generator [27] implemented into ARVE-DGVM to create daily values for temperature and precipitation from monthly means, and ran its soil physics submodel to simulate daily soil volumetric water content and soil temperature. We therefore did not run the ARVE-DGVM as a full DGVM for this study. Daily precipitation was generated based on the pollen-based reconstruction of precipitation at Lac Lautrey [22] (130 km from Gerzensee, 46.587 °N, 5.864 °E) for the Termination 1 transition. Annual precipitation reconstructions for Lac Lautrey before and after the transition were scaled to present-day annual precipitation at Lac Lautrey. The corresponding scaling factor was applied to present day annual precipitation at Gerzensee to obtain an estimate for annual precipitation amounts before and after the transition at Gerzensee.

The daily soil temperature and soil moisture values derived from ARVE-DGVM are required as drivers for the nitrogen compartment model, which includes routines to calculate litterfall and soil organic matter pools and was adapted from the ORCHIDEE-CN nitrogen module ([15], *S. Zaehle*, pers. comm.). The nitrogen model was parameterized by prescribing typical values published in literature for C/N ratios, biomass and soil organic matter for the three plant functional types (PFTs) that were present at Gerzensee during the transition (grass/herbal, needleleaf evergreen, broadleaf summergreen, figure 1). Given the current model setup, the nitrogen budget is not closed and vegetation changes are not modelled directly.  $N_2O$  and  $NO_x$  emissions are simulated separately for each PFT. Total emission values per unit area were obtained in a post-processing step by scaling the amount emitted by each PFT according to the prescribed fractional covers of the PFTs estimated from pollen accumulation rates from Gerzensee for the time of the transition (*W.O. van der Knaap*, pers. comm., [31]).



**Figure 2:** Simulated N<sub>2</sub>O emissions for the Oldest Dryas to Bølling transition at Gerzensee (Switzerland). Shown are total annual emissions (top margin of curve) and the breakdown of total emissions into seasonal fractions.

**Table 1:** Statistics of seasonal and annual N<sub>2</sub>O and NO<sub>x</sub> fluxes before and after the transition (SD: Standard Deviation; SEM: Standard Error in the Mean)

	N <sub>2</sub> O [mg m <sup>-2</sup> timespan <sup>-1</sup> ]					NO <sub>x</sub> [mg m <sup>-2</sup> timespan <sup>-1</sup> ]				
	spring	summer	fall	winter	annual	spring	summer	fall	winter	annual
	<i>before transition (14750 BP - 14660 BP)</i>					<i>before transition (14750 BP - 14660 BP)</i>				
Median	0.713	3.920	0.908	0.004	5.831	13.189	56.963	14.731	0.082	87.931
Mean value	0.759	4.031	1.030	0.043	5.863	13.318	58.580	16.061	0.755	88.715
1 SD	0.360	1.645	0.555	0.093	1.839	3.614	15.263	5.304	1.531	17.624
SEM	0.038	0.173	0.059	0.010	0.194	0.381	1.609	0.559	0.161	1.858
Minimum value	0.192	1.203	0.275	0.000	2.195	6.712	29.665	8.452	0.007	53.940
Maximum value	1.718	11.292	3.411	0.517	13.650	23.600	125.291	38.583	7.678	160.517
	<i>after transition (14630 BP - 14550 BP)</i>					<i>after transition (14630 BP - 14550 BP)</i>				
Median	1.799	10.092	2.386	0.218	14.568	23.248	113.944	30.125	3.024	171.153
Mean value	1.813	10.336	2.467	0.356	14.972	23.431	116.219	30.804	4.621	175.074
1 SD	0.539	2.809	0.795	0.362	3.210	4.924	24.222	7.291	4.215	28.542
SEM	0.060	0.310	0.088	0.040	0.354	0.544	2.675	0.805	0.465	3.152
Minimum value	0.792	4.690	0.995	0.009	8.147	14.789	68.180	17.550	0.195	108.531
Maximum value	3.168	16.732	4.637	1.702	22.128	37.139	178.884	51.762	18.742	238.429

### 3. Results

The combined increase in temperature and precipitation during the Oldest Dryas/Bølling transition resulted in a pronounced increase in simulated N<sub>2</sub>O (figure 2, table 1) and NO<sub>x</sub> emissions for the Ger-

zensee site. As we ran our simulations for just one single site, we cannot directly compare the magnitudes of the simulated changes with the ice core record, but the direction of the simulated pattern is consistent with the increase in atmospheric N<sub>2</sub>O concentration observed in Greenland ice [2]. For NO<sub>x</sub>, mean annual emissions increased by factor 1.97 from 88.7 (SD ±17.6; SEM ±1.86) mg m<sup>-2</sup> yr<sup>-1</sup> to 175.1 (SD ±28.5; SEM ±3.15) mg m<sup>-2</sup> yr<sup>-1</sup> when comparing the average of the time period 14750 – 14660 BP (before the transition) to the average of the time period 14630 – 14550 BP (after the transition). For N<sub>2</sub>O, the increase was even more pronounced with a factor of 2.55 from 5.9 (SD ±1.8; SEM ±0.19) mg m<sup>-2</sup> yr<sup>-1</sup> to 15.0 (SD ±3.2; SEM ±0.35) mg m<sup>-2</sup> yr<sup>-1</sup>. Similar variability characterizes the seasonal amplitude of N<sub>2</sub>O emissions at present day, e.g., a factor of 1.82 for the spruce site at Höglwald/Germany in 1995 (derived from figure 4 in [32]).

The annual mean soil moisture averaged over the 90 years prior to the transition increased by factor 1.64 from 16.80 (SD ±2.52; SEM ±0.27) % to 27.62 (SD ±2.72; SEM ±0.30) % as compared to the annual mean soil moisture averaged over the 80 years after the transition. The simulated difference in annual mean soil temperature between the coldest year within the 90 years before the transition and the warmest year of the 80 years after the transition was 4.9 °C, as compared to 6 °C for δ<sup>18</sup>O derived July air temperature. The increase in soil temperature is less pronounced than the increase in air temperature due to the dampening effect in soils. Moreover, the simulated 4.9 °C increase refers to annual mean temperature, while the proxy-derived 6 °C increase refers to the increase of July temperature only. Annual mean soil temperature averaged over the 90 years before the transition increased by 2.5 °C from 5.6 (SD ±0.5; SEM ±0.06) °C to 8.1 (SD ±0.5; SEM ±0.06) °C as compared to the annual mean soil temperature averaged over the following 80 years after the warming. As there is variability within both parts of the temperature time series, comparison of the averages over both time series shows a less pronounced increase in temperature than a comparison of extreme years before and after the transition.

The seasonal distribution of N<sub>2</sub>O emissions shows a clear maximum for summer (JJA) and a minimum for winter (DJF). For all seasons, the change from generally cold and dry conditions to warmer and moister conditions leads to an increase in emissions when comparing the 90 years before the transition to the 80 years after the warming. For spring and summer, mean N<sub>2</sub>O emissions increased by factor 2.39 from 0.8 (SD ±0.4; SEM ±0.04) mg m<sup>-2</sup> to 1.8 (SD ±0.5; SEM ±0.06) mg m<sup>-2</sup> and by factor 2.56 from 4.0 (SD ±1.6; SEM ±0.17) mg m<sup>-2</sup> to 10.3 (SD ±2.8; SEM ±0.31) mg m<sup>-2</sup>, respectively. Fall emissions increased by factor 2.40 from 1.0 (SD ±0.6; SEM ±0.06) mg m<sup>-2</sup> to 2.4 (SD ±0.8; SEM ±0.09) mg m<sup>-2</sup>. Winter emissions increased by factor 8.20, but in general were extremely low and showed a very high variability (< 0.1 mg m<sup>-2</sup> before the transition, and 0.4 (SD ±0.4, SEM ±0.04) mg m<sup>-2</sup> after the transition). The seasonal pattern and general behavior of NO<sub>x</sub> emissions (not shown here) are very similar to that of N<sub>2</sub>O, with an increase of emissions by factor 1.76, 1.98, 1.92 and 6.12 for spring, summer, fall and winter, respectively.

#### 4. Discussion

Nitrification (aerobic oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>), and, even more importantly, denitrification (anaerobic reduction of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub>), are the main processes of the terrestrial nitrogen cycle that result in N<sub>2</sub>O and NO<sub>x</sub> emissions from soils. Both processes are catalyzed by microorganisms whose kinetics is temperature dependent. Soil moisture exhibits an important control on denitrification, which takes place where anaerobic conditions exist in water-filled pores of soil. Apart from soil temperature and soil moisture, a group of other factors such as substrate quantity (depending on biomass and litter production), nitrogen input (deposition, biological N-fixation), and litter quality (C/N ratio of litter, which influences degradability) influence production and release of N<sub>2</sub>O from soils. The interplay of all these factors makes it hard to foresee which factors are dominantly influencing N<sub>2</sub>O emissions. Initial sensi-

tivity tests with our nitrogen model for the Oldest Dryas/Bølling transition at Gerzensee reveal that annual emissions of both trace gases show a good correlation with mean annual temperature ( $R^2 = 0.81$ ) and mean annual soil moisture ( $R^2 = 0.75$ ) when both factors are tested independently. This indicates that temperature and moisture are important factors influencing emissions. In addition to temperature and precipitation, the observed increase of emissions is reinforced by the change in vegetation cover from mostly herbaceous tundra vegetation to mostly forest (figure 1). A comparison of our vegetation change scenario to a sensitivity test where vegetation cover was kept constant with the conditions of the first simulation year for the entire simulation period reveals that approx. 33% of the increase in emissions is due to the change in vegetation cover. In our simulations, grasslands tend to produce less  $N_2O$  than forests, therefore the transition from mostly grassland to mostly forest cover amplifies the increase in emissions caused by the changes in meteorology. However, the phenomenon of pristine temperate grasslands producing less nitrogen trace gas emissions than forests under comparable climate conditions requires further evaluation.

As shown in figure 2, the magnitude of  $N_2O$  emissions during summer increases along with the variability of emissions. Before the transition, summer soil temperatures were high enough to allow microbial processes to result in the net emissions of some nitrogen trace gases. The temperature and moisture increases linked to the abrupt climate change event stimulates microbial activity and therefore emissions, but at the same time, the limiting effect of soil moisture during drier years becomes more pronounced. Total summer emissions are generally higher, which results in increased variability of emissions between drier years and wetter years. In contrast, wintertime emissions are controlled mainly by temperature rather than soil moisture. The increase in winter soil temperature leads to a decrease of days with soil frost and thus promotes microbial activity. Based on these model results, we suggest that emissions in summer are likely to be limited by the availability of water in the soil, while temperature controls emissions during winter.

With this study we could show the effect of soil temperature and soil moisture changes on  $N_2O$  and  $NO_x$  emissions. We did not intend to consider all aspects in the nitrogen cycle affecting nitrogen availability and nitrogen trace gas emissions yet, which requires simulation of a closed nitrogen cycle with actual vegetation dynamics instead of using prescribed biomass values from literature. A closed nitrogen budget with direct simulation of vegetation dynamics using the full DGVM with the nitrogen cycle directly integrated into it is a goal for future applications and will allow to address all effects of environmental changes on nitrogen availability, such as changes in quality and quantity of plant biomass, litter production, soil organic matter and microbial activity, as well as succession processes. Moreover, we only can judge the relative change in emissions at the moment, as the simulated total quantities of trace gas emissions per time unit still need to be evaluated. We used high-resolution reconstructions of mean annual temperature and precipitation for the Oldest Dryas/Bølling transition as a basis for creating a daily weather scenario to drive the nitrogen model. With roughly decadal resolution, the  $\delta^{18}O$  proxy record of the Gerzensee is an exceptionally detailed record of the abrupt climate change event. However, we acknowledge that our method of interpolating this paleoproxy record to an annual timestep, and then simulating daily weather based on these data with a weather generator, introduces additional uncertainty into our results. Nevertheless, we feel that the resulting data used to drive our model represents a plausible scenario of the climate changes that occurred during the Bølling warming event.

## 5. Conclusions

Our simulated  $N_2O$  emissions for the Oldest Dryas/Bølling transition at Gerzensee are in good accordance with the timing of the concentration changes observed in Greenland ice. We were able to show that terrestrial  $N_2O$  and  $NO_x$  emissions react very sensitively to small changes in temperature, moisture and vegetation cover, and can change significantly within a very short time span. As we only simulate

emission changes for a single site, we cannot directly transfer our results into estimates of atmospheric concentration changes. For the time between 14670 and 14620 cal. years BP, our simulated N<sub>2</sub>O emissions show increase rates as high as 1% per year. This indicates that short-term local reactions of emissions to changing climate could have been considerably more pronounced than visible from the atmospheric concentration changes recorded in Greenland ice (concentration change from approx. 210 to 258 ppmv from 14800 to 14500 cal. years BP, annual increase rate of approx. 0.06%). In the future we will expand the focus of our research from single sites such as Gerzensee to global simulations, allowing more direct comparison with ice core data. Moreover, additional simulations at Gerzensee with more detailed reconstructions of palaeoclimatic conditions, in particular a better way of reconstructing precipitation, will provide more information about the reaction of nitrogen trace gas emissions from terrestrial ecosystems to abrupt climate change.

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