Project Number 282910

ÉCLAIRE

Effects of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems

Seventh Framework Programme

Theme: Environment

D3.3 Soil NO emission model: Soil NO emission model (improved parameterization with regard to responses to changes in environmental conditions)

Due date of deliverable: **30/09/2014**

Actual submission date: **27/07/2015**

Start Date of Project: **01/10/2011**

Duration: **48 months**

Organisation name of lead contractor for this deliverable :
Karlsruhe Institute of Technology (KIT)

Executive Summary

- The objective of this task was to provide improved process descriptions and parameterizations of biotic (microbial metabolism) and abiotic (agricultural management) driven soil NO emissions including a robust response to climatic conditions that are predicted to change in the future. The objective is to improve the climate response characteristics of soil NO emissions within the LandscapeDNDC model.

- Within the project, a revised soil biogeochemical process description for LandscapeDNDC was developed.

- The validation study for the core Eclaire sites revealed the consistency and robustness of the new process description. The validation results report an excellent model performance for the simultaneous simulation/validation of nitric and nitrous oxide emissions for managed ecosystems across Europe.

- The validation study discovered deviations in the fertilizer induced emission factors for NO comparing simulation results with yearly emission estimates from field observations. The modelling study reported lower annual fertilized induced NO emissions. This emphasizes the uncertainty in upscaling a low number of observations to the annual budget.

1. Objectives:

The aim of this work package is to provide improved process descriptions and parameterizations of biotic and abiotic (agricultural management) driven soil NO emissions that include a robust response to climatic conditions that are predicted to change in the future. The objective is to improve the climate response characteristics of soil NO emissions within the LandscapeDNDC model.

The final deliverable is an improvement of the process description of the biogeochemical ecosystem model LandscapeDNDC. This has been achieved by developing a new soil biogeochemical module for LandscapeDNDC. The progress of the deliverable will be evaluated by validation of simulation studies of combined soil N_2O and NO emissions from managed ecosystems (forest, arable and grassland).

2. Activities:

The modelling and parameterization/calibration study using the LandscapeDNDC model was performed in conjunction with a parallel research effort to improve the model capabilities to simulate CH_4 production and emission pathways of flooded rice systems. Due to the synergies of the two research efforts a new biogeochemical process description was developed in order to improve the soil CH_4 and N_2O / NO emissions.

The process based ecosystem model LandscapeDNDC (Haas *et al.*, 2013) is a simulation framework, which comprises various sub-models accounting for processes describing water and matter fluxes in the atmosphere, hydrosphere, pedosphere and vegetation. LandscapeDNDC has been applied with different internal biogeochemical models i.e. MoBiLE-DNDC (Chirinda *et al.*, 2011), Forest-DNDC (Butterbach-Bahl *et al.*, 2009), Pnet-N-DNDC (Butterbach-Bahl *et al.*, 2001; Kiese *et al.*, 2005), ForestDNDC-tropica (Werner *et al.*, 2007), MiCNit (Blagodatsky *et al.*, 2011) and DECONIT (de Bruijn and Butterbach-Bahl, 2010). In view of a potential over-parameterization of the process description of denitrification in the DNDC model family de (de Bruijn *et al.*, 2009) developed the DECONIT module, which reduced the complexity of process description and amount of parameters of the denitrification routines. In addition, DECONIT introduced new concepts for the description of soil mineralisation stressing the influence of the chemical properties of plant litter i.e. concentrations of lignin and cellulose.

3.1 Development of a new soil biogeochemical process description

In order to improve the model response to biotic and abiotic drivers of the soil NO emissions, a new biogeochemical process description has been developed which combines different approaches that were used for describing soil microbial process dynamics in the DNDC model family and the DECONIT model. Microbial dynamics and process description for nitrification are still following the DNDC concept, whereas soil organic matter mineralisation and denitrification is following more closely the concepts developed for DECONIT. Main differences are the introduction of lignin and cellulose fractions for characterization of litter quality (same as DECONIT) and decomposition rates in conjunction with a new time integration scheme working on a hourly integration time step rather than a daily integration as done in DNDC. This development was in collaboration with parallel developments of the LandscapeDNDC model regarding photosynthesis based crop growth and the capability to simulate CH_4 production, oxidation and emission pathways for paddy rice production systems.

The new biogeochemistry module predicts carbon and nitrogen turnover and transport in soils. The main focus in this study lies on the calculation of emissions of NO and N_2O from forest, arable and grassland soils. Production and consumption of both gases are controlled by numerous microbial processes such as mineralisation, nitrification, denitrification, chemodenitrification and immobilization combined with vegetation interaction such as e.g. plant nitrogen uptake and plant litter production (Butterbach-Bahl *et al.*, 2013).

Decomposition of soil organic matter in LandscapeDNDC so far followed the DNDC approach based on carbon pool structured properties (Li *et al.*, 1997). The main difference between the previous and the new developed modules with regard to decomposition is the representation of their established pools. The biogeochemistry module of DNDC characterizes their pools entirely by conceptual C/N ratios, whereas the DECONIT concept uses the chemical structure i.e. concentration of cellulose and lignin as determining factor. Potential decomposition rates for all pools are further subject to several reduction factors accounting for different climatic and edaphic conditions.

The new biogeochemical module established the carbon pool structure following DECONIT and other decomposition modules (Corbeels *et al.*, 2005) with three plant litter pools representing contents of lignin, cellulose and solutes. The respective litter pools are decomposed either to microbial available dissolved organic carbon (DOC) or humified to microbial non-available humus.
There are three different humus pools: One represents recently humified material with a high turnover rate and the other two represent recalcitrant humus compounds (i.e. humic acids) with low turnover rates. The conceptual scheme of the module is shown in Figure 1.

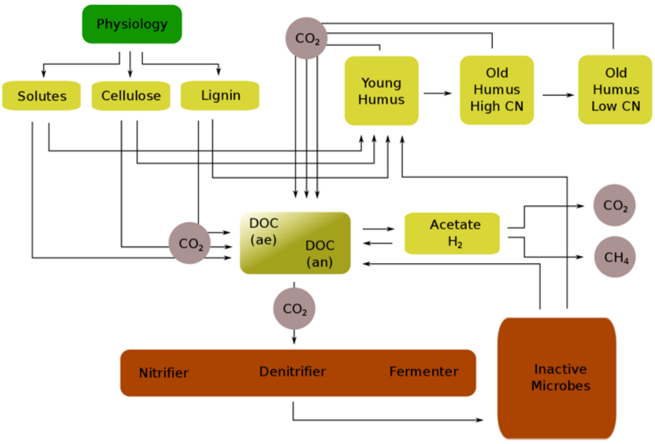

Figure 1 Flow diagram of carbon turnover in the new biogeochemical model (Kraus *et al.*, 2014)

Decomposition of a particular pool c_i is modelled as first-order kinetic subject to a potential decomposition constant k_i and various multiplicative modification factors:

$$r_{c_i} = k_i \, f_{tm} \, f_{C/N} \, f_{lig} \, f_{O_2} \, f_{clay} \, c_i$$

The temperature and moisture f_{tm} regulation is inherited from the DNDC concepts given by the harmonic mean of separately calculated factors (Figure 2). Likewise, the clay factor is derived from the DNDC model (Figure 2).

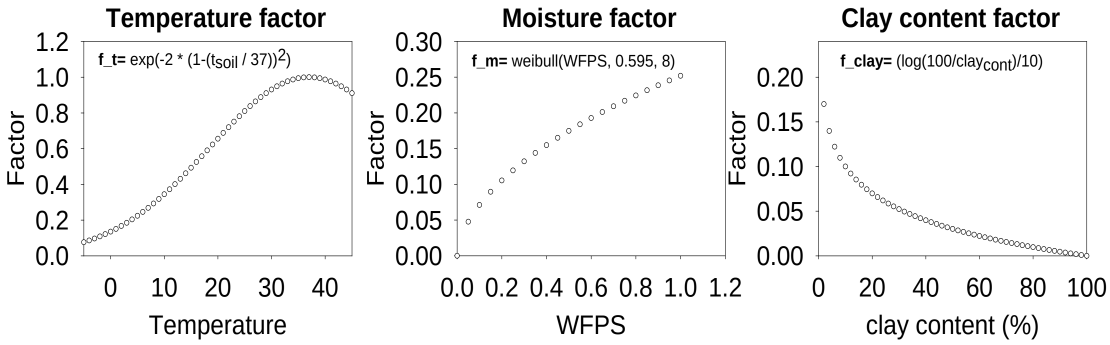

Figure 2 Multiplicative factors regulating the mineralization of soil organic carbon

For plant litter the model estimates a C/N ratio dependent reduction factor $f_{C/N}$, which decreases decomposability linearly starting from an optimal C/N ratio of 20 or smaller with no reduction to a maximum reduction of 0.1 approaching a C/N ratio of 300. According to Corbeels *et al.* (2005) and de Bruijn and Butterbach-Bahl (2010) plant litter decomposition is reduced by its lignin ratio:

$$f_{lig} = e^{-\beta \frac{c_{lig}}{c_{sol} + c_{cel} + c_{lig}}}$$

Decomposition rates are typically reduced under submerged conditions due to the lack of oxygen as electron acceptor. The biogeochemistry modules of DNDC introduced the concept of an anaerobic volume (AV) within the soil for the calculation of nitrification (in aerobic microsites of the soil) and denitrification (occurring in anaerobic microsites). This concept was adapted and broadened for the new description of aerobic and anaerobic decomposition. The AV depends on the partial pressure of oxygen (p_{O_2}) in the respective soil layer:

$$AV = e^{-(7\,p_{O_2})^2}$$

$$f_{O_2} = \begin{cases} 1, & aerob \\ 0.25, & anaerob \end{cases}$$

During aerobic decomposition a fixed proportion of 30% is directly released as CO_2. The microbial available aerobic and anaerobic DOC pools are further processed by microbial dynamics including nitrifier and denitrifier growth as well as fermentative, methanogenic and methanotrophic metabolisms (which are of minor importance in European arable systems). The humification of the different C pools (solutes, cellulose and lignin, humus 0 and humus 1) is modelled as first-order kinetic and it is subject to a potential humification constant k_i multiplied by the harmonic mean of a temperature and moisture factors (Figure 2) and the respective C fraction (C_i). This is not true for the humus pool 3.

$$r_{c_i} = k_i \; f_{tm} \, c_i$$

Nitrification, denitrification and chemo-denitrification

Microbial nitrification and denitrification have been identified as major sources for NO and N_2O whereas physicochemical processes such as chemodenitrification at soil pH values of < 5.0 for NO, occurring simultaneously in the soil (Braker and Conrad, 2011; Butterbach-Bahl *et al.*, 2013).

Nitrification is an aerobic process usually referred to as the biological oxidation of ammonia (NH_3) to nitrate (NO_3^-) via the intermediate products ammonium (NH_4^+), hydroxylamine (NH_2OH) and nitrite (NO_2^-):

$$NH_4^+ \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^-$$

During nitrification a certain amount of nitrogen is converted to NO and N_2O by nitrifier denitrification (Butterbach-Bahl et al. 2013; Conrad 1996; Firestone et al. 1989). The model is based on the DNDC concept of nitrifier dynamics (Li *et al.*, 2000; Stange *et al.*, 2000), which in turn is founded on the former work from (Blagodatsky and Richter, 1998) . The nitrification rate of ammonium to nitrite is given by

$$r_{NH_4} = \mu_{mic} \, c_{mic} \, a_{mic} \, f_{pH} f_{NH_4} \, \mu_{nit\_max}$$

wherein μ_{mic}, c_{mic} and a_{mic} are the potential growth rate, microbial biomass and microbial activity of the nitrifier community, respectively. f_{pH} corresponds to limits and best condition where the highest nitrification happens and it is given by one complex equation (not shown). f_{NH_4} belongs to the available NH_4 in the soil. Finally μ_{nit_max} factor regulates the amount of NH_4 that will be transformed to NO_2 and it depends on oxygen availability and on a N:O ratio for oxidation processes. Nitrification of NO_2^- to NO_3^- is modelled independent of microbial biomass using instead a Michaelis-Menten kinetic reduced by nitrifier activity:

$$r_{NO_2} = a_{mic} \, f_{NO_2}$$

The fraction of r_{NH_4}, which is lost as NO and N_2O depends on water saturation, pH and temperature (Johansson, 1984; Johansson and Granat, 1984; Slemr and Seiler, 1984, 1991). Respective factors are adapted from the biochemistry of the DNDC modules (Li *et al.*, 2000; Stange *et al.*, 2000). The amount of NO produced during the nitrification is given by

$$NO_{NH_4-NO} = a_{NH_4} \; f_{tm} \, f_{pH} \, K_{NO}$$

while the amount of soil N_2O produced during nitrification is given by

$$N2O_{NH_4-N2O} = a_{NH_4} \, f_{tm} \, f_{pH} \, K_{N2O}$$

where a_{NH_4} corresponds to the amount of available NH_4, f_{tm} to harmonic mean of temperature and moisture factors, f_{pH} to a pH factor, K_{NO} to the reaction rate for NO reductase and K_{N2O} accouunts for the reaction rate for N_2O reductase. The temperature and moisture and pH factors are different for NO and N_2O during the nitrification processes (Figure 3, Figure 4).

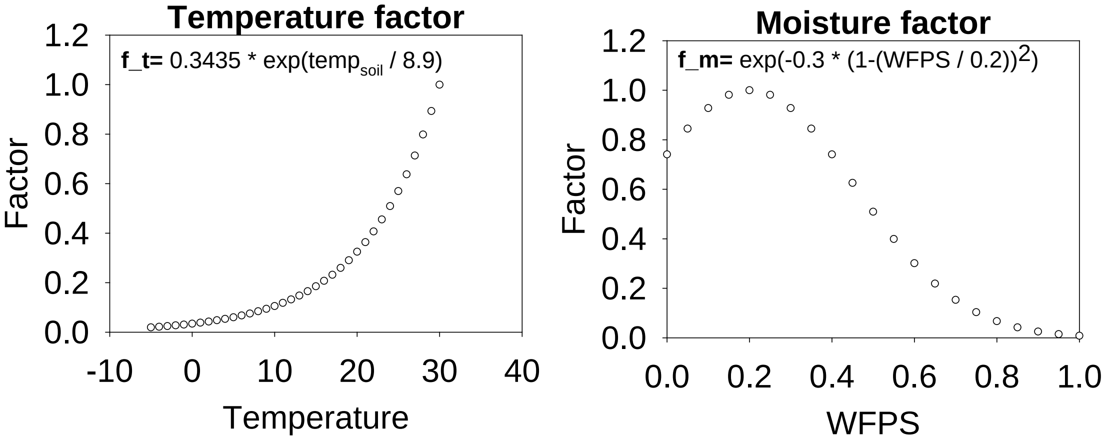

Figure 3 Temperature and moisture factors for NO emissions produced during nitrification

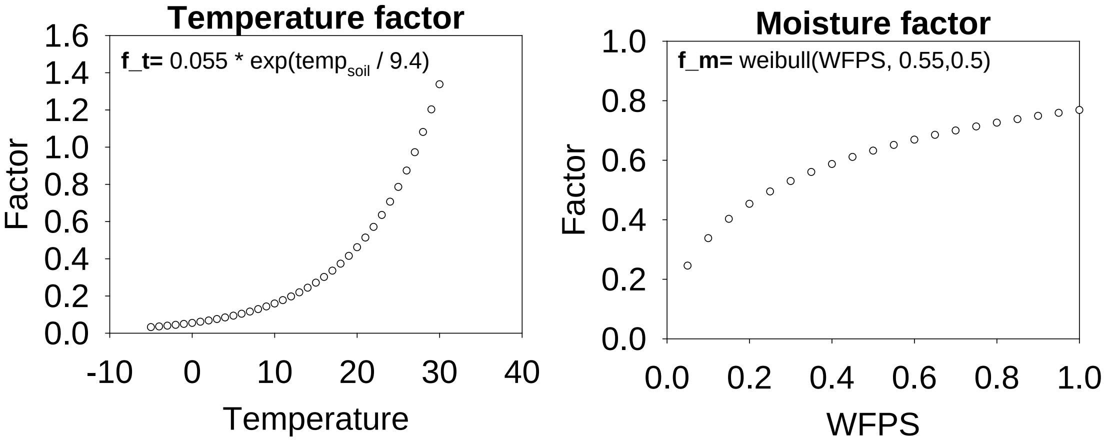

Figure 4 Temperature and moisture factor for N_2O emissions produced during nitrification step

Denitrification stands for the stepwise anaerobic reduction of NO_3^- to N_2 via the intermediate products NO_2^-, NO and N_2O:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Following the DECONIT approach denitrification of each substance is calculated proportional to its relative contribution. The underlying assumption is a supposed microbial usage priority for the most abundant substrate. The proportionality factor is given by denitrifier microbial growth and the harmonic mean of Michaelis-Menten reductions factors accounting for carbon and nitrogen availability:

$$r_i = \mu_{mic}\, c_{mic}\, a_{mic}\, f_{C,N} \frac{c_i}{c_{tot}}$$

In each reduction step a certain amount of denitrified nitrogen is directly released as N_2. The respective fraction depends on the pH value and the current size of the anaerobic volume. Decreasing oxygen availability leads to more complete reduction to N_2 whereas a decreasing pH value retards complete denitrification:

$$r_{N_x \rightarrow N_2} = 0.6 + 0.35\, AV - 0.5\, f_{pH}$$

A further source of NO emissions from soils by non-enzymatic process is the chemical denitrification or the chemodenitrification, i.e., the chemical decomposition of NO_2^- to NO. It occurs only when soil pH value is lower than 5.0. It was assumed that the main source of nitrite in soils is nitrification, since rates of nitrification in forest soils (200 –1000 kg N ha^{-1} y^{-1}) are usually higher than rates of denitrification (50 kg N ha^{-1} y^{-1}) (Barton *et al.*, 1999). Therefore chemodenitrification rates depend on soil pH, temperature, nitrification rates in the soil and a reaction rate factor for chemodenitrification.

$$r_{NO_2^- \to NO} = f_t \, K_{chemo} \, f_{pH} \, r_{NO_2}$$

3.2 Collection of data for site scale model validation

Within the Éclaire project, NO field observations have been conducted at nine sites across Europe. Due to incomplete data availability in the Eclaire database (3 out 9 sites have reported complete datasets necessary for the modelling) we have increased the data foundation for the validation to other sources such as e.g. the European fluxes database cluster (http://gaia.agraria.unitus.it/), IP NitroEurope and from the NOFRETETE project.

Forest ecosystems

The new soil module was applied for simulation of soil NO and N_2O emissions at 12 different forest stands including the dominating tree species across Europe (*Picea abies, Fagus sylvatica, Picea sitchensis, Betula pendula, Pseudotsuga menziesii and Quercus robur*). The area in which the stands are based is within a large latitudinal range representing Temperate and Mediterranean climatic conditions (Table 4). Mean annual temperature varied from 6.80 until 12.2 ^{o}C while annual precipitation ranged from 730 to 1500 mm. Similarly stand age was different in every single case. The youngest forest stand (31 years) corresponded to Glencourse-UK while the oldest forest was for the Austrian beech stand at Schottenwald (145 years). Atmospheric N deposition varied from 6.5 - 47 kg N ha-1 yr^{-1}. Humus type was moder except mull at beech forest of Hoeglwald, spruce forest at Achenkirchen and at the oak forest at Matrafuered. Data for model initialization regarding vegetation and soil properties (see details in Table 4) was obtained from publications (Kesik *et al.*, 2005), from the European fluxes database cluster (http://gaia.agraria.unitus.it/), IP NitroEurope and ECLAIRE databases and from the NORFRETETE project. Daily climate data for model driving as well as daily NO and N_2O flux measurements were obtained from the same aforementioned sources.

Arable and grassland ecosystems

For the model validation six arable and four grassland sites have been selected due to observation data availability (see Table 5). All studied systems are under intensive cultivation practices using synthetic fertilizers, farm yard manure and slurries as main N inputs (except at Bugac-Hungary and at the grassland site at Virginia-USA). The studied sites are located in the Central and Mediterranean part of Europe and at the north part of the American Continent. Properties of the studied sites are shown in Table 5. Model input data and measurements were provided by the IP NitroEurope and ECLAIRE databases as well as from previous work (Butterbach-Bahl *et al.*, 2009). The evaluation sites present different management regimes including the main commodity crops (maize, wheat, barley, rape seeds, etc). For details on management practices we refer to (Laville *et al.*, 2005; Venterea *et al.*, 2005; Ammann *et al.*, 2009; Butterbach-Bahl *et al.*, 2009; Loubet *et al.*, 2011).

Table 1 Mean site characteristics of studied forest ecosystems

Site/Country	Country Code_Site/tree specie	Forest type	Coordinates	Micrometereological conditions		Stand age	Annual N deposition (kg ha^{-1})	Organic layer		Mineral layer (5 cm depth)			
				Average temperature (ºC)	Mean Annual precipitation (mm)			Humus type	pH	soil type	clay (%)	pH	SOC (%)
Hoeglwald-Germany	DE_Hoeglwald_spruce	*Picea abies*	48°N 11°E	7.90	888	106	40.0	MODER	3.20	LOAM	19.00	3.50	2.90
Hoeglwald-Germany	DE_Hoeglwald_beech	*Fagus sylvatica*	48°N 11°E	7.90	888	120	40.0	MULL	3.00	SALO	19.00	3.70	5.10
Achenkirchen-Austria	AT_achenkirchen_spruce	*Picea abies*	47°N 11°E	6.80	1500	135	6.4	MULL	5.70	LOAM	19.00	7.00	7.70
Glencourse-United Kindom	UK_glencourse_sitka	*Picea sitchensis*	55°N 3°E	8.50	1000	29	10.5	MODER	4.20	SILO	18.00	4.20	7.00
Glencourse-United Kindom	UK_glencourse_birch	*Betula pendula*	55°N 3°E	8.50	1000	31	10.5	MODER	4.80	SILO	18.00	4.80	7.00
Speulderbos-Netherlands	NL_speulderbos_douglas	*Pseudotsuga menziesii*	52°N 5°E	10.40	769	53	47.0	MODER	3.70	SAND	3.00	3.70	9.00
klausenleopoldsdorf-Austria	AT_klausenleopoldsdorf_beech	*Fagus sylvatica*	48°N 16°E	8.20	804	65	10.0	MODER	5.20	SCLO	27.00	4.50	5.10
Schottenwald-Austria	AT_schottenwald_beech	*Fagus sylvatica*	48°N 16°E	10.10	940	145	31.0	MODER	5.00	SILO	18.00	4.20	6.80
Matrafuered-Hungary	HU_matrafuered_oak	*Quercus robur*	48°N 20°E	8.50	780	73	7.5	MODER	4.50	SALO	9.00	5.30	1.90
Matrafuered-Hungary	HU_matrafuered_spruce	*Picea abies*	48°N 20°E	8.50	780	45	10.3	MULL	5.70	SALO	9.00	5.30	3.60
Soroe_Denmark	DK_soroe_beech	*Fagus sylvatica*	48°N 16°E	8.70	730	90	28.4	MODER	4.30	LOSA	9.00	4.50	4.00
Ispra-Italy	IT_ispra_oak	*Quercus robur*	45°N 8°E	12.20	1300	65	13.5	MODER	4.20	SALO	11.00	4.20	8.20

Table 2 Mean site characteristics of studied arable and grassland systems

Site/Country	Code	Land use	Coordinates	Micrometereological conditions		Annual N deposition (kg N ha^{-1})	Mineral layer (5 cm depth)				Mineral layer (5 to 30 cm depth)		
				Average temperature (ºC)	Mean Annual precipitation (mm)		soil type	clay (%)	SOC (%)	pH	clay (%)	SOC (%)	pH
Grignon-France	FR_grignon	Arable	49°N 2°E	11.1	600	13.3	SILO	18.9	2.42	7.6	18.9	2.3	7.6
Virginia-United States of America	USA_virginia_maizwinbarley	Arable	37°N 77°W	14.9	582	26	LOAM	9	2	6.8	9	2	6.8
Virginia-United States of America	USA_virginia_soybeanmaiz	Arable	37°N 77°W	14.9	582	26	LOAM	9	2	6.8	9	2	6.8
Paris-France	FR_paris_wheat	Arable	49°N 2°E	11.5	565	14	CLLO	33	1.8	7.9	33	1.8	8
Colorado-United States of America	USA_colorado	Arable	40°N 104°W	9.2	392	7	SICL	41	0.8	7.2	41	0.8	7.2
Petrodolinskoe-Ukraine	UA_petrodolinskoe	Arable	46°N 30°E	10.3	700	18	CLAY	59	2.5	6.79	59	1.6	6.9
Oensingen-Switzerland	CH_oensingen_qa	Grassland	47°N 7°E	9.92	1250	9.2	SLCL	43	2.8	6.62	44	2	6.68
Bugac-Hungary	HU_bugac_extensive	Grassland	47°N 20°E	10.4	562	13	SLCL	13	5	7.3	13	4.3	7.3
Virginia-United States of America	USA_virginia_grass	Grassland	37°N 77°W	14.9	582	25	LOAM	9	2	6.8	9	2	6.8
Posieux-Switzerland	CH_posieux	Grassland	46°N 7°E	8.9	1075	8.5	LOAM	20	2.9	6.2	20	2.9	6.2

3.3 Model Parameterization

To improve the processes describing the soil carbon and nitrogen cycle a calibration of the process parameters was performed in order to optimize the prediction accuracy of the model. First a parameter sensitivity analysis for the new soil biogeochemistry module has been performed in order to identify the most sensitive parameters describing soil borne NO and N_2O emissions. In the next step parameter calibrations for different ecosystems including the available field observations of NO and N_2O emissions have been performed using a Bayesian Model Calibration method (BC) (Van Oijen *et al.*, 2005; Rahn *et al.*, 2012). The parameters addressed within the calibration are summarized in Table 1. The BC method has been proved to be a powerful approach to obtain very good optimized parameters sets for process-based models. Figure 5 illustrates the Metropolis algorithm for the Bayesian model calibration of the LandscapeDNDC soil biogeochemistry.

Table 3 The 15 most sensitive process parameters with respect to soil NO and N_2O emissions used for the calibration and Bayesian parameter uncertainty quantification

Symbol	**Description**	**Units**
CO_2_PROD_DECOMP	Factor of CO_2 production during decomposition	
F_DENIT_N_2O	Factor that regulates how much of the denitrified N goes to N_2 (directly)	
MUEMAX_C_DENIT	Microbial use efficiency for C consumption during de-nitrification	kg C d^{-1}
KF_NIT_N_2O	Factor reaction rate for N_2O reductase	
KMM_N_DENIT	Michaelis-Menten constant for N during denitrification	Kg N m^{-3}
AMAX	Maximal specific microbial death/reutilization rate	kg C d^{-1}
KR_HU_AORG	Humufication rate for heterotrophic microbial biomass	kg C d^{-1}
F_DENIT_NO	Factor of NO production during denitrification	
KMM_C_DENIT	Michaelis-Menten constant for C use during de-nitrification	Kg C m^{-3}
MUEMAX_C_NIT	Microbial use efficiency for C consumption during nitrification	kg C d^{-1}
KR_HU_HUM_1	Rate of Humufication of humus pool one	kg C d^{-1}
KR_DC_HUM_1	Rate of decomposition of humus pool one	kg C d^{-1}
KF_REDUCTION_ANVF	Reduction factor of the anaerobic volume fraction	
BIOSYNTH_EFF	Biosyntheis efficiency factor	
KR_DC_HUM_0	Rate of decomposition of humus pool cero	kg C d^{-1}

Performing four different Bayesian calibrations in parallel (Markov chains) for these parameter sets and using the convergence criteria of (Gelman and Rubin, 1992) a calibrated joint parameter distribution will be generated (Figure 6). This joint parameter distribution represents the posterior parameter distribution of the calibration, from where we sampled optimum sets for uncertainty quantification.

3. Results:

4.1 Model calibration

The Bayesian calibration resulted in a joint parameter distribution for the 15 most sensitive parameters (Figure 6). Model calibration was carried out for different sites using daily NO and N_2O measurement. Table 2 summarizes and Figure 5 illustrates the distribution of each parameter after the calibration.

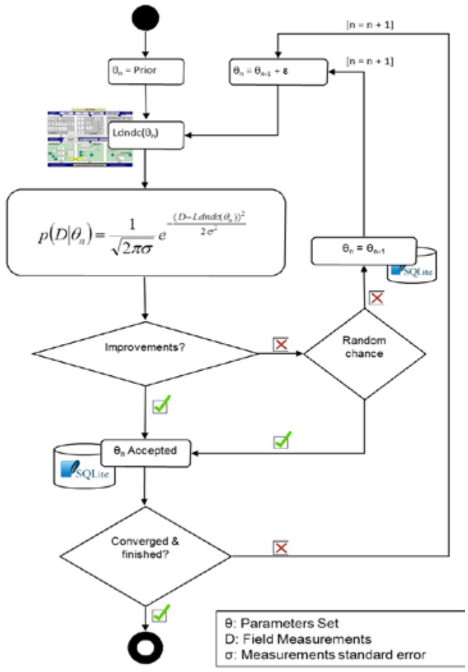

Figure 5 Metropolis algorithm for the Bayesian Calibration of the LandscapeDNDC soil biogeochemistry module following the approach of Van Oijen *et al.*, 2005, Rahn *et al.*, 2012.

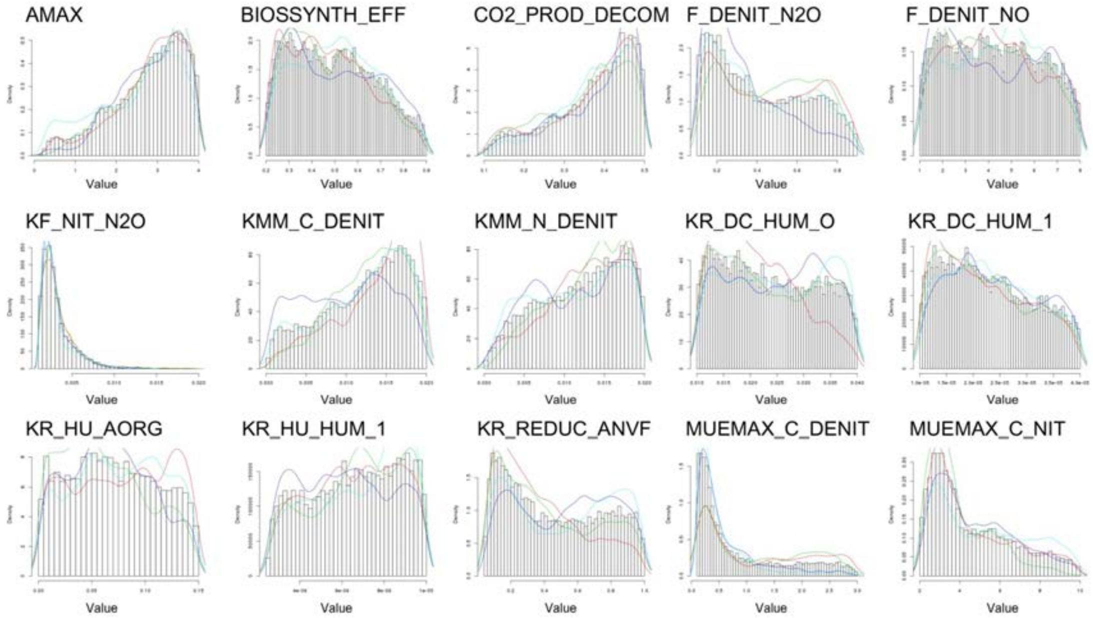

Figure 6 Joint parameter distributions resulting from the 4 parallel BC chains (indicated by the 4 coloured lines) after the conversion of the Markov-Chains was reached

The posterior parameter values were assigned uniform probability within their given ranges. The uncertainty of the prior parameter values (pre calibration model default values given with minimum and maximum values) were minimized considerably during the BC (e.g. see KF_NIT_N2O in Figure 6) while some parameters (like KR_HU_AORG, see Figure 6) did not reduce their uncertainty significantly. This parameter corresponds to the humification constant from heterotrophic microbes and it suggests that all values ranging from 0.001 to 0.15 present a similar probability. For this kind of parameter, uncertainty is not reduced by the BC method. Values exceeding 0.14 are less likely than the others.

4.2 Measured vs. simulated daily NO and N_2O emissions on site scale

The evaluation of the model performance to predict daily NO emissions was done based on commonly used model fitting indicators (Engeland *et al.*, 2010; Kiese *et al.*, 2011; Ritter and Muñoz-Carpena, 2013) such as the coefficent of determination (r^2), model efficiency (ME) and normalized root mean square prediction error ($RMPPE_n$). (Bouwman *et al.*, 2010) mentioned that r^2 values from model validation studies on daily time resolution are rarely reported for N_2O because model performance might be low and for validation of NO emissions model performance is in general even less precise. In our study the r^2 values indicate a fundamental good performance of the new calibrated process based module in LandscapeDNDC across the three different ecosystems.

Table 4 Summary of calibrated parameter values (default, minimum, maximum and optimized parameter value)

Parameter name	**default value**	**minimum**	**maximum**	**posterior**
CO_2_PROD_DECOMP	0.300	0.100	0.500	0.240
F_DENIT_N_2O	0.250	0.100	1.000	0.475
MUEMAX_C_DENIT	1.050	0.000	3.000	0.104
KF_NIT_N_2O	0.003	0.000	0.020	0.003
KMM_N_DENIT	0.083	0.000	0.020	0.019
AMAX	1.500	0.000	4.000	3.433
KR_HU_AORG	0.015	1.000	0.150	0.004
F_DENIT_NO	4.000	1.000	8.000	5.785
KMM_C_DENIT	0.002	0.000	0.020	0.010
MUEMAX_C_NIT	5.000	2.000	10.000	8.106
KR_HU_HUM_1	0.000	0.000	0.000	0.000
KR_DC_HUM_1	0.000	0.000	0.000	0.000
KR_REDUCTION_ANVF	0.200	0.000	1.000	0.278
BIOSYNTH_EFF	0.565	0.200	0.900	0.447
KR_DC_HUM_0	0.020	0.010	0.040	0.033

The best posterior parameter values obtained from the BC were applied for the arable, grassland and forest ecosystem simulations. Modelled soil NO and N_2O emissions were compared against high and low temporal resolution field data from semi-natural (forest) and cultivated lands (arable and grasslands) across Europe. This validation embraces also a model evaluation including short and long term data series which range from scattered point measurements up to continuous 15 years measurement campaigns. Table 3 summarizes the performance of the model to represent biogenic NO emissions. The evaluation on daily time scale results in r^2 values ranging from 0.01 to 0.79 while ME values ranged from - 3.42 to 0.67. $RMSPE_n$ values varied from 0.57 to 4.26 (Table 3). Measured mean soil NO flux per site was well simulated by LandscapeDNDC ($r^2= 0.92$, $p<0.05$, 3) (Figure 7). The best performance was seen for forest ecosytem ($r^2= 0.95$, $p<0.05$, comparing means of daily NO emission strengths, compare Figure 7) rather than for exploited lands $r^2= 0.82$, $p<0.05$. Slight model deviations were estimated for sites presenting high data resolution and long term measurements campaigns (i.e. Höglwald-Germany, Speulderbos-Netherlands, Grignon-France, Oensingen- Switzerland) while a higher deviation was seen for sites having scatter measurement points (i.e Matrafuered-Hungary, Virginia-United States, Klausenleopoldsdorf-Austria). Scattered measurements made it very difficult to value the performance of the model to represent soil NO fluxes. For example, the number of measurement points at the oak forest at Matrafuered-Hungary was 4000 times lower than the ones at the spruce forest of Höglwald-Germany. We observed that the model performed very well for sites having high resolution datasets (Table 3, Figure 8, Figure 9, Figure 10) rather than for the ones having few points (i.e. Figure 11). For this reason there is a strong need to support long term field experiment that analyse processes on the ecosystem scale (C, N and water cycles). This will guarantee a better representation of processes associated to NO production and will improve future modelling work.

Table 5 Summary of the performance of model simulations for validation of soil NO emissions

Site	number of obsvs.	Measured-mean NO (g N ha^{-1} d^{-1})	Stdev. mean NO (g N ha^{-1} d^{-1})	Simulated mean NO (g N ha^{-1} d^{-1})	r^2	ME	RPMSEn
DE_Hoeglwald_spruce	4382	24.03	3.09	22.5	0.31	0.03	0.99
DE_Hoeglwald_beech	1414	6.8	2.05	7.74	0.23	-0.15	1.07
AT_achenkirchen_spruce	254	0.14	NA	0.1	0.04	-1.50	1.58
UK_glencourse_sitka	358	6.21	1.18	5.67	0.15	0.01	1
UK_glencourse_birch	373	0.46	0.45	1.34	0.01	-1.25	1.5
NL_speulderbos_douglas_2006-2009	729	8.61	0.33	11.59	0.66	0.21	0.89
NL_speulderbos_douglas_2002-2003	341	18.78	1.11	15.02	0.76	0.67	0.58
AT_klausenleopoldsdorf_beech	63	0.17	NA	0.99	0.07	-2.50	2.35
AT_schottenwald_beech	240	4.63	NA	3.38	0.00	-0.73	1.31
HU_matrafuered_oak	4	0.58	0.24	1.59	0.55	-1.18	2.9
HU_matrafuered_spruce	19	0.38	0.32	1.93	0.79	-2.19	4.26
DK_soroe_beech	730	0.65	0.38	1.73	0.02	-3.43	2.1
IT_ispra_oak	154	5.44	3.48	4.6	0.65	0.54	0.68
FR_grignon	412	1.82	1.23	1.54	0.32	0.26	0.86
USA_virginia_maizwinbarley	30	9.44	6.82	5.2	0.02	-0.60	1.24
USA_virginia_soybeanmaiz	26	3.06	1.03	0.77	0.01	-2.25	1.77
FR_paris_wheat	42	6.49	1.53	3.9	0.00	-0.68	1.28
USA_colorado	10	2.54	1.29	1.78	0.28	-0.13	1.01
UA_petrodolinskoe	354	1.17	0.54	1.28	0.19	0.17	0.91
CH_oensingen_qa	361	1.28	1.16	1.78	0.11	-0.02	1.01
HU_bugac_extensive	1291	2.98	NA	1.5	0.05	-0.05	1.02
USA_virginia_grass	23	3.02	NA	2.1	0.02	-0.72	1.28
CH_posieux	103	0.55	NA	0.78	0.02	-1.88	1.69

A comparison of the new versus the default soil biogeochemistry module (the default module is based on a generalization of the DNDC soil biogeochemistry process description) to capture soil NO emissions is displayed in Figure 7. The inter-comparison indicates that the default module underestimated NO emissions by up 50% for forest ecosystems. For arable and grassland ecosystems, NO emissions were underestimated to a greater extent (see small values at Figure 7, b).

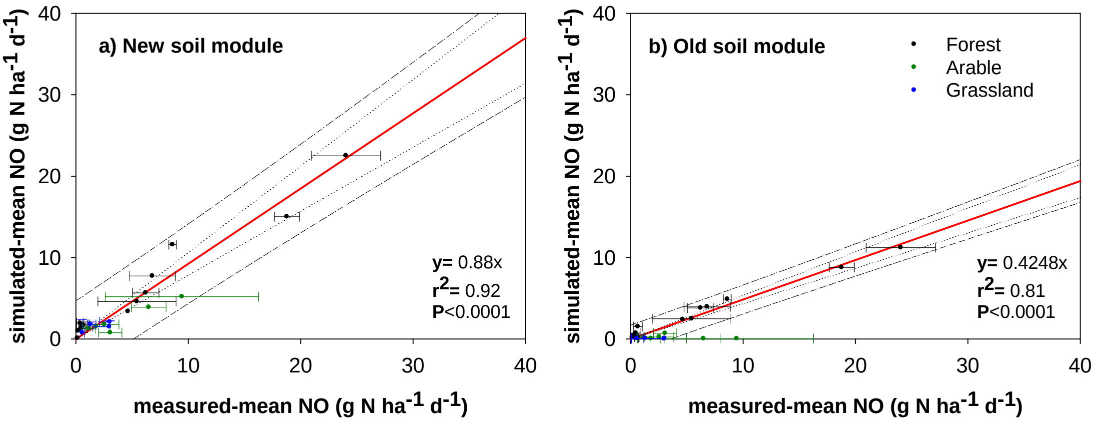

Figure 7 Comparison of the new developed versus the default soil biogeochemistry modules on the prediction of daily mean NO emissions. Data shown are means of paired data of daily simulated / observed NO emissions. As for some observations the number of observations is coarse, the data shown does not present yearly averages.

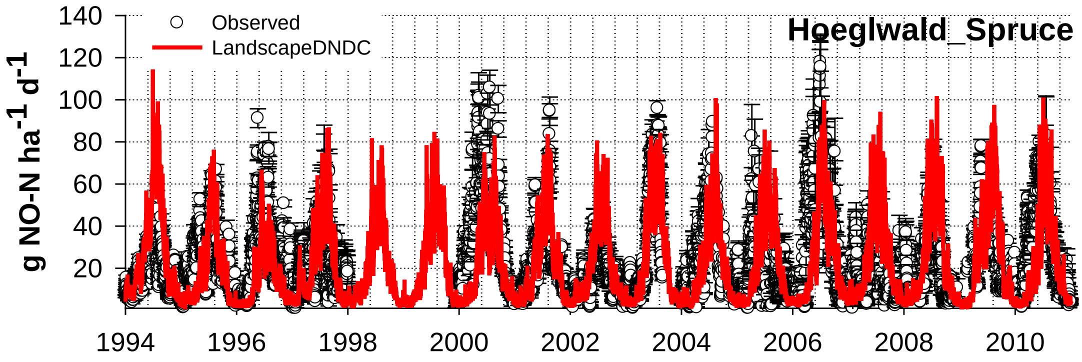

Figure 8 Daily NO emissions from a spruce forest (Höglwald, Germany)

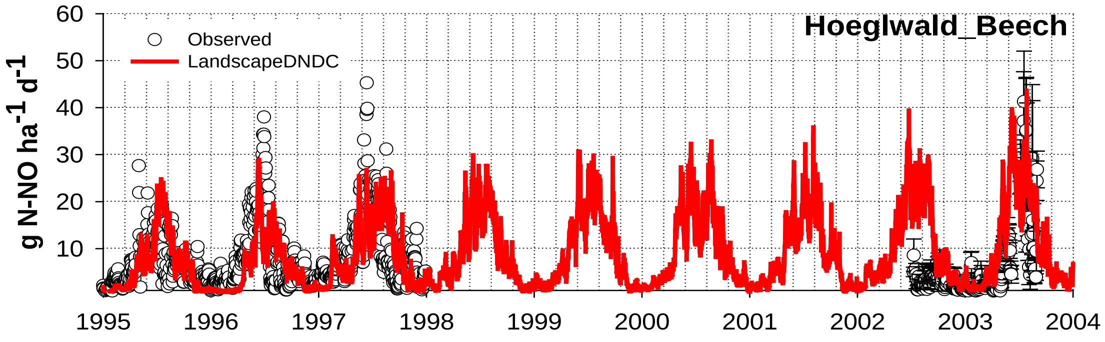

Figure 9 Daily NO emissions from a beech forest (Höglwald, Germany)

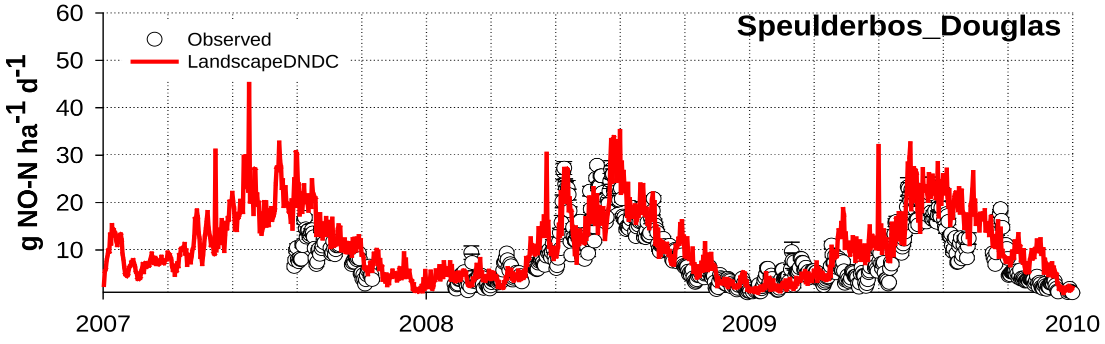

Figure 10 Daily NO emissions from a Douglas forest (Speulderbos, Netherlands)

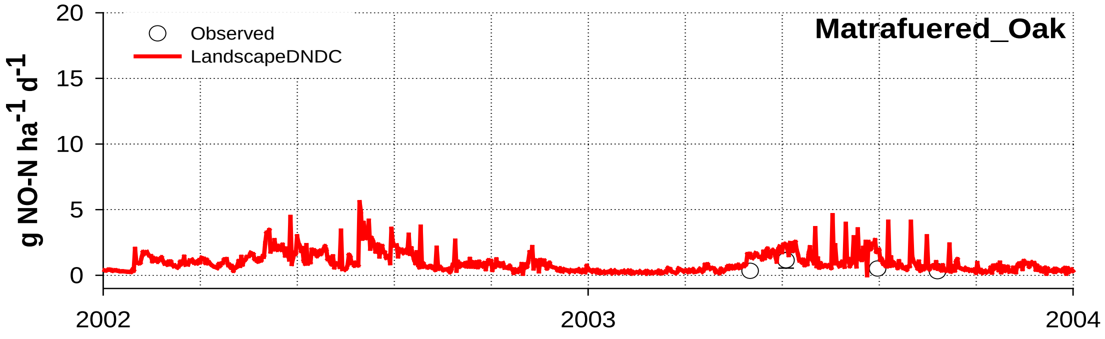

Figure 11 Daily NO emissions from an oak forest (Matrafuered, Hungary) with very scarce observation data resolution

In general, the model predicted successfully the inter-annual variations of the simultaneous emission patterns for biogenic NO and N_2O emissions which was the main task of our work. Outstandingly, the parameterization work improved the capability of the model to predict NO and N_2O emissions from managed ecosystems. For forest ecosystem, Figure 8 and Figure 12 show the simulated daily NO and N_2O emissions of a spruce forest in Germany and the model is capable of predicting both trace species simultaneously very well when comparing them to the high resolution observations. This was also true for the Douglas and Beech forests in the Netherlands (Figure 10 and Figure 13) and Denmark (Figure 14 and Figure 15). Model deviation for NO and N_2O was determined during winter seasons at the spruce forest in Germany. This might correspond to missing processes in the model such as e.g. the impact of freeze thaw events (de Bruijn and Butterbach-Bahl, 2010). During the wintertime, the model simulates soil temperature neglecting the influence of solar radiation and is therefore not able to distinguish between sunny and cloudy conditions.

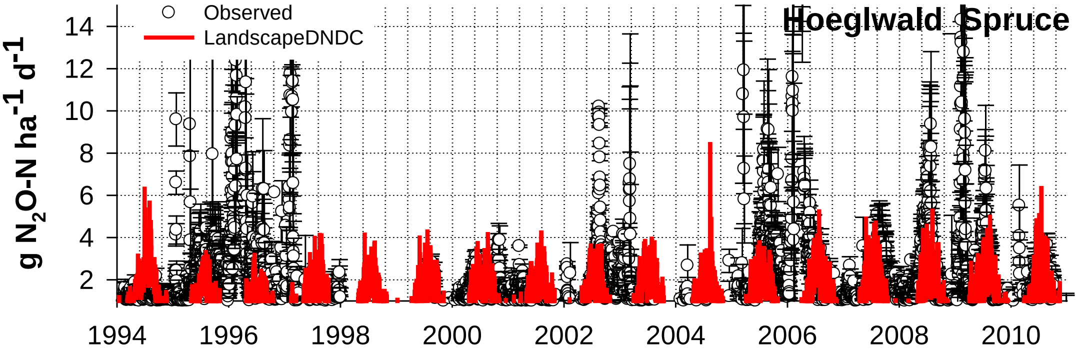

Figure 12 N_2O emissions from a spruce forest (Höglwald, Germany)

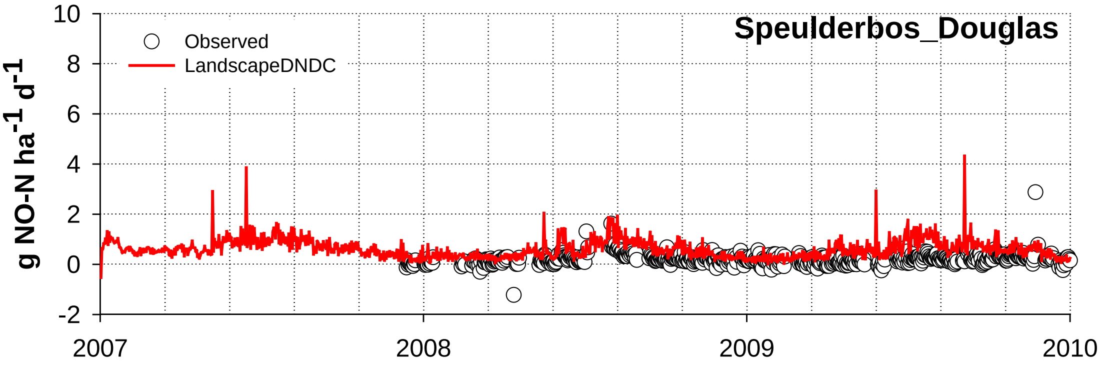

Figure 13 Daily N_2O emissions from a Douglas forest (Speulderbos, Netherlands)

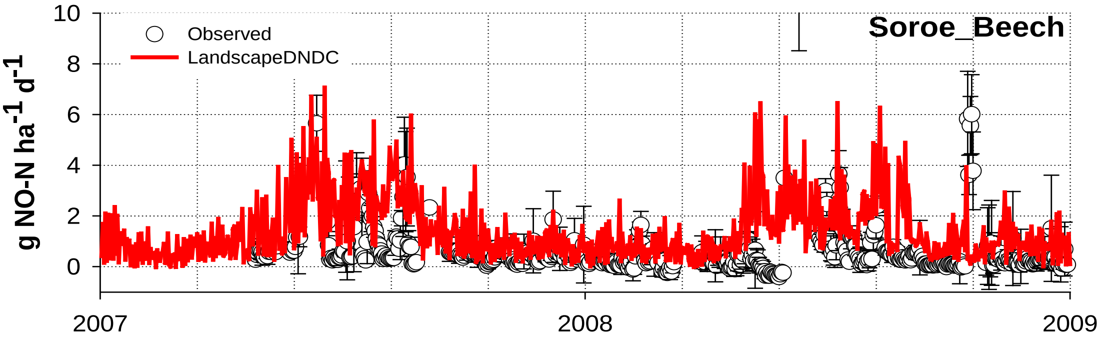

Figure 14 Daily NO emissions from a Beech forest (Soroe, Denmark)

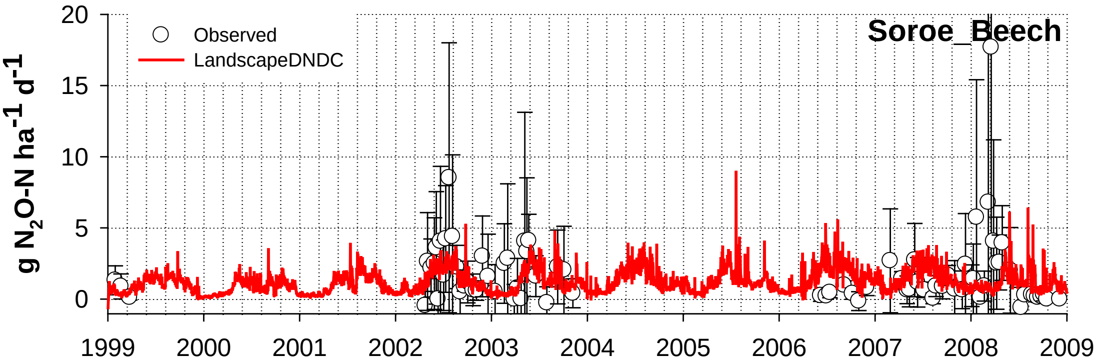

Figure 15 Daily N_2O emissions from a Beech forest (Soroe, Denmark)

High correlation between measurements and ecosystem properties such as soil pH values were determined. Figure 16 illustrates the correlation of soil NO emissions and the average soil pH value (organic layer and mineral soil) across different forest ecosystems across Europe. The high NO emissions for low pH values result mainly from chemo-denitrification. The atmospheric N deposition provides substrate for the microbial nitrogen cycle in the soil (see Figure 17) and via mineral nitrogen availability and it triggers microbial and chemical nitrogen transformation processes in the soil. Figure 17 illustrates the correlation between the N deposition and the NO emission which is therefore only indirect via the substrate availability respectively the N limitation of the system.

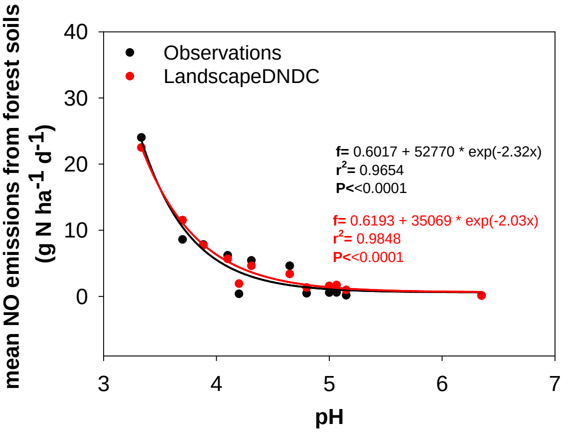

Figure 16 Correlation of mean NO emission and soil pH value

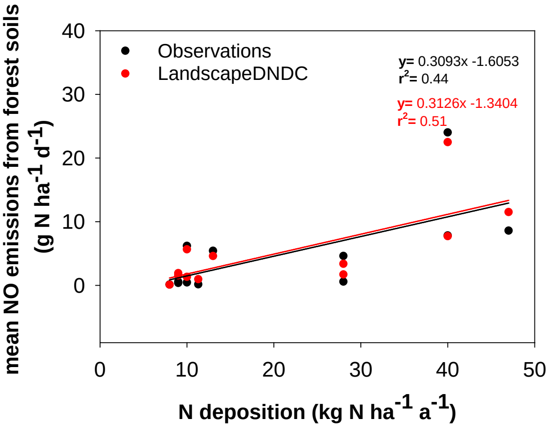

Figure 17 Correlation of mean NO emissions and N deposition rates

For forest ecosystem, the validation study found the main source for soil NO emissions was the chemodenitrification process and it was driven by low soil pH values of the topsoil. Figure 18 shows the partition of the NO produced during microbial and chemical processes. Nitrogen availability also plays a role but the pH value dictated the magnitude of the NO fluxes. For example the amount of N deposition at the spruce and beech forest of Höglwald is the same (40 kg N ha^{-1} a^{-1}, in Figure 8 and Figure 9) however the pH is much lower at the spruce stand. This indicates that vegetation cover type drives the chemistry in soil affecting pH and thus soil biogenic emissions.

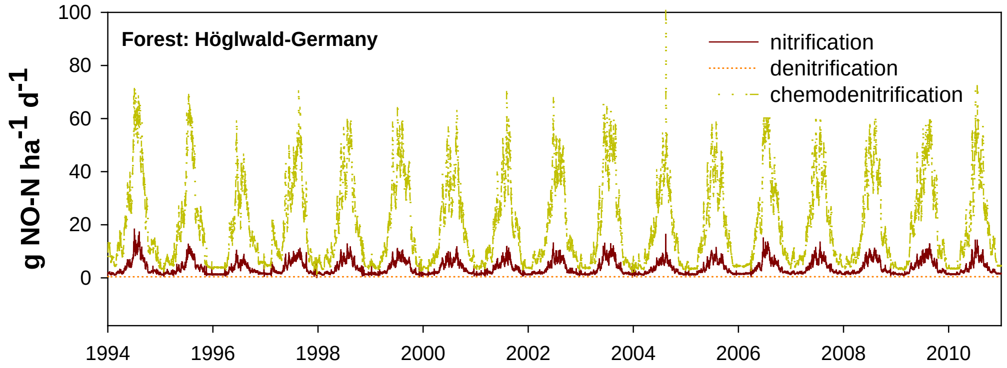

Figure 18 Sources of soil NO production from a spruce forest (Höglwald, Germany)

When focusing on arable systems, the abrupt availability of ammonium and nitrate throughout fertilization is governing the budget of soil NO and N_2O emissions, which can be demonstrated in Figure 19 and Figure 20. LandscapeDNDC is capable of predicting the diurnal pattern of soil NO and N_2O emissions with good agreement compared to the observations. The model captures the emission peaks well within the uncertainty of the observations.

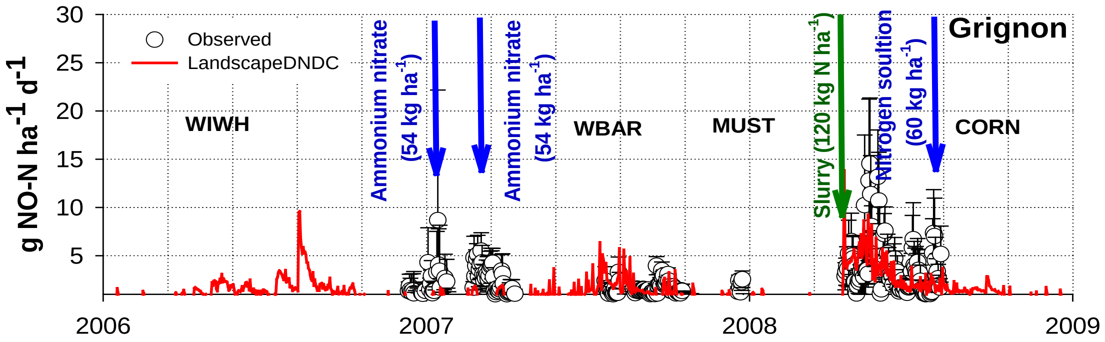

Figure 19 Daily NO emissions from arable soils at a research site close to Paris (Grignon, France)

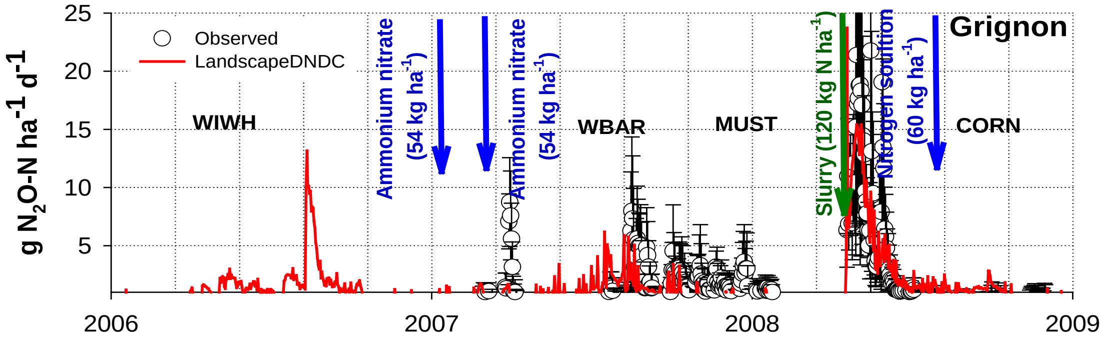

Figure 20 Daily N_2O emissions from arable soils (Grignon, France)

Performing an uncertainty quantification from the results of the BC by sampling parameters sets out of the joint parameter distribution and evaluating the model predictions for all sampled parameter sets (up to hundreds of site simulations) will result in uncertainty ranges of predicted NO and N_2O emissions when statistically analysing (see example Figure 25 and Figure 22). The uncertainty ranges for the predicted NO and N_2O emission strengths for all validation sites will be evaluated (publication in preparation).

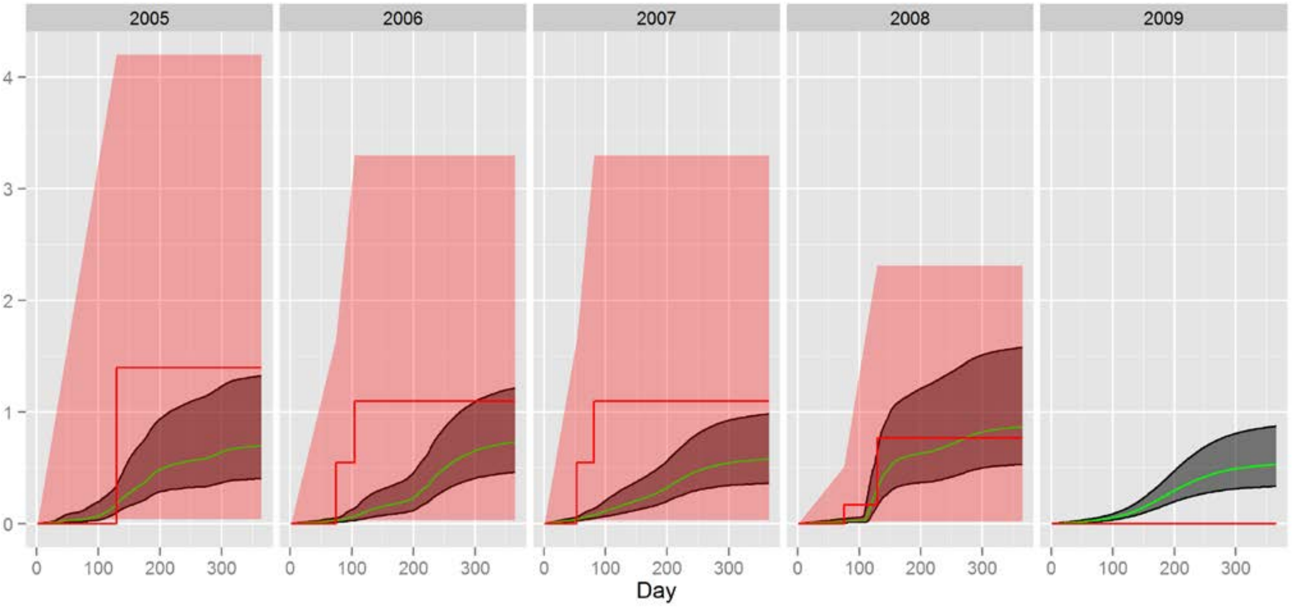

Figure 21 Uncertainty range in simulated soil N_2O emissions [kg N-N_2O / ha] for the Grignon-France site as resulting from the BC. Green line: median, black lines: 25 and 75 percentile, grey area: estimated uncertainty range, red line: N_2O emission estimated via IPCC direct N_2O EF (1.0 %), red area: IPCC uncertainty range for IPCC N_2O emission estimate. (For 2009, no N Fertilizer data was available)

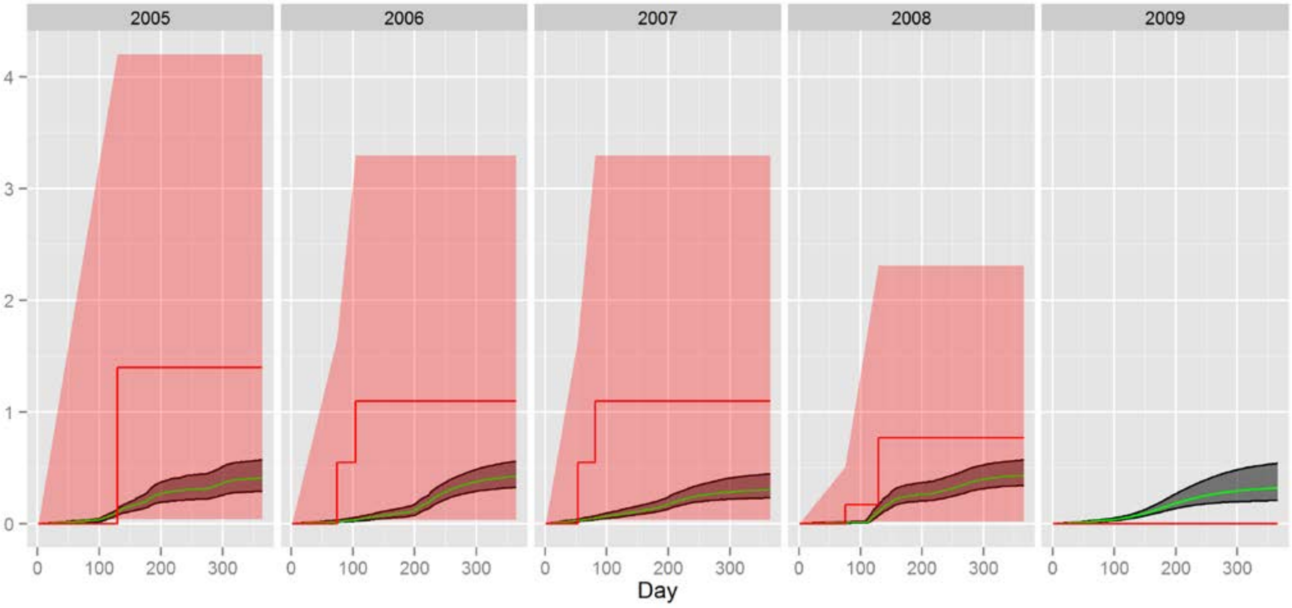

Figure 22 Uncertainty range in simulated soil NO emissions [kg N-NO / ha] for the Grignon-France site as resulting from the BC. Green line: median, black lines: 25 and 75 percentile, grey area: estimated uncertainty range, red line: NO emission estimated via IPCC direct NO EF (1.0 %), red area: IPCC uncertainty range for IPCC NO emission estimate. (For 2009, no N Fertilizer data was available)

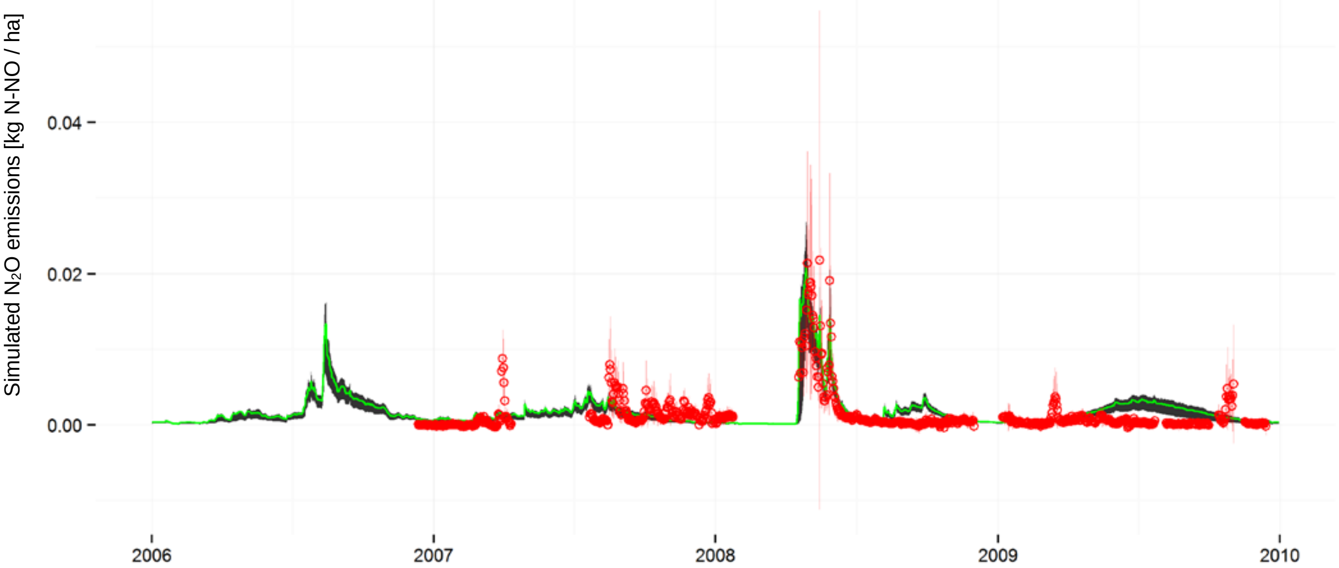

Figure 23 Simulated N_2O emissions [kg N-N_2O / ha] including the uncertainty bands resulting from the BC. Green line: median, black lines: 25 and 75 percentile, grey area: estimated uncertainty range, red circles: field measurements and measurement errors

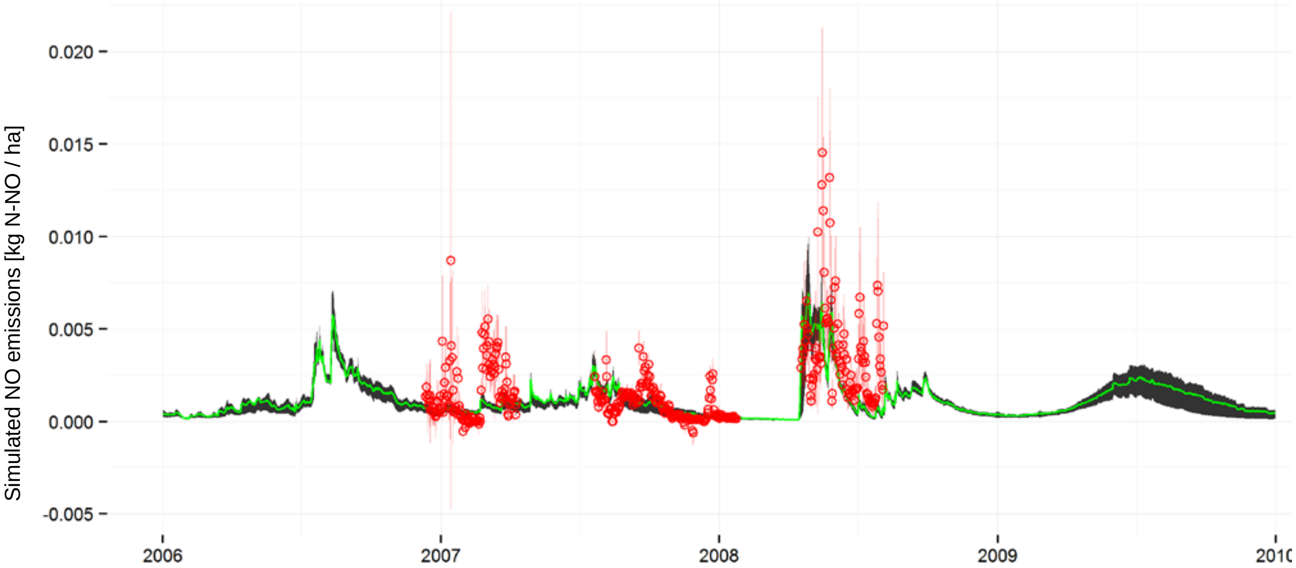

Figure 24 Simulated NO emissions [kg N-N_2O / ha] including the uncertainty bands resulting from the BC. Green line: median, black lines: 25 and 75 percentile, grey area: estimated uncertainty range, red circles: field measurements and measurement errors

Managed grassland ecosystems (i.e. intensive vs. extensive) are dominated by anthropogenic management practices determining the emission patterns of soil NO emissions. The model is able to simulate the NO and N_2O emission pulses following N fertilization (mineral and organic N) well within the uncertainty of the observations (Figure 25 and Figure 26): This was also true for sites under extensive management practices (Figure 27 and Figure 28). Discrepancies in low agreement of NO emissions with observations can result from uncertainties in the reported agricultural management and the resulting substrate availability in the soil. Parameter calibrations resulted in a well-balanced nitrogen cycle capable to resolve most of the NO emission pulses while maintaining the background emission patterns as well.

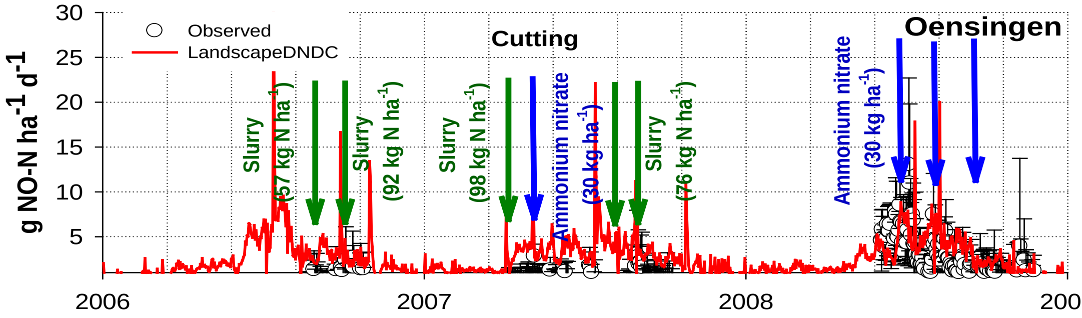

Figure 25 Daily NO emissions form managed grassland ecosystems (Oensingen Switzerland)

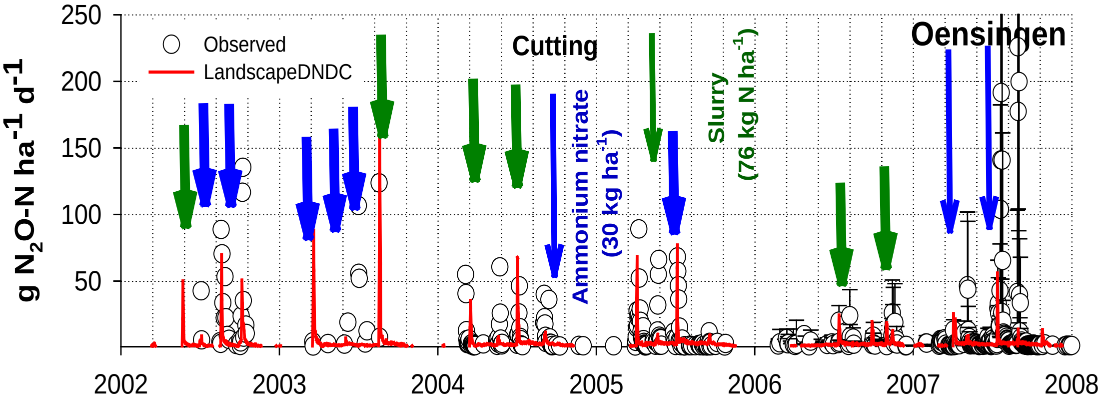

Figure 26 Daily N_2O emissions form managed grassland ecosystems (Oensingen Switzerland)

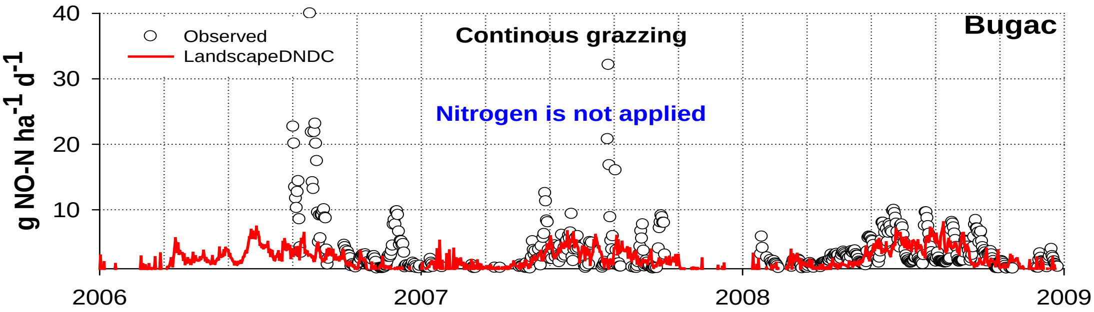

Figure 27 Daily NO emissions for managed grassland ecosystems (Bugac, Hungary)

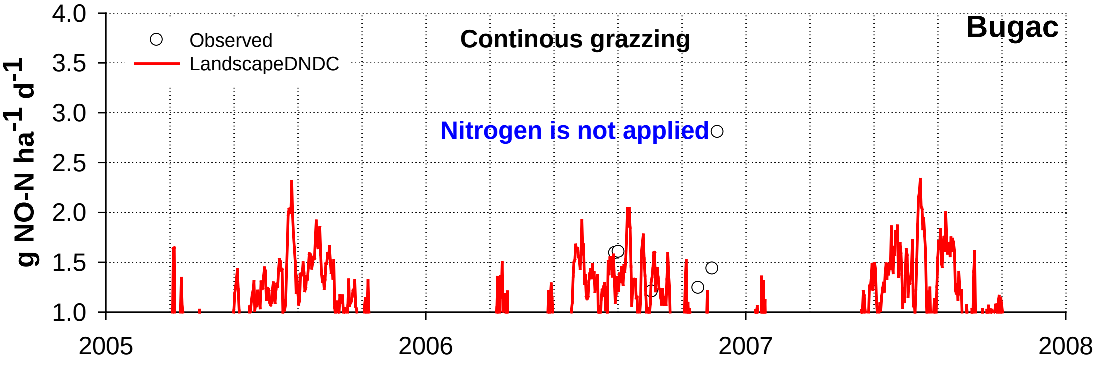

Figure 28 Daily N_2O emissions for an extensively managed grassland ecosystem (Bugac, Hungary)

NO emissions from cultivated lands were mainly produced during nitrification and denitrification (Figure 29). The effect of chemodenitrification was null since pH values exceed 6.0 for arable and grassland ecosystems Table 5.

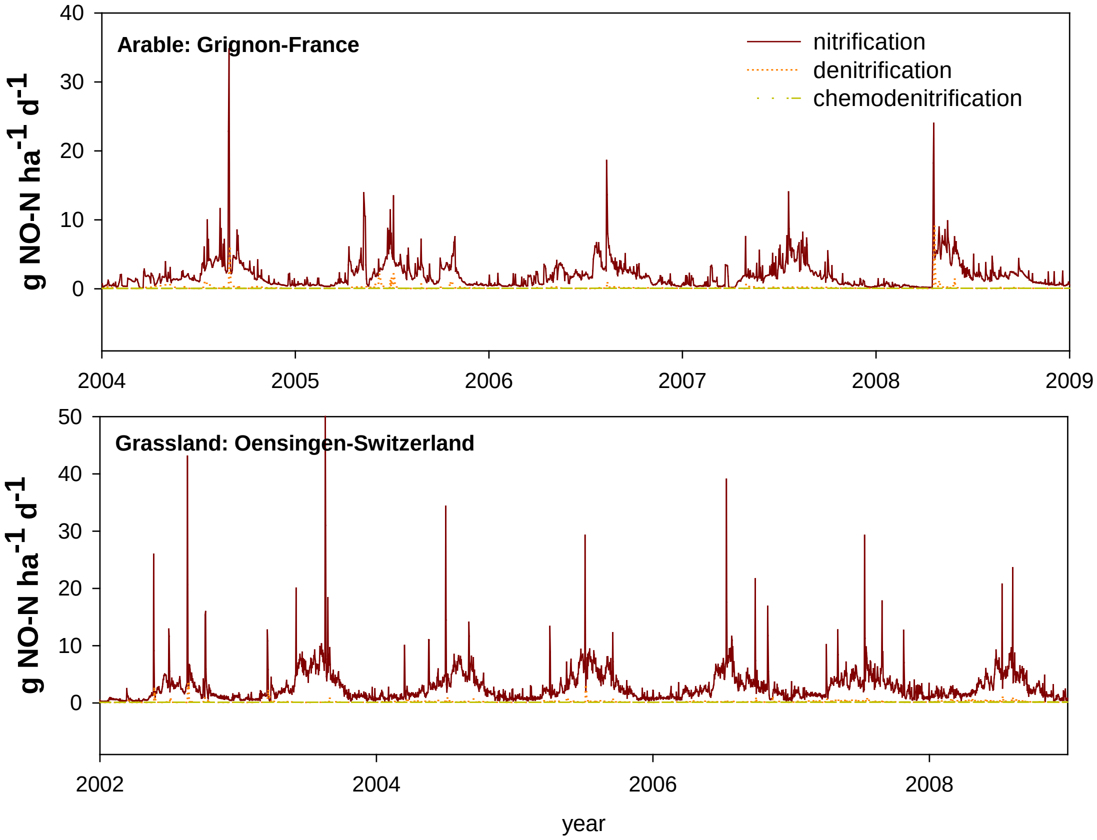

Figure 29 Sources of soil NO production and emission for three different ecosystem types

4.3 Regional scale simulations

LandscapeDNDC has been developed in recent years in order to be deployed on the site as well as at the regional scale and to take advantage of parallelism when running simulations on high performance computing systems. The model framework is ready to be used on the regional scale for assessments of soil NO and N_2O emissions.

LandscapeDNDC will be used with Éclaire in WP 6 for the assessment of soil NO and N_2O emissions from agricultural systems across Europe. This work is still in progress (due to a delay caused by the quality assurance of the regional input data of agricultural management at the EU scale).

The model capabilities for simulating regional emission strengths was proven instead for a test case simulating soil NO and N_2O emissions from arable soils for the federal state of Saxony, Germany (4400 polygons, 3 crop rotation, results averaged across the crop rotation, see Figure 30 and Figure 31). The application of the new parameterization for modelling N_2O emissions for the State of Saxony yielded fluxes within the uncertainty range (1.43 ± 1.25 SD kg N ha^{-1} a^{-1}) estimated by Klatt et al, 2014. The former author also applied the standard 2006 IPCC EF approach with mean direct N_2O emissions of 1.51 kg N ha^{-1} a^{-1}. With regard to arable soil NO emissions our simulations are in agreement with past studies (Yienger and Levy, 1995).

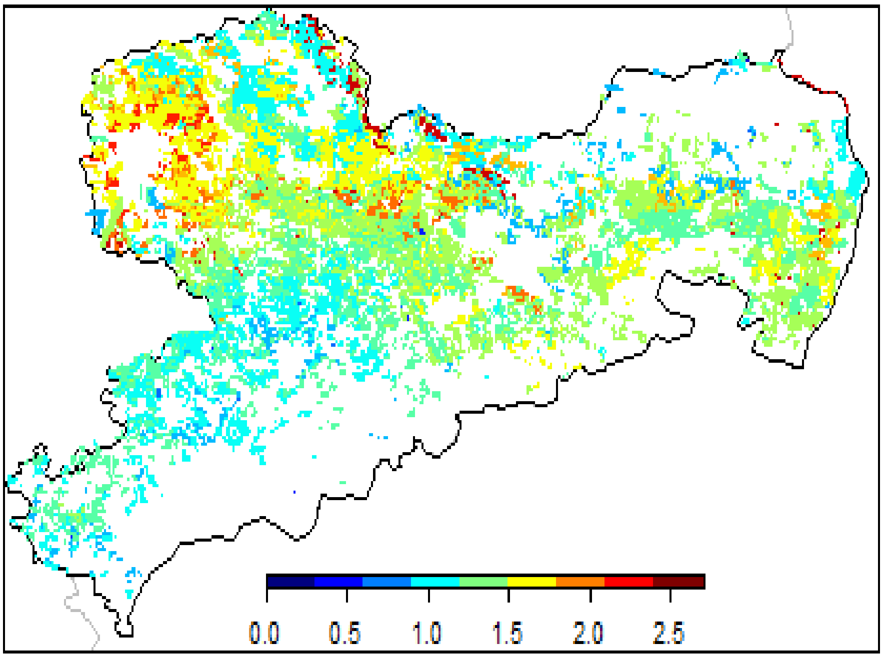

Figure 30 Soil N_2O emissions from arable, mean N_2O emissions: 1.08 kg N ha^{-1} a^{-1}

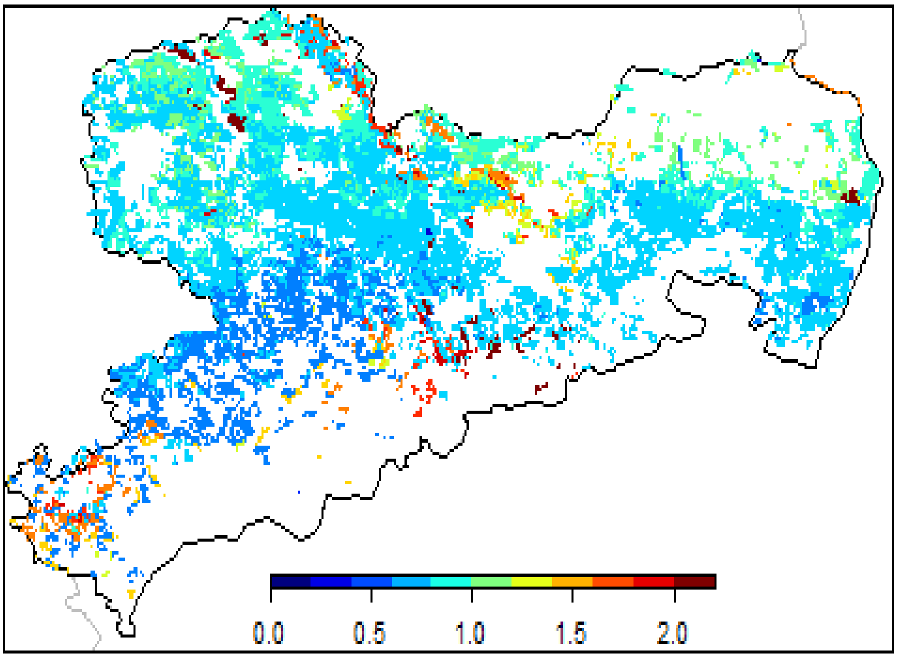

Figure 31 Soil NO emissions from arable, mean NO emissions: 0.63 kg N ha^{-1} a^{-1}

4. Milestones achieved:

The milestones associated to this task were:

- MS11 Workshop for summarizing state of the art of the different models (modules and to outline in detail the upcoming developing work and strategies for model uncertainty assessment (joined action with WP1.4)) to gather Eclaire experts on processes of litter decomposition and resulting NO and NH3 emissions.
  The Milestone MS11 was achieved and reported.

- MS13 Provision of site based estimates of NH3/NO and VOC exchange for ÉCLAIRE core sites for present and future environmental conditions.
  The Milestone MS13 is partly achieved with the work reported in this manuscript. The publication of the task outcome will contain emission estimates for the core sites for present and future environmental conditions. The milestone MS13 will be reported to the ECLAIRE website as soon as the manuscript is prepared.

5. Deviations and reasons:

The deliverable was delayed. Delays occurred due to delays in other deliverables, the results of which were needed to fulfil this deliverable. In detail, the results of the deliverable D2.2 provided essential results necessary for the calibration of the LandscapeDNDC model. D2.2 was delayed until month 36.

Measurement site data was needed to setup model simulations for the sites for the validation of the LandscapeDNDC model. To make progress with the work we have used all relevant data available from the ECLAIRE database in Month 37 and other available datasets. A manuscript is being prepared on the model validation study and this work will include any further data in the ECLAIRE database at its time of submission (anticipated for Q1/2015).

6. Publications:

Accepted publications:

1. Kraus D, Weller S, Klatt S, et al. (2014) A new LandscapeDNDC biogeochemical module to predict CH_4 and N_2O emissions from lowland rice and upland cropping systems. Plant Soil 1–25. doi: 10.1007/s11104-014-2255-x
2. Klatt Steffen, Kraus David, Rahn Karl-Heinz, Kiese Ralf, Butterbach-Bahl Klaus, Werner Christian and Haas Edwin (2014) Parameter-induced uncertainty quantification of regional N_2O emissions and NO_3 leaching using the biogeochemical model LandscapeDNDC, accepted for publication in ACSESS Books, Manuscript ID: ACSESS-2013-0001-MAV.R1, Book in print

Publications under review:

3. A modelling study on mitigation of N2O emissions and NO3 leaching at different agricultural sites across Europe using LandscapeDNDC, manuscript under review, manuscript number: STOTEN-D-15-03856, submitted at the 10th of September 2015 to the Journal “Science of the Total Environment”

Publications in preparation:

4. Validation of the MeTri^x soil biogeochemistry module of LandscapeDNDC for prediction of soil NO and N2O emissions and NO3 leaching from different ecosystems and sites across Europe, manuscript in preparation to be submitted in Q3 2015
5. Assessment of regional biogenic versus anthropogenic nitric oxide emissions for the state of Saxony Germany, manuscript in preparation to be submitted in Q3 2015

7. Meetings:

Edinburgh spring 2014

- Milestone MS11
  Meeting with experts from Éclaire on the process of litter decomposition of various ecosystems and resulting NO and NH3 emissions.

8. List of Documents/Annexes:

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