Article (refereed) - postprint

Machon, Attila; Horváth, László; Weidinger, Tamás; Grosz, Balázs; Moring, Andrea; Führer, Ernő. 2015. **Measurement and modeling of N balance between atmosphere and biosphere over a grazed grassland (Bugacpuszta) in Hungary.** *Water, Air, & Soil Pollution*, 226 (3), 27. 19, pp. 10.1007/s11270-014-2271-8

Measurement and modeling of N-balance between atmosphere and biosphere over a grazed grassland (Bugacpuszta) in Hungary

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Abstract – This work is a synthesis of a 5-year estimation of nitrogen-balance at a semi-arid, semi-natural, undisturbed grassland site (Bugac). We measured the N input of atmospheric pollutants by wet and dry deposition of gases and aerosols whilst we considered N output as NO, N_2O gases volatilized from soil. Beside measurements of soil fluxes the denitrification-decomposition (DNDC) ecological model was also used and simulations were compared to and validated against the measured values. The daily flux simulations generally did not match well the measured data for N_2O and NO. In most cases the mean fluxes were underestimated, though results of the comparison of monthly values suggest that model data, together with observed deposition data, are applicable to estimate the net N-balance for grasslands. The calculated yearly N-balance (net flux) between atmosphere and surface, without biological fixation and effect of grazing ranged between –9.4 and –14 kg N $ha^{-1}year^{-1}$ as the sum of the measured deposition and emission terms: –11 to –15 and 0.9-2.9 kg N $ha^{-1}year^{-1}$, respectively, between 2006 and 2010. Observed and modeled soil emissions were lower by one order of magnitude than atmospheric deposition. Considering the biological nitrogen fixation and the effect of grazing (effects of both grazed plant and excreta) the net nitrogen balance varies within –6.6 and –11 kg N $ha^{-1}year^{-1}$. It seems - taken into account the high uncertainty in calculation due to the effect of grazing - that sources of nitrogen exceed the sinks; the surplus is probably mineralized in the soil.

Keywords: nitrogen exchange, deposition, soil emission, denitrification, DNDC model, grassland

1. Introduction

Among elements nitrogen (N) has one of the most complex biogeochemical cycles. It is mostly affected by human activities both directly and indirectly resulting in altered concentration, distribution and flux of reduced and oxidized N species (Erisman et al. 2011). Anthropogenic emissions of reactive N compounds have a direct and manifold impact on N cycle. The released compounds undergo numerous sequences of transformations in the atmosphere and water as well as soil ecosystems until they are immobilized or de-nitrified to nitrogen gas (N_2); this system of processes is termed as N cascade (Galloway et al. 2003). The indirect impact of human activities further complicate the cycle of N species through affecting metabolic processes of animals, plants, and a large variety of microorganisms. Depending on the lifetime of various N compounds - from hour to hundred years - their environmental impacts can range from local direct damage to climate change (Galloway et al. 2003; Moldanová et al. 2011).

Due to the complexity of N cycle many transformation processes and influencing factors have not been completely explored yet. However, it is essential to monitor them to determine the rate of pollutant emissions and the harmful effects in current and future context. There are some synthesis studies of N cycles on continental and global scale (Erisman et al. 2003; 2010; Galloway et al. 2003; Vitousek et al. 1997); nevertheless, the uncertainty in estimation of N-balance and emissions from vegetation remains high because of the relatively sparse number of available, appropriate (both lab and field) measurements.

The N-balance of non-intensively managed ecosystems is dominantly determined by atmosphere-surface exchange processes. For non-fertilized grasslands, atmospheric deposition is the main source of N (Machon et al. 2011), but we also have to consider the N fixation by legumes (Ammann et al. 2009). On the other hand, a significant amount of N compounds is emitted by the biosphere. For some compounds (e.g. for ammonia) the exchange is bi-directional (e.g. Sutton et al. 2001; Zhang et al. 2010). In this case the sum of deposition and emission rates is called as net flux.

Several N compounds (e.g.: nitrogen dioxide (NO_2), nitric acid vapor (HNO_3), ammonium (NH_4^+) and nitrate (NO_3^-) ions in fine and coarse mode of particle phase) have only negative flux (deposition) from atmosphere to the ecosystems, i.e. they are not released by soil and vegetation (Watt et al. 2004; Wesely and Hicks 2000). Atmospheric gases and particles are deposited in two ways to the surfaces, partly by precipitation (wet deposition) during cloud formation and below cloud scavenging, and partly by turbulent flux onto the plants and soil surface (dry deposition) (Erisman et al. 2005). In general, the rate of dry are wet deposition in grasslands is in the same magnitude in Hungary (Kugler et al. 2008; Machon et al. 2011).

N compounds are emitted partly by soil and stomata of plants. Nitrogen has different forms in soil with wide-range of oxidation number from NH_4^+ (–3) to NO_3^- (+5). Nitrification and denitrification processes fundamentally affect the soil N-balance (Robertson and Groffman 2007), through producing intermediate gases as nitric oxide (NO), nitrous oxide (N_2O) and elemental N_2. All of those can be emitted to the atmosphere. By vegetation N compounds are emitted dominantly as ammonia gas (NH_3) (Horváth et al. 2005; Massad et al. 2010). Ammonia emission from soil can be observed as well but only for alkaline soils. The role of NH_3 gas in the troposphere, the dynamics of exchange (Massad et al. 2010), as well as its role in N load and in nutrient supply and other aspects of NH_3 in ecosystems are well known (Sutton et al. 2008; 2011).

Trace gas exchange within surface-biosphere-atmosphere system strongly depends on meteorological conditions (Nagy et al. 2007), concentrations, as well as characteristics of ecosystem and soil physical, chemical and biological properties (Horváth et al. 2008; Meixner and Yang 2006; Smith et al. 2003; Sutton et al. 2011). For this reason investigation of N-exchange processes above different ecosystems is important and necessary. Over grassland ecosystems our knowledge is quite comprehensive concerning these processes; however, there are still some remaining uncertainties e.g. the contribution of N compounds to the whole N budget for a given ecosystem and how the contribution varies in response to external natural and anthropogenic drivers, such as changing climate and land management (Skiba et al. 2009).

Several European integrated research programs (e.g. GRAMINAE, GreenGrass, NOFRETETE and NitroEurope) (Pilegaard et al. 2006; Soussana et al. 2007; Sutton et al. 2001; 2007) have been dealing with the N turnover of various terrestrial ecosystems. N flux measurements have been carried out by different scientific communities at many different sites from different points of view (e.g. air pollution, greenhouse effect, water pollution, nutrient load, biodiversity etc.) (Hicks et al. 2011; Sutton et al. 2007; 2011; INI; and EU initiatives like NinE and COST Action 729), while there are just a sparse number of total N-balance estimations on landscape scale involving all major sources and sinks.

For detailed investigation of the biosphere-atmosphere exchange of different N compounds including plot measurements over different types of ecosystems and for modeling of N fluxes from plot to continental scale, the EU Framework 6th Integrated Project (NitroEurope – www.nitroeurope.eu, Sutton et al. 2007) was started in 2006 coordinating the N researchers across Europe. One of the grassland stations with intensive measurement program of the NitroEurope network was established in central Hungary, on the Hungarian Great Plain, in Bugacpuszta.

Our task in the project was to determine the N-exchange between the atmosphere and semi-natural grassland in a semi-arid continental climate representative for the Hungarian Great Plain, in central Hungary, based on measurements of N-fluxes, taking into account also their dependence on climatic conditions and on the possible feedbacks to soil/vegetation dynamics. In addition, we employed the DNDC (DeNitrification DeComposition) model to estimate soil fluxes of N-gases. This paper summarizes the results of the five year measurement record of the N-exchange, taking into account all of the significant N species.

The current study is not the first one dealing with N-turnover above Bugacpuszta. In Horváth et al. (2010) solely the measured soil NO and N_2O fluxes were published for 2002-2004. Machon et al. (2010) reported a preliminary net nitrogen balance based only on one year observation record. In Machon et al. (2011) preliminary results for the whole nitrogen balance were reported including wet and dry deposition and soil emission focusing mostly on weather induced variability of nitrogen exchange.

The main aim of our work was to determine the surface-atmosphere N-balance balance over the grassland on the basis of measured and/or modeled upward and downward N-fluxes. In addition, we attempted to give a rough estimation for the total nitrogen balance, including the effect of grazing.

2. Materials and methods

2.1 Site of investigations

The selected location was Bugacpuszta (46.69 °N, 19.60 °E, 113 m a.s.l.) in the Hungarian Great Plain, between the rivers Danube and Tisza. This semi-natural, semi-arid, sandy grassland is one of the most characteristic landscape types in Hungary; therefore, the area is protected and part of the Kiskunság National Park.

The climate is semi-arid temperate continental, where the mean annual temperature is 10.7 °C and the average yearly precipitation (1989–2006) is 550 mm. The region has Chernozem-type sandy soil (according to

the World Reference Base (WRB) classification, see www.fao.org) with high sand (79%) and low clay (13%) contents in the upper 10 cm soil layer. The total carbon, organic carbon, total nitrogen content and pH in the soil extracted by KCl solution in the 0-10 cm layer are: 7.0% (SD=3.2); 6.3% (SD=3.2); 0.69% (SD=0.32) and 7.7 (SD=0.36), respectively. The same parameters in the 0-60 cm layer are: 4.1% (SD=1.2); 3.2% (SD=0.88); 0.32% (SD=0.09) and 8.2 (SD=0.27), respectively. The area was never ploughed around at least 200 m away from the measurement plot. Except grazing the soil has been undisturbed. The plant association is semi-arid sandy grassland (*Cynodonti Festucetum pseudovinae*) dominated by *Festuca pseudovina*, *Carex stenophylla*, *Salvia pratensis* and *Cynodon dactylon*. During their evolution, endemic plant and animal species (e.g. Hungarian Grey Cattle) have developed extraordinary strategies to survive heat and drought. The plant community is sensitive to physical or chemical disturbances. For this reason, the area is a nature reserve and management is not allowed. The only exception is the traditional extensive grazing by a herd of the ancient Grey Cattle breed at an average grazing pressure of 0.5–0.8 stock ha^{-1} in the grazing season (220 days in each year), which has been going on for centuries in dynamic equilibrium with the grass ecosystem (Machon et al. 2010).

2.2 DNDC (denitrification-decomposition) modeling

2.2.1 Description of the model

Ecological models like DNDC can predict the rate of processes and fluxes in different scales. These models are also applicable to support climatic or land use scenarios for the future planning. One of the main aims of biogeochemical models is to simulate C and N exchange and cycles. DNDC, a process-based biogeochemical model (Li et al. 1992a;b) was used in this study to calculate soil fluxes of all important gaseous N forms including NO, N_2O, NH_3, and N_2 that are difficult to determine by field or laboratory measurements. Advantage of the model is the online access (www.dndc.sr.unh.edu/); it has been used by many research groups all over the world (Giltrap et al. 2010; Hsieh et al. 2005; Levy et al. 2007; Smith et al. 2010). The model has been continuously developed and modified (e.g. Brown et al. 2002; Neufeldt et al. 2006; Saggar et al. 2007; Xu-Ri et al. 2003); therefore, a lot of experiences of operation are available in the literature.

Ecological drivers, like i) soil properties (soil texture, density, slope, field capacity, wilting point, clay fraction, pH, SOC, NO_3^-, and NH_4^+ content), ii) meteorological variables (daily minimum and maximum temperature, precipitation, and global radiation), iii) vegetation characteristics (crop type, plant, and harvest time, details of crop phenology), iv) and farming management as tillage, fertilizers, manure, weed, irrigation, grazing pressure, and type (cattle, horse, sheep) with start and end date of grazing etc. as daily input parameters are required to simulate trace gas fluxes. These are mainly determined by soil climate and soil processes such as denitrification, nitrification, mineralization, decomposition etc. (Li 2007).

Vertical profiles of soil parameters as well as trace gas fluxes are calculated based on these input data. Firstly, DNDC predicts daily soil temperature, moisture, redox potencial (E_h), pH, and substrate concentration, and then uses these to drive nitrification, denitrification, CH_4 production/oxidation, and other relevant geochemical or biochemical reactions. Most parts of the model run at a daily time step except the soil climate and denitrification submodels which run at an hourly time step. Output parameters from the model runs are daily soil profiles of temperature, moisture, E_h, pH, and concentrations of total soil organic carbon, nitrate, nitrite, ammonium, urea, ammonia, as well as daily fluxes of CO_2, NO, N_2O, CH_4, and NH_3.

For parameterization and validation of the model the meteorological (global radiation, min., max., and average air temperature, precipitation) and the botanical (plant species composition, areal coverage of plant, functional group e.g. legumes) datasets were gained by field observations of Szent István University (SzIU). The site-specific soil information (texture, pH, clay fraction, organic C content, bulk density etc.) was provided by the Research Institute for Soil Science and Agricultural Chemistry (RISSAC) of the Hungarian Academy of Science (HAS). Sensitivity analyses were also performed to identify main input model parameters responsible for the majority of changes in soil emission (for more details see Machon et al. 2010).

The model treats nitrogen inputs from atmospheric deposition, fertilizer usage as well as nitrogen fixation and accounts for soil (in)organic turnover, allowing the calculation of leaching of nitrogen as well as gaseous emissions. The model consists of two components (Li 2000).

The first component consists of three different submodels.

a) Soil climate submodel. It simulates soil temperature and moisture profiles based on soil physical properties, weather, and plant water use in one dimension. The soil is divided into horizontal layers, water fluxes and heat flows which are determined by soil texture and the gradients of soil moisture potential (for water fluxes) and soil temperature (for heat flows).

b) Crop growth submodel. It simulates crop biomass accumulation and partitioning of biomass into grain, stalk, and roots based on thermal degree days and daily N and water uptake. If N or water stress occurs, crop growth will be suppressed. Biomass partitioning is determined by the physiological parameters stored in the crop library files.

c) Decomposition sub-model. It simulates daily decomposition, ammonification, ammonia volatilization and CO_2 production by soil microbes. The submodel calculates turnover rates of soil organic matter at a daily time step. In the DNDC model SOC resides in four major pools: plant residues or litter, microbial biomass, humads, and passive humus. Each pool consists of one or more sub-pools with different properties. The daily decomposition rate for each sub-pool is regulated by pool size, its specific decomposition rate or fraction lost per day, soil clay content, N availability, soil temperature and moisture, and effective depth of the soil profile. The effects of cropping practices on C and N dynamics are also considered in the model. The effect of soil properties such as soil temperature, clay fraction and water content is modeled using reduction factors that constrain decomposition rate from the maximum in non-optimum conditions. Nitrogen mineralized during decomposition enters the inorganic nitrogen pool as NH_4^+, where it accumulates, or is nitrified to NO_3^- (with gaseous losses as NO and N_2O), or is removed via plant uptake, leaching, transformation to NH_3 and volatilization, or adsorption onto clay minerals. Soluble carbon levels, which fuel both nitrification and denitrification, are related to the fraction of carbon released by the decomposition of litter, labile humus, and dead microbial biomass that is re-assimilated in microbial biomass each day.

The second component consists of three submodels as well (Li et al.1992 a;b; Li 2000; 2007).

a) Nitrification submodel. It tracks growth of nitrifiers and turnover of ammonium to nitrate. Nitrification rate is calculated as a function of ammonium concentration, nitrifier population, temperature and pH.

b) Denitrification submodel. It operates at an hourly time step to simulate denitrification and the production of nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), and dinitrogen (N_2). based on soil redox potential and dissolved organic carbon (DOC) concentration. The rates for each step in the denitrification reduction sequence are a function of soluble C, soil temperature (or E_h for frozen soils), soil pH, N-substrate availability, and denitrifier biomass. As the soil dries following a rain event, the denitrifying part of each model layer decreases with soil water content. The growth and the death of denitrifier populations are simulated, which enables consumption of DOC, NO_3^-, NO_2, NO, and N_2O. The hourly time-step denitrification sub-model in DNDC is activated by three conditions which increase soil moisture and/or decrease soil oxygen availability: rain or irrigation events, flooding (as in irrigated rice agriculture), and freezing temperatures. Air temperature below −5 ºC is assumed to freeze the soil and thus, inhibit oxygen diffusion into the soil. An oxidation-reduction potential (E_h) is calculated depending on soil organic matter content as a proxy for oxygen consumption and denitrification rate is computed by using E_h as a multiplication factor. For any initiation of denitrification the initial status of the available NO_3^- and soluble carbon pools is provided by the decomposition submodel.

c) Fermentation submodel.

Classical laws of physics, chemistry, and biology, as well as empirical equations generated from laboratory studies, have been employed in the model to parameterize each specific geochemical or biochemical reaction (Li 2000).

During the model calibration (according to the test runs) we modify some default settings and also redefine some preliminary field data such as atmospheric CO_2 and NH_3 concentration, atmospheric N deposition, soil texture parameters (e.g. clay fraction, SOC profile etc.), crop biomass/yield and grazing time. To adjust the fluxes of N gases there was no direct approach, so it could be done only by modifying crop or soil parameters to alter the biogeochemical processes. After the refinement with calibration all parameter were fixed and with the final setting we ran simulations (different time period than the calibration period) in plot scale and compared directly with the field measurement (measurement had also a local scale footprint).

The model can be run in two modes: in plot and regional scale. In the last decade this widely used model was calibrated and validated by field measurements by many research groups (e.g. Beheydt et al. 2007; Brown et al. 2002; Butterbach-Bahl et al. 2004; Cai et al. 2003; Jagadeesh et al. 2006; Pathak et al. 2005; Smith et al. 2002). The entire model links C and N biogeochemical cycles and the basic ecological drivers.

2.2.2 Sensitivity test of the model

We ran different simulations to examine the main input parameters and the relevant processes (mentioned above) responsible for the majority of the change in soil emission. Analyses were done by varying one input factor within commonly observed range, while keeping all the other input conditions at a constant value (without exhaustive explanation the input variables can be seen in Table 1). Variation of these parameters results in slight differences in the total soil nitrogen fluxes; however, they significantly affect the share of different nitrogen compounds (NH_3, NO, N_2O, and NO_2) in total emission (Table 1).

According to our results, there are relationships between emitted trace gases and meteorological conditions. In the case of temperature exponential relationship can be assumed because thermal reaction rate generally exponentially increases with the temperature. Overall, the model is sensitive to the changes of meteorological parameters. Some soil properties were also varied. Parallel simulations were performed by changing initial parameters e.g. pH, clay fraction, SOC (soil organic carbon). We concluded that the model is

sensitive to clay content, pH as well as microbial processes and variations in surface carbon content (Table 1). During sensitivity analysis we examined the effect of variation in land management. DNDC is able to consider various land use practices, e.g. use of organic or inorganic fertilizers, irrigation, cutting and grazing by cattle, horses, sheep, etc. We varied the number of cattle per hectare and the grazing time. Grazing seems to have a strong effect on ammonia emission, while other N-gas emissions are not significantly affected.

The model is also sensitive to the vegetation properties: for instance, grass classification determines the yearly amount of dry matter. Additionally, plants also affect other processes, like decomposition of organic compounds, and affect the C/N ratio or the microbial activities. The sensitivity analysis has shown the most critical input parameters which have to be measured accurately.

2.3 Measurement of plant/soil C/N content

Total carbon and nitrogen content in soil and plant samples were analyzed by EuroVector EA 3000 type elemental analyzer based on dynamic flash combustion principle. The lowest absolute detection limit is 0.2 µg in 1 g sample. Analyses were preformed at the laboratory of Hungarian Forest Research Institute.

2.4 Measurement of wet nitrogen deposition

Wet depositions of ammonium and nitrate ions were determined based on concentration measurements by spectrophotometry (indophenol-blue) and ion chromatography methods, respectively in daily wet-only precipitation samples. Relative error (precision) of both analytical methods was below 5% while the minimum detection limit (MDL) was 0.05 mg N L^{-1}. The estimated bulk error of the concentration measurements and precipitation sampling was around 10%. Fluxes can be calculated as follows:

$$-F_{wet} = c \times p_d \,, \qquad (1)$$

where F_{wet} is the deposited nitrogen in the precipitation (mg N m^{-2} day^{-1}), c is the concentration of ammonium or nitrate in the precipitation (mg N L^{-1}) and p_d is the amount of daily precipitation (L m^{-2} day^{-1}).

Meteorological parameters like precipitation, air temperature, soil temperature, and soil moisture were also measured at the station.

2.5 Determination of dry nitrogen deposition based on the inferential method

24-hour sampling by the three-stage filter pack method by EMEP (1996) was used to determine the concentrations of NH_3 gas, HNO_3 vapor, NH_4^+, and NO_3^- particles. Concentrations of nitrate/nitric acid and ammonium/ammonia (c) were measured by ion chromatography and spectrophotometry (indophenol-blue method), respectively. For all components the bulk relative error (precision) of sampling and measurements was around 10% and the detection limit (MDL) was 0.1 µg N m^{-3}. Concentration of NO_2 was monitored by a HORIBA APNA 350 instrument (detection limit: 0.2 µg N m^{-3}, precision: <5%).

Dry deposition fluxes F_{dry} (mg N m^{-2} day^{-1}) of nitrogen components mentioned above were determined by the inferential method according to Eq. (2) based on the measured concentration c of the given compound (µg N m^{-3}) using inferred deposition velocities v_d (mm s^{-1}) from the literature (Table 2):

$$-F_{dry} = f \times v_d \times c \,, \qquad (2)$$

where f is a conversion factor among different length, mass, and time units. Deposition velocities of nitric acid vapor and ammonia gas were estimated from measurement of Horváth et al. (1992; 2005) (see Table 2) where the climate, soil characteristics and grass surface were similar as to our site. The deposition velocity of NO_2 above grass varies between 0.4 and 2.8 mm s^{-1} caused by climate dependence, annual and diurnal variations at different sites. Yearly mean deposition velocity (1.35 mm s^{-1}) was adopted and used based on the literature data of Hesterberg et al. (1996): 1.1 to 2.4 mm s^{-1}; Horváth et al. (2005): 0.4 mm s^{-1}; Marner and Harrison (2004): 0.8 to 2.5 mm s^{-1}; Yamulki et al. (1997): 0.67 mm s^{-1}; and Watt et al. (2004): 2.77±0.17 mm s^{-1}.

Limited number of dry deposition velocity values can be found for nitrate and ammonium particles in the literature. Mean particle diameter can be a good approximation for estimation of v_d due to the dependence of deposition velocity on particle size. As the rate of sedimentation (deposition by gravitation) is proportional to the size the ammonium has lower deposition velocity rate than nitrate, in accordance with the deposition velocities recommended by Borrell et al. (1997) and Gallagher et al. (2002) for nitrate and ammonium ions, respectively (Table 2).

2.6 Soil nitrous oxide flux measurements by static chambers

Soil N_2O flux was measured by weekly samplings during non-freezing periods (between 2006 and 2010) using 8 parallel static soil chambers (A=0.25 m^2; h=5 cm) (Christensen et al. 1996; Clayton et al. 1994; Horváth et al. 2006). The installation of the chambers, the sampling protocol and the concentration measurement by GC-ECD were described earlier in Machon et al. (2010). To eliminate the effect of non-linearity caused by saturation effect during sampling (Stolk et al. 2009) some pilot measurement were done to justify the linearity of concentration changes in the static chambers. Above the sandy soil linear concentration changes were observed in the first 30 minutes of the enclosure period. The relatively constant atmospheric background concentrations (320 ppb) were sampled immediately after closure. The detection limit was determined taking into account a minimum 10% change in concentration during sampling from the initial background values. According to this criterion, the calculated detection limit of fluxes is 1.3 μg N m^{-2} h^{-1}.

Flux was determined according to Horváth et al. (2008):

$$F_{N_2O} = \frac{2 \times \Delta C \times A_N \times V_{ch} \times 60 \times f}{V_m \times A_{ch} \times t} = 3.5 \times \Delta C \times \frac{f}{t} \quad , \tag{3}$$

where F_{N2O} is the flux (μg N m^{-2} $hour^{-1}$), 2 is a conversion factor from ppb unit into μg N m^{-3} (being two N in the N_2O molecule), ΔC is the difference in mixing ratios (nL L^{-1} or pbb) in chambers at the end and the start of samplings, t=30 min: the time of samplings, A_N is the relative atomic weight of N (14 g), V_{ch} the volume of chambers (m^3), 60 is the time conversion factor from minutes to hours (min/hour), f=1.090 is a dimensionless correction factor taking into account the residual pressure in the evacuated tubes after evacuation, V_m is the temperature dependent molar volume of ideal gases (m^3), and A_{ch} is the surface area (m^2) of soil covered by chambers.

Results of the statistical analysis showed that the non-systematic bulk error (coefficient of variation) of sampling and analysis was always below 10%. It was estimated by 10-10 parallel chambers in the field using t=0 samples where accumulation of soil emitted N_2O is zero and the background mixing ratio is measured in chambers (≈320 ppb). Taking into account that the average accumulation rate is of 30%, the estimated error is in the same magnitude for samples taken in t= 10; 20 and 30 min.

2.7 Soil nitric oxide flux measurements by dynamic chambers

Soil emission of NO has been determined by the dynamic chamber method as described in Horváth et al. (2006). The installation of the chambers, the sampling protocol and the concentration measurement by Horiba APNA/APOA 350 instruments were described earlier in Machon et al. (2010).

Chemical correction of rapid reaction of NO with ozone ($NO+O_3 \rightarrow NO_2+O_2$) was taken into account. NO flux was estimated according to Meixner et al. (1997). Under steady-state conditions the mass balance equation for NO can be written as follows (the photolysis rate of NO_2 inside the dark chambers was estimated to be zero):

$$F_f + F_m + F_{bl} + F_{gp} = 0 \, , \tag{4}$$

where F_f is the soil flux, F_m is the difference between fluxes entering and leaving the chamber, F_{bl} is the term for the wall effect which was negligible because of the relatively short residence time (40 s) of the gas mixture in the chamber, and F_{gp} is the loss of NO due to the chemical reaction with ozone. After solving Eq. (4) soil flux of NO (F_f, μg N m^{-2} $hour^{-1}$) can be calculated as:

$$F_f = \left([NO]_{out} - [NO]_{in} \right) \times f_1 \times f_2 \times \frac{Q}{A} + k \left([NO]_{out} [O_3]_{out} \right) \times f_1 \times \frac{V}{A} \, , \tag{5}$$

where Q is the flow rate (1.5×10^{-3} m^3 $minute^{-1}$), A is the area of the chamber (20×10^{-3} m^2), $[NO]_{out}$ and $[NO]_{in}$ are the mixing ratio of NO in the air (ppb or nL L^{-1}) leaving and entering the chamber, respectively, while

$$f_1 = \frac{A_N}{V_t} \, , \tag{6}$$

where A_N is the relative atomic weight of N, V_t is the molar volume (m^3) of air at the given temperature, f_2=60 is the conversion term from minutes to hours (min/hour). V is the volume of the chamber (m^3), and k is the reaction

rate constant: $k = 1.8\times10^{2}\times\exp(-1400/T)$ ($ppb^{-1}\,hour^{-1}$ or $L\,nL^{-1}\,hour^{-1}$), after Seinfeld and Pandis (1998), where $[O_3]_{out}$ is the mixing ratio of ozone ($nL\,L^{-1}$) leaving the chamber.

Soil emissions of N_2 and NH_3 have not been measured because of practical reasons (field measurements would have been difficult and/or expensive).

3.1 Measured wet deposition of inorganic and organic N

Based on the 5 year measurement average NO_3^- and NH_4^+ content of the precipitation were 2.84 and 0.78 mg L^{-1} (0.64 and 0.61 mg N L^{-1}), respectively (Table 3). The average share of ammonium and nitrate in the total inorganic N wet deposition is balanced in the average of 5 years (51% and 49%, respectively), but ratios vary significantly in different years.

It has to be noted that generally not negligible amount of organic nitrogen is also deposited by the precipitation (Cape et al. 2001). The difference between total N and inorganic N concentrations gives the dissolved organic N (DON) but the approach has some analytical artifacts. DON may take approximately 20%-30% of the total N deposition in precipitation although it is generally not included in N deposition estimates (Cornell et al. 2003). Annual average of DON in precipitation correlates better with ammonium than with nitrate and has seasonal pattern suggesting an agricultural source (Cape et al. 2004).

In some areas (e.g. in United Kingdom) the share of organic N in precipitation can be 24-40% in the total wet deposition (Cape et al. 2004), while in other regions (e.g. Soroe in Denmark) this ratio is only 9% (Skiba et al. 2009). Within the NitroEurope Integrated Project organic nitrogen content of our precipitation samples collected between October 2008 and February 2009 were analyzed in CEH (Centre for Ecology and Hydrology, Edinburgh). Based on the results (Neil Cape, CEH, Edinburgh personal communication) the organic N fraction in Bugac samples is around 16% of the total N content in the rainfall (Fig. 1). Because of the high uncertainty mostly caused by the short sampling period this value was not considered in our N-balance estimation.

3.2 Inferred dry deposition fluxes of nitrogen compounds

The share of different nitrogen compounds in dry deposition calculated by the inferential method can be seen in Table 3. Reduced and oxidized forms contribute 55% and 45%, respectively as an average during the observation period (5 years). These results agree with other European measurement sites (Skiba et al. 2009), although they found slightly larger differences among years. Dry deposition is dominated by ammonia and nitric acid (Table 3). It can be also noticed that the contribution of the deposited N gases (NH_3, HNO_3, and NO_2) is 83-89%, while the aerosol particles (NH_4^+, NO_3^-) takes only 11-17% of the total amount of dry nitrogen downward flux. The multi-year variation in share among dry deposition of N-forms derives solely from the year-by-year variation in atmospheric concentrations of pollutants according to Eq. (2) taking into account the constant inferred dry deposition velocity.

3.3 Measured soil emission flux of NO and N_2O

The multi-year average of the soil N_2O flux measurement (Table 3) is 0.67 kg N $ha^{-1}year^{-1}$ although there are large differences among years. This value is close to the mean emission (0.93 kg N $ha^{-1}year^{-1}$) determined during a survey by nine European grassland measurement sites (Flechard et al. 2007). The observed lower N_2O emission levels can be explained by the differences in rainfall, by the low N-input, and by differences in water-management features of the area of our measurements.

Precipitation is highly responsible for changes in the microclimate of soil, influencing the metabolisms, changing the favoring circumstances to (de)nitrification processes. The optimum range of wetness for denitrification at our site is 40-50% WFPS (Machon et al. 2011). In "regular" or dry years of 2006-2009 with an average precipitation of 480 mm and a soil moisture of 32% mean soil N_2O flux was 0.38 kg N $ha^{-1}year^{-1}$ in contrast with 2010 when soil moisture was within the optimum range (43%) caused by doubled precipitation (967 mm) and the N_2O emission increased nearly by a factor of 5. As a consequence, lower soil humidity in 2006-2009 influenced the soil processes through water stress and indirectly affected the nutrient uptake by plants and the cycle of N. The annual mean temperatures in 2007-2010 were 0.5 °C warmer than the long term average mainly caused by the mild winters (soil generally was not frozen).

There are some flux estimations by DNDC model for European grasslands in the literature. Average emission of N_2O from grasslands was estimated by DNDC at 1.0 kg N $ha^{-1}year^{-1}$ (Levy et al. 2007). This figure is higher but it is in relatively good agreement in order with our measured and annual average values, if we consider that the well aerated and dry sandy soil is not favorable for anaerobic denitrification producing N_2O.

The multi-year mean NO emission was around 1.1 kg N $ha^{-1}year^{-1}$. Soil emission of NO exceeds that of N_2O in each year (4-5 times higher in the drier years 2006-2009) with the exception of highly precipitated year 2010. It is in accordance with the fact that denitrification process producing N_2O is more effective in wet soils in contrast with NO production (Davidson 1991). In 2006-2009 the soil moisture content of the well-ventilated dry soil is close to the optimum for NO formation that is around at 20-30% WFPS for Bugac soil (Machon et al. 2011). Due to the properties of sandy soil (i.e. easy aeration in contrast to clay rich soils), generally nitrification dominates, favoring the formation of NO. The soil becomes anaerobic after rain events, thus significant emission peaks of N_2O and N_2 by denitrification can be observed or modeled only for short periods. The rate of N_2O/N_2 production depends on WFPS (water-filled pore space) controlled by the amount of precipitation.

Within the NitroEurope IP cooperation program different soils from Europe, including soil from Bugac station, were analyzed by incubation technique using oxygen and nitrogen isotopes. With this technique O-exchange between water and intermediate forms of the N-transformations during metabolism, and the change of isotope ratio could be measured (Kool et al. 2007; 2009a). By this methodology they described that NH_4^+ especially in our soil can be the source for nitrous oxide production instead of NO_3^- i.e. in our soil nitrifier denitrification is an alternative N_2O formation pathway (Kool et al. 2009b and 2010). This alternative metabolic process, i.e. the nitrifier denitrification of ammonia by oxidizing bacteria may control the formation of N_2O. This biochemical pathway can be a contributor to the majority of N_2O production at our measurement site, thus N_2O can also be produced at lower humidity levels in soil, resulting in a secondary peak in the range of lower wetness (20-30% WFPS) (Machon et al. 2011).

Comparing our N_2O+NO fluxes to another NitroEurope managed grassland site in Switzerland (Ammann et al. 2009) we can see that although the main drivers of soil processes are quite different (e.g. the clay fraction is 40% there and the amount of yearly precipitation at Swiss site was two times higher) the soil fluxes of N_2O and NO were at the same level (<1 kg N $ha^{-1}year^{-1}$).

3.4 The net atmosphere-surface flux based on measurements

The summary of atmospheric deposition and soil emission rates can be seen in Table 3. There are large variations in deposition and emission fluxes among years especially due to different meteorological conditions. In the year of 2010 annual precipitation was 967 mm; significantly higher than long-term (1989-2006) average (550 mm). Years 2007 and 2009 were slightly arid with 446 mm and 486 mm of precipitation, respectively. Comparing both years to the long term seasonal pattern it can be concluded that the deficit in the yearly precipitation generally occurred in spring and summer. In 2008 the yearly precipitation (567 mm) reached the regular level, whilst the annual mean temperature was a bit higher than the long term average. All of these variations in meteorological parameters show that the conditions were different in every year.

Analyzing the deposition dataset it is assumed that ratio of dry to wet deposition of nitrogen is influenced by the amount of yearly precipitation because of the generally observed linear relationship between wet deposition and precipitation rate. The ratio of dry to wet deposition varied within the range of 1.5-2.3 between 2006 and 2010.

The share of different N-gas soil emissions is influenced year-by-year by different atmospheric concentrations and weather conditions such as precipitation or soil/air temperature at our measurement site. Both soil N-fluxes and ratio of N_2O/NO soil emission varies in a wide range and we can observe that meteorological conditions affect soil processes in larger extent than the rate of dry or wet deposition. Consequently, the ratio of total deposition and soil gas emission (NO+N_2O) varies between 6 and 13 year-by-year and the magnitude of the deposition is higher approximately by one order of magnitude than soil emission. The measured N net flux between the atmosphere and the surface at the study site ranged between –9.4 and –13.3 kg N $ha^{-1}year^{-1}$ as the sum of the measured deposition and emission terms. Depending on the year 2–10% of the deposited N returns to atmosphere in the form of greenhouse gas N_2O and 5-13% of it in the form of NO.

3.5 Modeled soil fluxes

For validation of the DNDC model we compared the simulated NO and N_2O soil flux data and C/N ratio with measured values (see Figs. 2, 3 and Tables 4, 5). At our measurement site there were N_2O flux measurements in 2002-2004 in the framework of the GreenGrass project on a fortnightly sampling basis (Horváth et al. 2010). So, together with our current measurements, we can compare the simulation results with almost a whole decade of measured dataset of N_2O flux (Table 5). Comparison for a shorter period was published by Hidy et al. (2011).

Monthly fluxes modeled and measured by static/dynamic chambers show a slight agreement ($r=0.74$ for N_2O and $r=0.83$ for NO at the probability level of $p<0.01$). In winter months the agreement is worse caused by a number of reasons: e.g. in winter smaller number of sampling was taken due to snow or frost, or the model probably does not predict well the emissions around 0 °C (e.g. rain or snow, soil layers are frozen or not etc).

The significant proportion of the annual N_2O emission is produced during winter at low soil temperature. The thawing events (when the upper soil layer is not frozen) can cause large emission peaks (Müller et al. 2002).

It can be seen (Fig. 3) that DNDC model systematically underestimates the NO emission peaks. Though the simulation was not able to capture the measured emission peaks, trend of the monthly emissions gives a relatively good agreement. Model simulations of daily soil N_2O fluxes follow well the emission immediately after the rain events. In contrast, by conducting weekly measurements we have probably missed some N_2O emission peaks. Comparing the data of Table 4 it can be concluded that simulation (with a given uncertainty) gives good estimation for C/N ratios in each year.

Seasonal changes in N_2O and NO soil fluxes can be observed both for measured and modeled values (Figs. 2, 3). In summer months the microbial activity of both nitrification and denitrification is increasing with the soil temperature. Most of the measurement period between 2006 and 2009 can be characterized by aerobic condition favoring nitrification; therefore, measured soil flux of NO was generally higher than N_2O flux. It can be explained partly by the fact that the sandy soil dried out within a short time after the rain events. That is, the effective time for denitrifier bacteria community, preferring anaerobic condition, was shorter than in soils with higher water-retaining capacity. On the other hand, in extreme wet soils, loss of nitrous oxide is decreasing; reduction goes on to molecular nitrogen (N_2). Weather conditions (heat or water stress) prevented keeping the optimum soil condition for nitrous oxide production in extended periods of the observation.

The emission peaks in the simulation correlate with temperature, and reflect the rain events. After rain the denitrification processes can produce an N_2O emission peak due to the anaerobic period. In winter time, the soil surface used to be frozen for the cold period and the produced trace gases are stored in the unfrozen subsoil (Müller et al. 2002). For this reason the first thawing events results in high emission peaks for N_2O (Priemé and Christensen, 2001; Müller et al. 2002). In spring of 2007 N_2O emission peak was missing as we expected because the mild winter (soil was not frozen) so the phenomenon mentioned above was not occurred.

Soil emissions of N_2 and NH_3 have not been measured because of practical reasons. Hence, validation of the model for these parameters was not possible due to the lack of measurement. However, taking into consideration the relatively good agreement (especially in yearly rate) between modeled and measured fluxes for NO and N_2O, we can make a rough estimation (assuming a similar relationship) for N_2 and NH_3 fluxes, emphasizing that uncertainty of these values are higher than for other components.

Based on model results it can be concluded that the rate of annual soil N emissions including all of gases (N_2, NH_3, NO, N_2O) varies within a relatively narrow range, with an average of 2.1 (SD=0.44) kg N ha^{-1} $year^{-1}$ in Bugac station. There are significant differences between the shares of different N-components in the given year, which was influenced by change in meteorological variables and soil physics.

It can be observed that in years with extremely dry and hot summer (2003 and 2009) the model significantly underestimated the N_2O fluxes. It can be explained by the fact that biosphere is adapted to these conditions (drought-tolerant species); on the other hand, biosphere (through life processes) try to moderate the extreme environmental conditions, which is difficult to model due to the complexity of the system. All ecological models are based on simplifications therefore we can not eliminate the deviations caused by simplifications. Overall, there is a relatively good correlation between the simulated and measured fluxes.

It should be emphasized that the three-dimensional heterogeneity of the ecosystem (even on meter scale) was the main reason why the measurements were taken at several places simultaneously. The microbial activity often responds much quicker to the environmental changes, such as biomass, but the biomass remains an important character. The major simulated trace gas emissions and short-term events are often driven by meteorological extreme events (heat and water stress, freezing-thawing), drying/rewetting (nitrification-denitrification), and management (grazing/cutting/fertilization etc).

On the basis of multi-year simulation DNDC model underestimates the emissions of N_2O and NO but the standard deviation of the measured data are much larger than the simulated values. The modeled annual emission level of N_2O is 0.55 kg N $ha^{-1}year^{-1}$ (which gives slight agreement with our measurements). This value is lower by one order of magnitude compared to the 5.6 kg N $ha^{-1}year^{-1}$ average value calculated by the IPCC method determined for many European areas (Boeckx and van Cleemput 2001). In the IPCC method the cultivated arable lands are also included, where the N_2O emission is generally higher caused by the crop N-fertilization.

3.6 Estimated effect of leaching, biological N-fixation, and grazing

The surface run-off and N-leaching are strongly dependent on slope, soil type, depth of the groundwater level, precipitation etc. as ecological drivers. On a flat area surface run-off practically does not occur. The groundwater level is about 6 m deep, and the sandy surface tends to dry out quickly, thus the nitrate measurement from soil moisture were usually unsuccessful due to the soil water content in soil is often below 20%, therefore the nitrate leaching is probably negligible. While in Bugac N-leaching was neglected for an

extensively managed (fertilized) grassland site in Swiss Central Plateau it was estimated to be 3.5 kg N $ha^{-1}year^{-1}$ in the period of 2002-2009 (Ammann et al. 2009).

The biological N-fixation by plants (BNF) is not negligible because of the 8-17% share of legumes observed according to our surveys in different years; however, we were not able to determine the N-fixation by direct measurement. Biological nitrogen fixation for natural grasslands ranges within 2.3-3.1 kg N $ha^{-1}year^{-1}$ estimated by Butterbach-Bahl et al. (2011). As to the N-fixation by legumes the European outlook is the follows: although the measurement of N-fixation by ^{15}N isotope technique is not resolved everywhere yet, according to a preliminary study the estimated N-fixation is less than 1–2 kg N $ha^{-1}year^{-1}$ at most of the sites of NitroEurope project (Skiba et al. 2009) except Oensingen (Switzerland) where a higher value was calculated since the legumes ratio is 48%.

Based on land cover ratio of the legumes (8-17%) the estimated average N-fixation by plants at Bugac site is around 2.9 kg (1.9-3.9) N ha^{-1} $year^{-1}$ (personal communication of Christof Ammann, Agroscope Reckenholz-Tanikon ART, Swiss Federal Research Station, Zürich, Switzerland). This value was considered in our N-exchange estimation (see next chapter). Nevertheless, the main N-input of our grassland is the dry and wet depositions (altogether 11–15 kg N $ha^{-1}year^{-1}$).

The research area is usually grazed by a herd of gray cattle for about 220 days yearly with 0.5-0.8 LU ha^{-1} (500-800 livestock unit in 1074 ha) grazing pressure. The Hungarian Grey Cattle breed is protected for genome conservation and propagation for other farms; hence there is no extensive meat or milk producing and consequently the number of animals is relatively constant. We estimated the output and input of nitrogen by grazing on the basis of literature and simulated data. Waldrip et al. (2013) reported an average of 162 (SD=50) g N $day^{-1}LU^{-1}$ nitrogen uptake by grazing. Using this figure the N content of grazed grass is 21.6 ± 9 kg N ha^{-1} $year^{-1}$. Based on DNDC simulations (Table 4) the annual average of the removal by grazing is 21± 5 kg N ha^{-1} which shows good agreement with the calculated data.

With grazing nitrogen temporarily leaves ecosystem and it is partly supplied back with excreta except the amount of nitrogen built into the bodies of cattle. Waldrip et al. (2013) estimated 119 (SD=38) g N day^{-1} LSU^{-1} excreted nitrogen. The calculated N uptake at our site using this figure is 15.8±5 kg N $ha^{-1}year^{-1}$. Another calculation of Skiba et al. (2009) estimated of 16 kg N $ha^{-1}year^{-1}$ as N input by excretion at Bugac site.

3.7 Total N-balance including measured, modeled, and estimated data

The net surface atmosphere balance can be seen in Fig. 4. In the lack of direct measurements of soil N_2 and NH_3 emission we can make a rough estimation for the orders of magnitude of these processes. Hence, we used the modeled emission fluxes to compare the soil emission to the N-uptake including deposition and biological fixation (Fig. 4). All of soil emission rates are derived from DNDC modeling. Total N-balance in Fig. 4 does not involve the effect of grazing and excreta.

For estimation of net balance of nitrogen including BNF and the effect of grazing and excreta these data were delivered as it was described in section 3.6 (Table 3). The net budget shows negative balance (input terms exceed the outputs) but we have to take into consideration the large uncertainty in estimation of the effect of grazing. We can only state with caution that the ecosystem has a surplus of nitrogen or it is close to the equilibrium. Probably the excess (if any) is mineralized and stored in the soil in inorganic form. This might be supported by the increase in total nitrogen content in the 0-30 cm layer between 2006 and 2010: 0.28; 0.33; 0.37; 0.38; 0.34%. According to a previous study (Sophie Zechmeister-Boltenstern, BOKU, personal communication) the mineralization rate is 194 μg NH_4^+ $g^{-1}week^{-1}$ related to dry weight of soil.

3.8. Climatic and ecological effects

Based on that global warming potential of N_2O is 298 times higher than that of CO_2 on 100-year time horizon (IPCC 2007), both measured and simulated yearly N_2O emissions range between 71-849 and 108-409 kg CO_2-eq. $ha^{-1}year^{-1}$, respectively during the period examined.

Temperature and precipitation mainly affect the formation of N_2O and NO, and the seasonal fluctuation of their soil emission. In the measurement period the soil flux of N_2O was less than 1 kg N $ha^{-1}year^{-1}$. The forecasted potentially drying climate in the Hungarian Great Plan can lead to reduced N_2O emission, which may mean a potential negative feedback on greenhouse effect. On the other hand, Pintér et al. (2008) and Barcza et al. (2009) argued that grass can turn into a net CO_2 source in extreme dry years like 2003 and 2007 as a positive feedback for climate change. Though the impact of these two phenomena is opposite we should not neglect them, considering that the ratio and the strength of both processes are unknown. In addition, in Hungary the area of the surface covered by the temperate grass is large and will be growing with increasing aridity of climate.

The residence time of N in intensively managed grassland is potentially lower than at untreated grasslands. Soil nitrogen pool depends on the consumption and exchange of both living roots and bacteria which are competitors for the same nutrients. Function of plant physiology (plant N-uptake demand), plant growing,

microbial metabolism are highly affected by air and soil temperature and water deficit etc. Plant association of Bugac becomes open grassland if it is exposed many times to naturally induced droughts. So plants also induce effect on soil N transformation. The selection of herbivore is important, because every species have plant preferences. The optimum number of animals (0.5-0.8 ha^{-1}) is also required to preserve the treeless condition and the diversity of plant species through small disturbance. With overgrazing the nitrogen can be mobilized faster in the soil due to manure and urine and may lead faster biochemical processes. The compaction of the upper soil layer due to animal trampling can cause airless condition (decreasing porosity). This may increase the denitrification activity, which can lead to increased N losses.

4. Conclusions

Based on measurements and model simulations we quantified the extent of dry and wet N deposition with soil N-gas fluxes originated from microbiological processes in different years for semi-arid, semi-natural, extensively grazed grassland. The ammonia dry deposition is the main N-source (35-40%) of the area. The dry deposition of nitric acid vapor (20-25%) and wet deposition of ammonium and nitrate ions (30-35%) have also relatively large influence in the different years. The average modeled N-gas emission (2.1±0.4 kg N $ha^{-1}year^{-1}$) of the area is lower by one order than deposition rate. Both the rate of nitrogen load and soil emission are less than at other European sites due to the low atmospheric deposition, lack of intensive management, and fertilization. Bugac (nature reserved, undisturbed area) seems to be representing background levels of fluxes caused by the absence of local air pollution or N-sources (fertilizers etc). This statement is in accordance with the work of Skiba et al. (2009), where various N deposition and emission values were overviewed for different grasslands and other sites.

The calculated yearly N-balance (net flux) between the atmosphere and the surface ranged between –9.4 and –14 kg N $ha^{-1}year^{-1}$ as the sum of the measured deposition and emission terms: –11.2 to –15.1 and 0.9-2.9 kg N $ha^{-1}year^{-1}$, respectively, between 2006 and 2010 (without BNF and effect of grazing).

If we take into account the biological nitrogen fixation and the effect of grazing (effects of both grazed plant and excreta) the net nitrogen balance varies within –6.6 and –11 kg N $ha^{-1}year^{-1}$. It seems - taken into account the high uncertainty in calculation of grazing effect - that sources of nitrogen exceed the sinks; the surplus is probably mineralized in the soil.

We applied and validated the DNDC model first time in Hungary (built up a database of the air, soil and other parameters and using the measured data of Bugac). Soil trace gas emissions are strongly controlled by soil organic carbon and soil mineral N-content, and by soil temperature and moisture.

Using the DNDC model we are able to give N-gas flux prediction for those lands where measurements are missing and we are able to simulate fluxes of parameters and soil processes where field or laboratory measurements are difficult or expensive. This provides some support for future use of the DNDC model in regional mode for scaling up the soil fluxes for different ecosystem types or give climate scenario estimation up to country scale.

Acknowledgements– The authors are grateful for the permission of the Management of Kiskunság National Park to conduct the studies in the territory of the park in Bugacpuszta. This work has been supported by the NitroEurope EU 6th FP, the ÉCLAIRE EU 7 th FP (282910), National Research and Innovation Programs (NKFP/088/2004, NKFP6- 00028/2005 and NKFP6-00079/2005), COST Action 0804, and partly by the European Union and co-financed by the European Social Fund grant agreement no.: TAMOP 4.2.1/B-09/1/KMR-2010-0003. Authors thank to dr. Neil Cape (CEH) for organic N analyses.

References

Ammann, C., Spirig, C., Leifeld, J. and Neftel, A. (2009). Assessment of the nitrogen and carbon-balance of two managed temperate grassland fields. Agr. Ecosyst. Environ. 133, 150–162.

Barcza, Z., Haszpra, L., Somogyi, Z., Hidy, D., Lovas, K., Churkina, G. and Horváth, L. (2009). Estimation of the biospheric carbon dioxide balance of Hungary using the BIOME-BGC model. Időjárás 113, 203–219.

Beheydt, D., Boeckx, P., Sleutel, S., Li C. and van Cleemput, O. (2007) Validation of DNDC for 22 long-term N_2O field emission measurements. Atmospheric Environment 41, 6196–6211.

Boeckx, P. and van Cleemput, O. (2001). Estimates of N_2O and CH_4 fluxes from agricultural land in various regions of Europe. Nutr. Cycl. Agroecosyst. 60, 35–47.

Borrell, P., Builtjes, J.H., Grennfelt, P. and Hov, Ø. (eds.) (1997). Transport and chemical transformation of pollutants in the troposphere. Photo-Oxidants, Acidification and Tools: Policy Applications of Eurotrac Results, vol. 10. Springer, pp. 116.

651 Brown, L., Syed, B., Jarvis, S.C., Sneath, R.W., Phillips, V.R., Goulding, K.W.T. and Li, C. (2002).
652 Development and application of a mechanistic model to estimate emission of nitrous oxide from UK
653 agriculture. Atmospheric Environment 36, 917–928.
654 Butterbach-Bahl, K., Kesik, M., Miehle, P., Papen, H. and Li, C. (2004). Quantifying the regional source
655 strength of N-trace gases across agricultural and forest ecosystems with process based models. Plant Soil.
656 260, 311–329.
657 Butterbach-Bahl, K., Gundersen, P., Ambus, P., Augustin, J., Beier, C., Boeckx, P., Dannenmann, M., Sanchez
658 Gimeno, B., Ibrom, A., Kiese, R., Kitzler, B., Rees R.M., Smith, K.A., Stevens, C.,Vesala, T. and
659 Zechmeister-Boltenstern, S. (2011). Nitrogen processes in terrestrial ecosystems, in: Sutton, M.A., Howard,
660 C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H. and Grizzetti B. (eds.), The
661 European Nitrogen Assessment. Cambridge University Press. New York 2011, ISBN 978-1-107-00612-6.
662 Chapter 6, pp. 99–125.
663 Cai, Z., Sawamoto, T., Li, C., Kang, G., Boonjawat, J., Mosier, A.R., Wassmann, R. and Tsuruta, H. (2003).
664 Field validation of the DNDC model for greenhouse gas emissions in East Asian cropping systems. Global
665 Biogeochem. Cycles. 17(4), 1107.
666 Cape, J. N., Kirika, A. , Rowland, A. P. Wilson, D.R., Jickells, T.D. and Cornell, S. (2001). Organic nitrogen in
667 precipitation: real problem or sampling artifact? The Scientific World 1, 230–237.
668 Cape, J.N., Anderson, M., Rowland, A.P. and Wilson, D. (2004). Organic nitrogen in precipitation across the
669 United Kingdom. Water Air Soil Pollut. 4, 25–35.
670 Clayton, H., Arah, J.R.M. and Smith, K.A. (1994). Measurement of nitrous oxide emissions from fertilized
671 grassland using closed chambers. J. Geophys. Res. 99, 16599–16607.
672 Christensen, S., Ambus, P., Arah, J.R.M., Clayton, H., Galle, B., Griffith, D.W.T., Hargreaves, K.J.,
673 Klemedtsson, L., Lind, A.-M., Maag, M., Scot, A., Skiba, U., Smith, K.A., Welling, M. and Wienhold, F.G.
674 (1996). Nitrous oxide emission from an agricultural field: comparison between measurements by flux
675 chamber and micro-meteorological techniques. Atmos. Environ. 30, 4183–4190.
676 Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P. and Duce, R. A. (2003). Organic nitrogen deposition
677 on land and coastal environments: a review of methods and data. Atmospheric Environment 37, 2173–2191.
678 Davidson E.A. (1991). Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems, in: J.E. Roger and
679 W.B. Whitman (eds.) Microbial production and consumption of greenhouse gases: Methane, nitrogen oxides
680 and halomethanes. Am. Soc. Microbiol. Washington DC. pp. 219-235.
681 EMEP (1996). EMEP Manual for sampling and chemical analysis. EMEP/CCC-Report 1/95, NILU, Kjeller,
682 Norway.
683 Erisman, J. W., Grennfelt, P. and Sutton M. (2003). The European perspective on nitrogen emission and
684 deposition. Environ. Internat. 29, 311–325.
685 Erisman, J.W., Vermeulen, A., Hensen, A., Flechard, C., Dammgen, U., Fowler, D., Sutton, M., Grünhage, L.
686 and Tuovinen, J.P. (2005). Monitoring and modelling of biosphere/atmosphere exchange of gases and
687 aerosols in Europe. Envir. Poll. 133, 403–413.
688 Erisman, J. W., van Grinsven, H., Grizzetti, B., Bouraoui, F., Powlson, D., Sutton, M. A., Bleeker, A. and Reis
689 S. (2011). The European nitrogen problem in a global perspective, in: Sutton, M.A., Howard, C.M.,
690 Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H. and Grizzetti B. (eds.), The European
691 Nitrogen Assessment. Cambridge University Press. New York 2011, ISBN 978-1-107-00612-6. Chapter 2,
692 pp. 9–31.
693 Flechard, C. R., Ambus, P., Skiba, U., Rees, R.M., Hensen, A., van Amstel, A., van den Pol-van Dasselaar, A.,
694 Soussana, J.-F., Jones, M., Clifton-Brown, J., Raschi, A., Horvath, L., Neftel, A., Jocher, M., Ammann, C.,
695 Leidfield, J., Fuhrer, J., Calanca, P.L., Thalman, E., Pilegaard, K., Di Marco, C., Campbell, C., Nemitz, E.,
696 Hargreaves, K.J., Levy, P., Ball, B.C., Jones, S., van de Bulk, W.C.M., Groot, T., Blom, M., Domingues, R.,
697 Kasper, G., Allard, V., Ceshia, E., Cellier, P., Laville, P., Henault, C., Bizouard, F., Abdalla, M., Williams,
698 M., Baronti, S., Berretti, F. and Grosz, B. (2007). Effects of climate and management intensity on nitrous
699 oxide emissions in grassland systems across Europe. Agric. Ecosys. Environ. 121, 135–152.
700 Gallagher, M.W., Nemitz, E., Dorsey, J.R., Fowler, D., Sutton, M.A., Flynn, M. and Duyzer, J. (2002).
701 Measurements and parameterizations of small aerosol deposition velocities to grassland, arable crops and
702 forests: influence of surface roughness length on deposition. J. Geophys. Res. 107, AAC1–AAC8.
703 Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., and Cosby, B. J.
704 (2003). The nitrogen cascade. BioScience 53, 341–356.
705 Giltrap, D.L., Li, C. and Saggar, S. (2010). DNDC: A process-based model of greenhouse gas fluxes from
706 agricultural soil. Agric. Ecosys. Environ. 136, 292–300.
707 Hesterberg, R., Blatter, A., Fahrni, M., Rosset, M., Neftel, A., Eugster, W. and Wanner, H. (1996) Deposition of
708 nitrogen containing compounds to an extensively managed grassland in central Switzerland. Envir. Poll. 30,
709 1247–1254.

Hicks, W.K., Whitfield, C.P., Bealey, W.J. and Sutton, M.A., (eds.) (2011). Nitrogen Deposition and Natura 2000: Science and practice in determining environmental impacts. COST729/Nine/ESF/CCW/JNCC/SEI Workshop Proceedings, published by COST. Available at: http:// cost729.ceh.ac.uk/n2kworkshopISBN 978-91-86125-23-3

Hidy, D., Machon, A., Haszpra, L., Nagy, Z., Pintér, K., Churkina, G., Grosz, B., Horváth L. and Barcza, Z. (2011). Modeling of biosphere-atmosphere exchange of greenhouse gases. Part III, Chapter 10 Grasslands, in: Haszpra, L. (ed.), Atmospheric Greenhouse Gases: The Hungarian Perspective. Spinger, Dordrecht, Heilderberg, London, New York.

Horváth, L., Bozó, L., Haszpra, L., Kopacz, J., Molnár, Á., Práger, T. and Weidinger, T. (1992). Gradient measurement of air-soil exchange of gases, in: Schwartz, S.E. and Slinn, W.G.N. (eds.), Precipitation Scavenging and Atmosphere–Surface Exchange, vol. 2, Hemisphere Publishing Corporation, Washington, Philadelphia, London, pp. 637–648.

Horváth, L., Asztalos, M., Führer, E., Mészáros, R. and Weidinger, T. (2005). Measurement of ammonia exchange over grassland in the Hungarian Great Plain. Agric. Forest Meteor., 130, 282–298.

Horváth, L., Führer, E. and Lajtha, K. (2006). Nitric oxide and nitrous oxide emission from Hungarian forest soils; linked with atmospheric N-deposition. Atmos. Envir. 40, 7786–7795.

Horváth, L., Grosz, B., Machon, A., Balogh, J., Pintér, K. and Czóbel, Sz. (2008). Influence of soil type on N_2O and CH_4 soil fluxes in Hungarian grasslands. Commun. Ecol. 9 (Suppl.), 75–80.

Horváth, L., Grosz, B., Machon, A., Tuba, Z., Nagy, Z., Czóbel, Sz., Balogh, J., Péli, E., Fóti, Sz., Weidinger, T., Pintér, K. and Führer, E. (2010). Estimation of nitrous oxide emission from Hungarian semi-arid sandy and loess grasslands; effect of grazing, irrigation and application of fertilizer. Agric. Ecosys. Environ. 139, 255–263.

Hsieh, C., Leahy, P., Kiely, G. and Li, C. (2005). The effect of future climate perturbations on N_2O emissions from fertilized humid grassland. Nutrient Cycling Agroecosys. 73, 15–23.

IPCC (2007) The physical science basis – contribution of working group I to the fourth assessment report of the IPCC. Cambridge University Press, Cambridge, New York.

Jagadeesh Babu, Y., Li, C., Frolking, S., Nayak, D.R. and Adhya, T. K. (2006). Field validation of DNDC model for methane and nitrous oxide emissions from rice-based production systems of India. Nutrient Cycling Agroecosys. 74, 157–174.

Kool, D.M., Wrage, N., Oenema, O., Dolfing, J. and van Groenigen, J.W. (2007). Oxygen exchange between (de)nitrification intermediates and H_2O and its implications for source determination of NO_3^- and N_2O: a review, Rapid Commun. Mass Spectrom. 21, 3569–3578.

Kool, D.M., Müller, C., Wrage, N., Oenema, O. and van Groenigen, J.W., (2009a). Oxygen exchange between nitrogen oxides and H_2O can occur during nitrifier pathways. Soil Biol. Biochem. 41, 1632–1641.

Kool, D.M., Wrage, N., Oenema, O., Harris, D. and van Groenigen, J.W. (2009b). The ^{18}O signature of biogenic nitrous oxide is determined by O exchange with water. Rapid Commun. Mass Spectrom. 23, 104–108.

Kool, D.M., Wrage, N., Zechmeister-Boltenstern, S., Pfeffer, M., Brus, D., Oenema, O. and van Groenigen, J.W. (2010). Nitrifier denitrification can be a source of N_2O from soil: a revised approach to the dual isotope labelling method. NitroEurope Open Science Conference: Reactive Nitrogen and the European Greenhouse Gas Balance. February 3-4, 2010, Solothurn, Switzerland. Book of abstracts: pp. 12.

Kugler, Sz., Horváth, L. and Machon, A. (2008). Estimation of nitrogen flux between the atmosphere and aquatic/terrestrial ecosystems in Hungary. Environ. Poll. 154, 498–503.

Levy, P.E., Mobbs, D.C., Jones, S.K., Milne, R., Campbell C. and Sutton, M.A. (2007). Simulation of fluxes of greenhouse gases from European grasslands using the DNDC model. Agric. Ecosys. Environ. 121, 186–192.

Li, C., Frolking, S. and Frolking, T.A. (1992a). A model of nitrous oxide evolution from soil driven by rainfall events: 1. Model structure and sensitivity. J. Geophys. Res. 97, 9759–9776.

Li, C., Frolking, S. and Frolking, T.A. (1992b). A model of nitrous oxide evolution from soil driven by rainfall events: 2. Model applications. J. Geophys. Res. 97, 9777–9783.

Li, C. (2000) Modeling trace gas emissions from agricultural ecosystems. Nutrient Cycling Agroecosys. 58, 259–276.

Li, C. (2007) Quantifying greenhouse gas emissions from soils: Scientific basis and modeling approach, Soil Sci. Plant Nutrition 53, 344-352.

Machon, A., Horváth, L., Weidinger, T., Grosz, B., Pintér, K., Tuba Z. and Führer, E. (2010). Estimation of net nitrogen flux between the atmosphere and a semi-natural grassland ecosystem in Hungary. Eur. J. Soil Sci. 61, 631–639.

Machon, A., Horváth, L., Weidinger, T., Pintér, K., Grosz, B., Nagy, Z. and Führer, E. (2011) Weather induced variability of N-exchange between the atmosphere and a grassland in the Hungarian Great Plain. Időjárás 115, 219–232.

Marner, B.B. and Harrison, R.M. (2004). A spatially refined monitoring based study of atmospheric nitrogen deposition. Atmos. Envir. 38, 5045–5056.

Massad, R. S., Nemitz, E. and Sutton, M. A. (2010). Review and parameterisation of bi-directional ammonia exchange between vegetation and the atmosphere. Atmos. Chem. Phys. Discuss. 10, 10359–10386.
Meixner, F.X., Fickinger, Th., Marufu, L., Serca, D., Nathaus, F.J., Makina, E., Mukurumbira, L. and Andreae, M.O. (1997). Preliminary results on nitric oxide emission from a southern African savanna ecosystem. Nutrient Cycling Agroecosys. 48, 123–138.
Meixner F.X. and Yang W.X. (2006). Biogenic emissions of nitric oxide and nitrous oxide from arid and semi-arid land, in: D'Odorico P., Porporato A. (eds.), Dryland ecohydrology. Springer, Dordrecht, Berlin, Heidelberg, New York. ISBN 1-4020-4260-7. Chapter 14, pp. 233–255.
Moldanová, J., Grennfelt, P., Jonsson, A., Simpson, D., Spranger, T., Aas, W., Munthe, J. and Rabl A., Nitrogen as a threat to European air quality (2011). in: Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H. and Grizzetti B. (eds.), The European Nitrogen Assessment. Cambridge University Press. New York 2011, ISBN 978-1-107-00612-6. Chapter 18, pp. 405–433.
Müller, C., Martin, M., Stevens, R.J., Laughlin, R.J., K. Ammann, C., Ottow, J.C.G. and Jager H.J. (2002) Processes leading to N_2O emissions in grassland soil during freezing and thawing. Soil Biol. Biochem. 34, 1325–1331.
Nagy, Z., Pintér, K., Czóbel, Sz., Balogh, J., Horváth, L., Fóti, Sz., Barcza, Z., Weidinger, T., Csintalan, Zs., Dinh, N.Q., Grosz, B. and Tuba, Z. (2007). The carboN-balance of semi-arid grassland in a wet and a dry year in Hungary. Agric. Ecosys. Environ. 121, 21–29.
Neufeldt, H., Schafer, M., Angenendt, E., Li, C., Kaltschmitt, M. and Zeddies, J. (2006). Disaggregated greenhouse gas emission inventories from agriculture via a coupled economic-ecosystem model. Agric. Ecosys. Environ. 112, 233–240.
Pathak, H., Li, C. and Wassmann, R. (2005). Greenhouse gas emissions from India rice fields: calibration and upscaling using the DNDC model. Biogeosci. 1, 1–11.
Pilegaard, K., Skiba, U., Ambus, P., Beier, C., Brüggemann, N., Butterbach-Bahl, K., Dick, J., Dorsey, J., Duyzer, J., Gallagher, M., Gasche, R., Horvath, L., Kitzler, B., Leip, A., Pihlatie, M.K., Rosenkranz, P., Seufert, G., Vesala, T., Westrate, H. and Zechmeister-Boltenstern, S. (2006). Factors controlling regional differences in forest soil emission of nitrogen oxides (NO and N_2O). Biogeosci. 3, 651–661.
Pintér, K., Barcza, Z., Balogh, J., Czóbel, Sz., Csintalan, Zs., Tuba, Z. and Nagy, Z. (2008). Interannual variability of grasslands' carbon-balance dependson soil type. Commun. Ecol. 9 (Suppl), 43–48.
Priemé, A. and Christensen, S. (2001). Natural perturbation, drying-wetting and freezing-thawing cycles and the emission of the nitrous oxide, carbon dioxide and methane from farmed organic soil. Soil Biol. Biochem. 33, 2083–2091
Robertson, G.P. and Groffman P.M., (2007) Nitrogen transformation, in: Paul. E.A. (ed.), Soil Microbiology, Biochemistry, and Ecology. Springer, New York, New York, USA. Chapter 13, pp. 341–364
Saggar S., Giltrap D.L., Li C. and Tate K.R. (2007). Modelling nitrous oxide emissions from grazed grasslands in New Zealand. Agric. Ecosys. Environ. 119, 205–216.
Seinfeld, J.H. and Pandis, S.N. (1998). Atmospheric chemistry and physics: From air pollution to climatic change. John Wiley and sons Inc., New York, Chichester, Weinheim, Brisbane, Singapore, Toronto.
Skiba, U., Drewer, J., Tang, Y.S., van Dijk, N., Helfter, C., Nemitz, E., Famulari, D., Cape, J.N., Jones, S.K., Twigg, M., Pihlatie, M., Vesala, T., Larsen, K.S., Carter, M.S., Ambus, P., Ibrom, A., Beier, C., Hensen, A., Frumau, A., Erisman, J.W., Bruggemann, N., Gasche, R., Butterbach-Bahl, K., Neftel, A., Spirig, C., Horvath, L., Freibauer, A., Cellier, P., Laville, P., Loubet, B., Magliulo, E., Bertolini, T., Seufert, G., Andersson, M., Manca, G., Laurila, T., Aurela, M., Lohila, A., Zechmeister-Boltenstern, S., Kitzler, B., Schaufler, G., Siemens, J., Kindler, R., Flechard, C. and Sutton, M.A. (2009) Biosphere–atmosphere exchange of reactive nitrogen and greenhouse gases at the NitroEurope core flux measurement sites: Measurement strategy and first data sets. Agric. Ecosys. Environ. 133, 139–149.
Smith, W.N., Desjardins, R.L., Grant, B., Li, C., Lemke, R., Rochette, P., Corre, M.D. and Pennock, D. (2002). Testing the DNDC model using N_2O emissions at two experimental sites in Canada. Can. J. Soil Sci. 82, 365–374.
Smith, K.A., Ball, T., Conen, F., Dobbie, K., Massheder, J. and Rey, A. (2003). Exchange of greenhouse gasesbetween soil and atmosphere: interactions of soil physical factors and biological processes, Eur. J. Soil Sci. 54, 779–791.
Smith, W.N., Grant, B.B., Desjardins, R.L., Worth, D., Li, C., Boles, S.H. and Huffmann, E.C. (2010). A tool to link agricultural activity data with the DNDC model to estimate GHG emissions factors in Canada. Agric. Ecosys. Environ. 136, 301–309.
Soussana, J. F., Allard, V., Pilegaard, K., Ambus, P., Amman, C., Campbell, C., Ceschia, E., Clifton-Brown, J., Czóbel, SZ., Domingues, R., Flechard, C., Fuhrer, J., Hensen, A., Horvath, L., Jones, S. M., Kasper, G., Martin, C., Nagy, Z., Neftel, A., Raschi, A., Baronti, S., Rees, R. M., Skiba, U., Stefani, P., Manca, G., Sutton, M., Tuba, Z. and Valentini, R. (2007). Full accounting of the greenhouse gas (CO_2, N_2O, CH_4) balance of nine European grassland sites. Agric. Ecosys. Environ. 121, 121–134.

Stolk, P.C., Jacobs, C.M.J., Moors, E.J., Hensen, A., Velthof, G.L. and Kabat, P. (2009). Significant non-linearity in nitrous oxide chamber data and its effect on calculated annual emissions. Biogeosci. Discuss. 6, 115–141.

Sutton, M.A., Milford, C., Nemitz, E., Theobald, M.R., Hill, P.W., Fowler, D., Schjørring, J.K., Mattsson, M.E.,, Nielsen, K.H., Husted, S., Erisman, J.W., Otjes, R., Hensen A., Mosquera, J., Cellier, P., Loubet, B., David, M., Genermont, S., Neftel, A., Blatter, A., Hermann, B., Jones, S.K., Horvath, L., Führer, E., Mantzanas, C., Koukoura, K., Gallagher, M., Williams, P., Flynn M., and Riedo, M. (2001). Biosphere-atmosphere interactions of ammonia with grasslands: Experimental strategy and results from a new European initiative. Plant Soil 228, 131–145.

Sutton, M.A., Nemitz, E., Erisman, J.W., Beier, C., Butterbach-Bahl, K. and Cellier, P. (2007). Challenges in quantifying biosphere-atmosphere exchange of nitrogen species. Environmental Pollution 150, 125–139.

Sutton, M. A., Erisman, J. W., Dentener, F. and Möller, D. (2008). Ammonia in the environment: From ancient times to the present. Envir. Poll. 156, 583–604.

Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H. and Grizzetti B., (eds.) (2011). The European Nitrogen Assessment, Cambridge University Press. New York 2011, ISBN 978-1-107-00612-6. www.nine-esf.org/ENA

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W H. and Tilman, D.G. (1997). Human alteration of the global nitrogen cycle: sources and consequences. Ecol. Appl. 7, 737–750.

Waldrip, H.M., Todd R.W. and Cole, N.A. (2003). Prediction of nitrogen excretion by beef cattle: A meta-analysis. J. Anim. Sci. 91, 4290–4302.

Watt, S.A., Wagner-Riddle, C., Edwards, G. and Vet, R.J. (2004) Evaluating a flux-gradient approach for flux and deposition velocity of nitrogen dioxide over short-grass surfaces. Atmos. Environ. 38, 2619-2626.

Wesely, M.L. and Hicks, B.B. (2000). A review of the current status of knowledge on dry deposition. Atmos. Environ. 34, 2261–2282.

Yamulki, S., Harrison, R.M., Goulding, K.W.T. and Webster, C.P. (1997). N_2O, NO and NO_2 fluxes from a grassland: effect of soil pH. Soil Biol. Biochem. 29, 1199–1208.

Zhang, L., Wright, L.P. and Asman, W.A.H. (2010). Bi-directional air-surface exchange of atmospheric ammonia: A review of measurements and a development of a big-leaf model for applications in regional-scale air-quality models. J. Geophys. Res. D20310.

Xu-Ri., Wang, M. and Wang, Y. (2003). Using a modified DNDC model to estimate N_2O fluxes from a semi-arid grassland in China. Soil Biol. Biochem. 35, 615–620.

Internet sources:

Cost 729 Action: http://www.cost729.ceh.ac.uk (Assessing and managing nitrogen fluxes in the atmosphere-biosphere system in Europe)

INI: http://www.initrogen.org (International Nitrogen Initiative, Optimizing nitrogen use in food and energy production and minimizing the consequent harm to humans and the environment)

NinE: http://www.nine-esf.org (Nitrogen in Europe, current problem and future solution)

NitroEurope: http://www.nitroeurope.eu

Table 1: Summary of the sensitivity test of DNDC

Parameters	**Fluxes**			
	N_2O	NO	N_2	NH_3
	(kg N ha^{-1} $year^{-1}$)			
Original run	0.76	0.96	0.10	0.69
+1 °C	0.44	1.05	0.05	0.74
+2 °C	0.08	1.13	0.01	0.79
–1 °C	1.30	0.87	1.32	0.63
–2 °C	1.35	0.79	1.07	0.59
125% precipitation	0.83	1.10	0.10	0.73
75% precipitation	0.63	0.84	0.10	0.63
+10% SOC	0.95	1.04	0.14	0.69
–10% SOC	0.62	0.88	0.08	0.69
+10% clay content	0.68	0.98	0.08	0.69
–10% clay content	0.89	0.94	0.13	0.68
+ 0.5 pH	0.51	0.84	0.06	0.88
– 0.5 pH	0.96	1.04	0.14	0.58
Microbial activity index = 0.5	0.27	0.67	0.02	0.61
Without grazing	0.78	0.90	0.10	0.17

Table 2: Yearly average data for inferential estimation of dry fluxes

N–form	Average concentration	Mean deposition velocity
	($\mu g\ N\ m^{-3}$)	($mm\ s^{-1}$)
HNO_3	0.26	27[a]
NO_2	1.77	1.35[b]
NO_3^-	0.52	5.0[c]
NH_4^+	1.07	0.87[d]
NH_3	1.29	9.9[a]

[a]Horváth et al. (1992; 2005)
[b]Hesterberg et al. (1996); Horváth et al. (2005); Marner and Harrison (2004); Yamulki et al. (1997); Watt et al. (2004)
[c]Borrell et al. (1997)
[d]Gallagher et al. (2002)

Table 3: Annual sum of N-exchange between the biosphere and the atmosphere and the main physical parameters

Exchange processes	**2006**	**2007**	**2008**	**2009**	**2010**	**mean**
			(kg N $ha^{-1}year^{-1}$)			
Wet deposition of NO_3^-	–2.26±0.11	–2.04±0.10	–2.19±0.11	–2.15±0.11	–2.34±0.12	–2.19±0.11
Wet deposition of NH_4^+	–1.12±0.06	–2.17±0.11	–3.01±0.15	–2.35±0.12	–3.43±0.17	–2.42±0.88
Total wet deposition	–3.38±0.17	–4.21±0.21	–5.20±0.26	–4.50±0.23	–5.77±0.29	–4.61±0.92
Dry deposition of HNO_3	–1.57±0.16	–1.73±0.17	–2.64±0.26	–2.35±0.24	–2.95±0.29	–2.25±0.59
Dry deposition of NH_3	–4.18±0.21	–4.54±0.23	–5.32±0.27	–4.27±0.21	–3.79±0.19	–4.42±0.57
Dry deposition of NO_3^-	–1.01±0.05	–0.62±0.02	–0.83±0.04	–0.86±0.04	–0.72±0.04	–0.81±0.15
Dry deposition of NH_4^+	–0.35±0.02	–0.23±0.01	–0.27±0.01	–0.30±0.02	–0.32±0.02	–0.29±0.05
Dry deposition of NO_2	–0.75±0.04	–0.45±0.02	–0.80±0.04	–0.79±0.04	–0.95±0.05	–0.75±0.18
Total dry deposition	–7.86±0.37	–7.57±0.35	–9.86±0.62	–8.57±0.55	–8.73±0.59	–8.52±0.89
Total deposition	–11.2±0.54	–11.8±0.56	–15.1±0.88	–13.1±0.78	–14.5±0.88	–13.1±1.68
Soil emission of N_2O	0.18±0.02	0.15±0.02	0.57±0.06	0.63±0.06	1.80±0.18	0.67±0.07
Soil emission of NO	1.63±0.16	0.79±0.08	1.19±0.12[a]	1.18±0.12	0.78±0.08	1.11±0.35
Total soil emission ($NO+N_2O$)	1.81±0.18	0.94±0.10	1.76±0.18	1.81±0.18	2.58±0.26	1.78±0.58
Total soil emission[c] ($NO+N_2O+NH_3+N_2$)	2.21	1.48	1.99	1.67	2.91	2.08
Net flux (surface-atmosphere)	**–9.39±0.72**	**–10.9±0.66**	**–13.3±1.1[b]**	**–11.3±0.96**	**–11.9±1.14**	**–11.3±1.4**
Net flux[c] (surface-atmosphere)	**–9.66**	**–11.7**	**–14.0**	**–12.7**	**–11.6**	**–11.9**
Biological nitrogen fixation	–2.9±1.0	–2.9±1.0	–2.9±1.0	–2.9±1.0	–2.9±1.0	–2.9±1.0
Output by grazing	22±9.0	22±9.0	22±9.0	22±9.0	22±9.0	22±9.0
Input by excreta	–16±5.0	–16±5.0	–16±5.0	–16±5.0	–16±5.0	–16±5.0
Net balance (inc. BNF and grazing)[c]	**-6.6±9.0**	**-8.6±9.0**	**-10.9±9.0**	**-9.6±9.0**	**-8.5±9.0**	**-8.8±9.0**
Physical parameters	**2006**	**2007**	**2008**	**2009**	**2010**	**mean**
Temperature T_{air} (°C)	10.1	11.1	11.0	11.2	11.0	10.9±0.4
Temperature T_{soil} (°C)	10.2	11.5	11.1	11.4	10.9	11±0.5
Precipitation p (mm)	524	446	467	486	967	578±219
Soil wetness *WFPS* (%)	34.6±12	33.6±17	30.2±14	27.9±9.7	43±12	33.9±5.7

[a]No data for technical reason, calculated from the mean NO emission for 2006–2007 and 2009
[b]Estimated from the average of 2006–2010
[c]Soil flux estimated by DNDC modeling

Table 4: Measured and simulated C and N content in plant and soil and yearly grazed C and N estimated by the model

Year	C/N ratio in soil[a]		C/N ratio in plant[b]		C in plant	N in plant	Grazed C	Grazed N
	measured	simulated	measured	simulated		simulated		
		(%)				(kg $ha^{-1}year^{-1}$)		
2006	13.9	12.5	20.7	19.3	522	27	398	22
2007	13.0	12.5	21.2	19.1	458	24	302	17
2008	12.5	12.6	21.1	18.9	624	33	405	23
2009	14.9	12.6	20.5	18.9	435	23	270	15
2010	17.3	12.6	19.5	19.0	805	42	487	27
Average	14.3	12.6	20.6	19.0	568	30	372	21
SD	1.80	0.10	0.80	0.20	151	7.8	87	5.0

[a]average of 0–15 and 15–30 cm depths
[b]average of the below and above ground biomass

Table 5: Comparison of the measured and simulated (DNDC) soil N-fluxes

Year	I_2O		NO		N_2	NH_3	Total
	measured	simulated	measured	simulated	simulated	simulated	simulated
	(kg N ha^{-1} $year^{-1}$)						
2002	0.86	0.48	–	0.76	0.41	0.55	2.20
2003	0.80	0.64	–	0.50	0.45	0.37	1.96
2004	0.74	1.00	–	0.62	0.38	0.45	2.45
2005	–	0.43	–	0.67	0.31	0.43	1.84
2006	0.18	0.38	1.63	1.12	0.37	0.36	2.21
2007	0.15	0.23	0.79	0.57	0.39	0.29	1.48
2008	0.57	0.52	0.42	0.59	0.46	0.42	1.99
2009	0.63	0.24	1.18	0.47	0.68	0.28	1.67
2010	1.80	1.04	0.78	0.70	0.66	0.50	2.91
Average	0.72	0.55	0.96	0.67	0.46	0.41	2.08
SD	0.51	0.29	0.46	0.19	0.13	0.89	0.43

Fig. 1: Distribution of organic and inorganic nitrogen in the precipitation

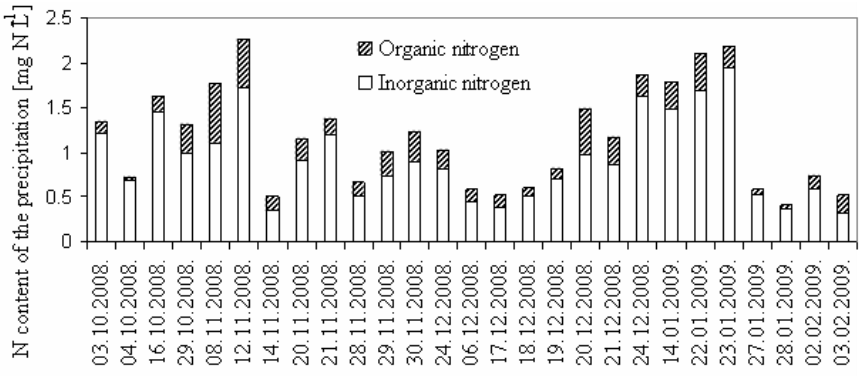

Fig. 2: Measured and simulated flux of N_2O (a) and their monthly correlation (b)

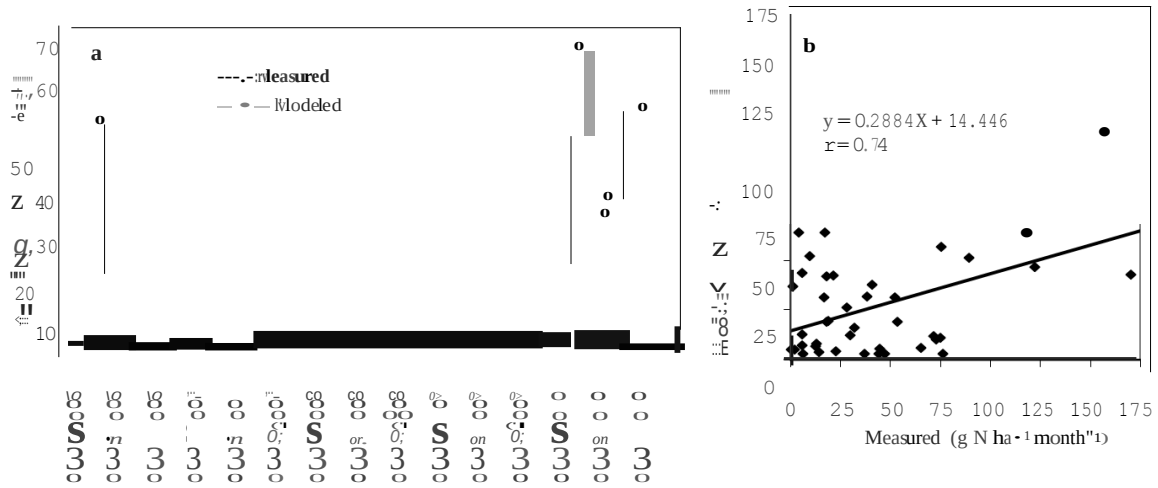

Fig. 3: Measured and simulated flux of NO (a) and their monthly correlation (b)

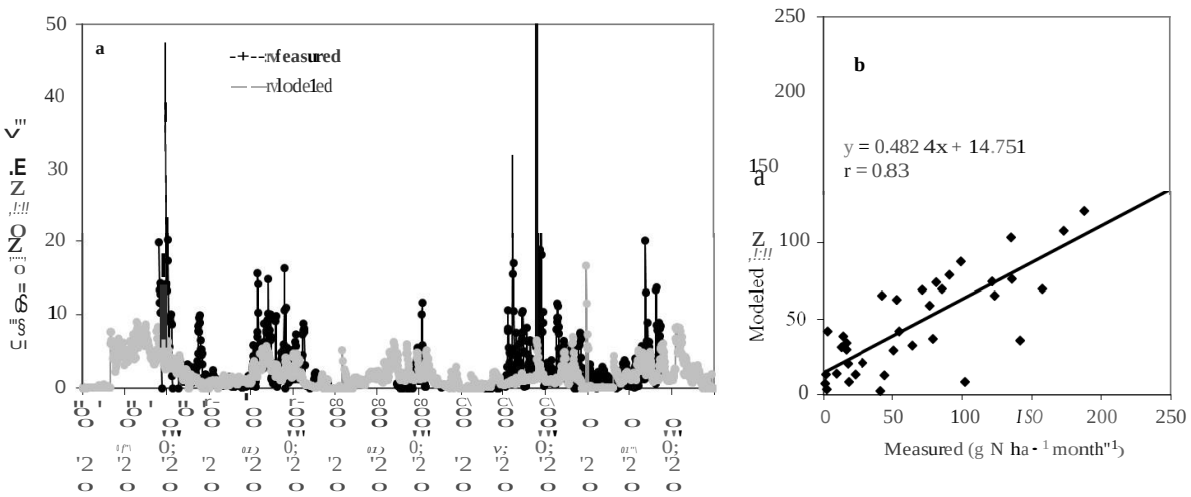

Fig. 4: Contribution of different N-forms to the N-budget in each year based on measurement and simulation (negative sign mean deposition and vice versa).