

**Project Number 282910**

**ÉCLAIRE**

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

**Seventh Framework Programme**

**Theme: Environment**

**MS13: Provision of site based estimates of NH<sub>3</sub>/NO and VOC exchange for  
 ÉCLAIRE core sites for present and future environmental conditions**

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

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Dissemination Level		
<b>PU</b>	Public	<input type="checkbox"/>
<b>PP</b>	Restricted to other programme participants (including the Commission Services)	<input checked="" type="checkbox"/>
<b>RE</b>	Restricted to a group specified by the consortium (including the Commission Services)	<input type="checkbox"/>
<b>CO</b>	Confidential, only for members of the consortium (including the Commission Services)	<input type="checkbox"/>

## 1) Executive Summary

- Ammonia volatilisation following nitrogen fertilisation is mostly temperature dependent: it increases by 12 to 30% (% TAN) with increasing temperature (2-6°C increase) and decreases slightly (a few percent) with increasing rainfall (20% rainfall increase).
- The variability in these emission changes is however high because of the short duration of the emissions which are therefore more sensitive to variability in local meteorology.
- NO emissions following nitrogen fertilisation are mostly temperature dependent: They increase by approximately 4 % (of average yearly NO emissions) with an increase / decrease in temperature (per °C) and decrease slightly (below one percent) with increasing/decreasing rainfall (per change of 10% of the yearly average rainfall).
- The variability in these emission changes is however extremely high because of the pulsing nature of the NO emissions following fertilization which are therefore much more sensitive to variability in future management compared to local meteorology.

**Objectives:**

The aim of WP3 was to provide improved parameterisations of biogenic and agricultural emissions to the modellers which include a robust response to climatic conditions that are predicted to change in the future. The individual objectives were to:

- To improve the climate response characteristics of NH<sub>3</sub> emission models for agricultural sources and vegetation,
- To improve the climate response characteristics of soil NO emission models,
- To improve European BVOC emission models and their response to meteorological drivers and stresses

The milestone MS13 objective was to give a summary report on site applications of improved NH<sub>3</sub> / NO and VOC models for present and future environmental conditions.

However, due to delayed availability of VOC emissions datasets, the VOC is not reported here. Moreover parts of the MS13 have been reported in the Deliverable D3.2 and D3.3.

**2) Activities:****a) Site based estimates of the NH<sub>3</sub> emissions with Volt'air and its meta-model for present and future environmental conditions****The Volt'air model**

The Volt'air ammonia volatilisation model is described at length in Générumont and Cellier (1997). It is a process-based model accounting for the water and solutes transfer and energy balance in the soil as well as the thermodynamic and chemical equilibria between phases. The soil is discretized in shallow layers at the surface. Volt'air is a process-based model, which is therefore adapted to simulations under climate changes. The Volt'air model was used to simulate NH<sub>3</sub> volatilisation following slurry spreading which constitutes one of the major NH<sub>3</sub> emission process to the atmosphere.

Since Volt'air is only adapted to crop sites with nitrogen fertilisation it can only be applied at these ÉCLAIRE sites. The model was therefore used for present conditions (2008, 2009 and 2012) for the Grignon site and for conditions where temperature was increased by +2°C, +4°C and +6°C and changes in rainfall of -20% -10%, 0%, +10% and +20%. This is intended to show the sensitivity of the model to the variables mainly influenced by climate change and which will also have a known effect on the emission processes. Indeed, NH<sub>3</sub> volatilisation results from a Henry thermodynamic equilibrium where a change of 5°C leads to a doubling of the gas-to-liquid partitioning (Sutton et al., 1995). In total three simulations times four temperature changes and five rain changes were run. No interactions between rain and temperature were simulated.

**The ammonia volatilisation meta-model based on Volt'air**

In order to generalise the simulations performed at the Grignon site with Volt'air, the NH<sub>3</sub> volatilisation meta-model described in the deliverable 3.1 was used to simulate the influence of climate change on NH<sub>3</sub> volatilisation in the 512 European sites and the two application periods (spring and summer). The combined effect of temperature increase (0, 2, 4, 6°C) and rainfall change (-20, -10, 0, +10, +20%) was evaluated for these 1024 situations. This provides a much more robust estimate of climate change effects on NH<sub>3</sub> volatilisation that complements the Volt'air simulations. Since the meta-model is itself derived from Volt'air it means that these results are equivalent to running Volt'air at the same sites.

**Results**

Volt'air NH<sub>3</sub> volatilisation sensitivity to climate change at the Grignon site

The simulations for showing the effect of temperature on the NH<sub>3</sub> volatilisation rates at the Grignon site, shows that median NH<sub>3</sub> volatilisation will increase by 5-6% with a 2- 6°C increase in temperature (Figure 1). Decrease in rainfall seems to increase median NH<sub>3</sub> volatilisation rates but an increase will also increase volatilisation (Figure 2). However, Figure 1 and Figure 2 also shows that there is a large variability in the simulations, as a result of the small number of runs. A pairwise T-test shows that the ammonia volatilisations for increased temperature and changed rainfall are not significantly different. This shows that such a sensitivity test performed on such a small number of fertilisation events (1 per year in Grignon), does not allow conclusions to be made on the sensitivity of NH<sub>3</sub> volatilisation to climate change. The meta-model has therefore been used to produce more generalised results.

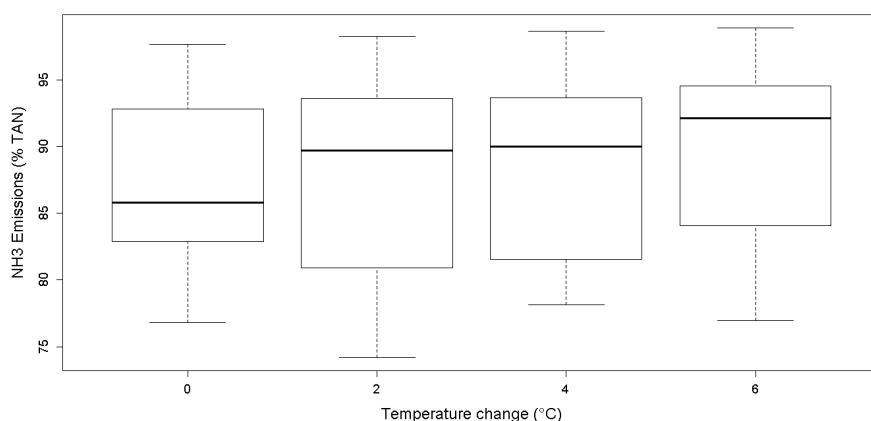


Figure 1. Boxplot of the NH<sub>3</sub> emission simulated by Volt'air as a function of the temperature change (rainfall changes are embedded in the statistics). Bold line is the median, the box shows the 25 and 75 percentile and the error-bars show the minimum and the maximum.

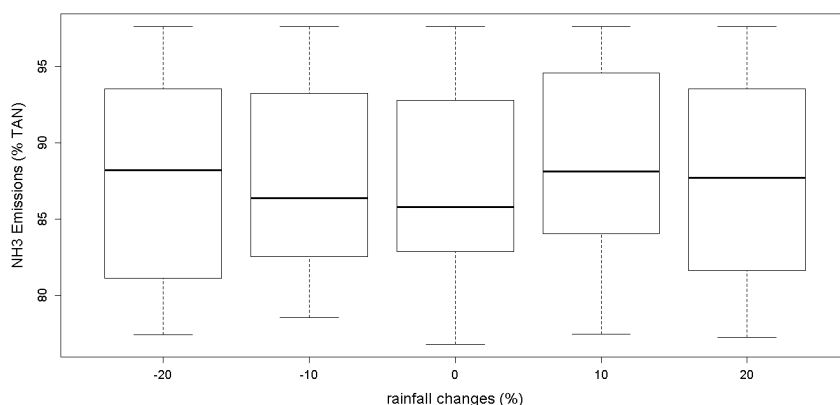


Figure 2. Boxplot of the NH<sub>3</sub> emission simulated by Volt'air as a function of the rainfall changes (temperature changes are embedded in the statistics). Bold line is the median, the box shows the 25 and 75 percentile and the error-bars show the minimum and the maximum.

### Generalisation of the sensitivity to climate change over Europe with the volatilisation Meta-model

Based on the 1024 dataset (multiplied by the temperature and rainfall changes studied cases), the sensitivity of the NH<sub>3</sub> volatilisation to both temperature and rainfall changes is much clearer. Figure 3 shows that volatilisation increases with temperature and decreases with rainfall regardless of fertiliser type. The effect of temperature, however, is more significant than the effect of rainfall (over the range of 6°C and ±20% rainfall tested here). Overall the increase with temperature is 30% for slurry, 12% for Farmyard manure and urea ammonium nitrate, over the 6°C increase simulated (Figure 3 and Figure 4).

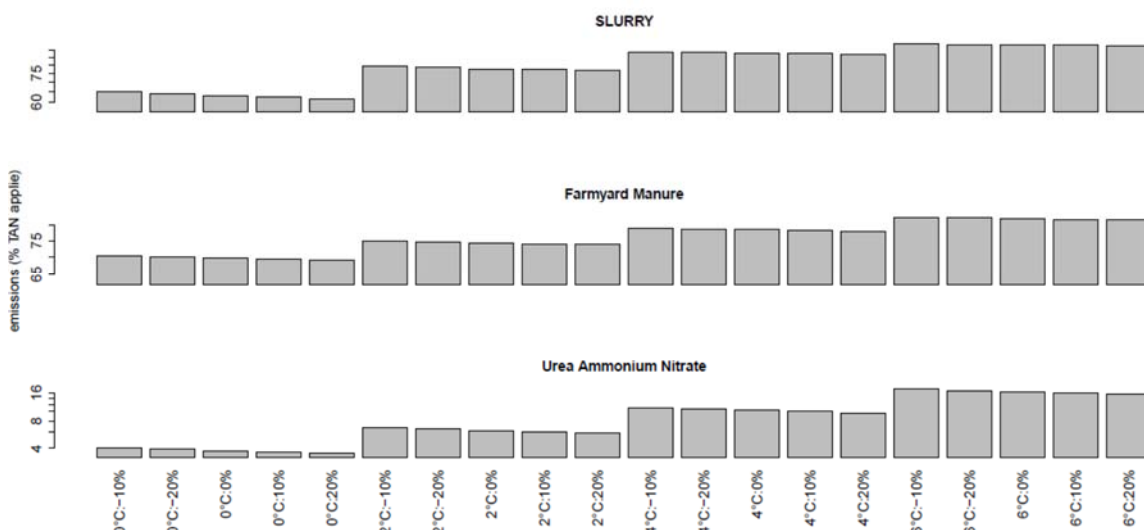


Figure 3. Median NH<sub>3</sub> emission simulated by the NH<sub>3</sub> volatilisation meta-model as a function of temperature and rainfall changes for each nitrogen fertiliser.

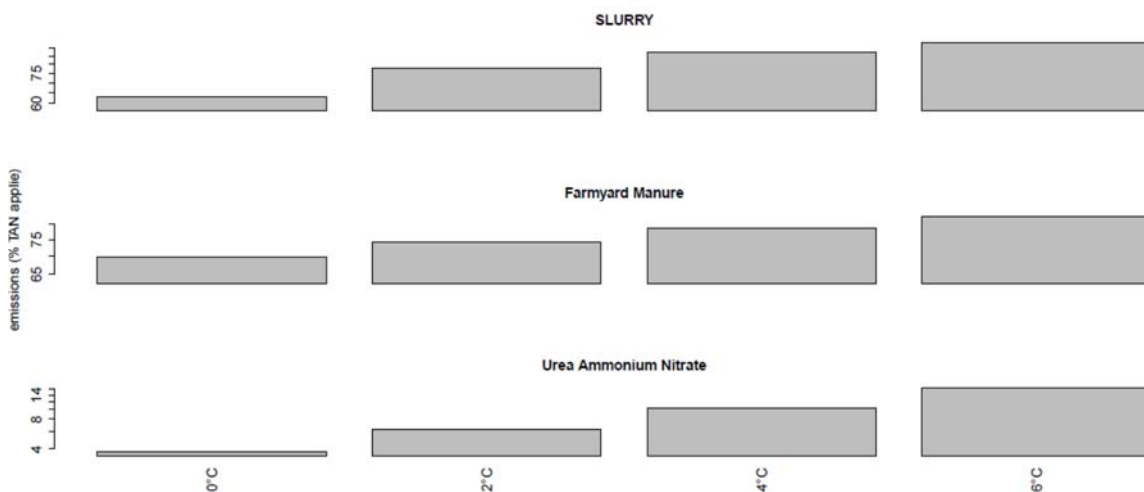


Figure 4. Median NH<sub>3</sub> emission simulated by the NH<sub>3</sub> volatilisation meta-model as a function of temperature changes for each nitrogen fertiliser.

Table 1 shows the linear regression coefficients and statistics of the NH<sub>3</sub> emissions (as a percentage of TAN applied) against temperature and rainfall changes. It shows that temperature is a significant factor while rainfall is not except for farmyard manure. Ammonia volatilisation is not greatly sensitive to rainfall changes (emissions (%tan) ~ -0.035 × (% rain change)). The sensitivity of NH<sub>3</sub> volatilisation to temperature is twice as large for slurry than for farmyard manure and urea ammonium nitrate, which can be explained by the much larger emission potential of the slurry compared to manure and mineral fertilisation (see deliverable 4.1, Figure 3). This means that slurry emissions are much less dependent on other factors (infiltration, adsorption on clay, etc.) than manure and mineral fertilisers are. Additionally, Table 1 shows that the product of rainfall and temperature increases is not an explanatory variable for NH<sub>3</sub> emissions.

**Table 1. Coefficient values and statistics of the linear regression between the 30 days cumulated emissions predicted by the NH<sub>3</sub> volatilisation meta-model, and the climate change variables (temperature and rain increase). The coefficient gives the response coefficient of the corresponding factor; Std. Error is its standard error; t value gives the t-test value; and Pr(>|t|) gives the probability of the null hypothesis (if lower than 0.0001, the parameter significantly affects the regression).**

	Coefficient	Std. Error	t value	Pr(> t )
<b>Slurry</b>				
Intercept	60.7	0.258	235.8	< 0.00001
Rain increase (% of actual rain)	-0.062	0.018	-3.4	0.0006
Increase in temperature (°C)	4.652	0.069	67.6	< 0.00001
product of the two factors above	0.005	0.005	1.0	0.32
<b>Farmyard manure</b>				
Intercept	68.6	0.108	634.2	< 0.00001
Rain increase (% of actual rain)	-0.035	0.008	-4.6	< 0.00001
Increase in temperature (°C)	2.078	0.029	71.9	< 0.00001
product of the two factors above	0.002	0.002	0.8	0.43
<b>Urea ammonium nitrate</b>				
Intercept	7.8	0.207	37.7	< 0.00001
Rain increase (% of actual rain)	-0.021	0.015	-1.4	0.15
Increase in temperature (°C)	2.546	0.055	46.1	< 0.00001
product of the two factors above	-0.004	0.004	-1.1	0.28

## Conclusions

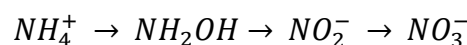
- Ammonia volatilisation following nitrogen fertilisation is mostly temperature dependent: it increases by 12 to 30% (% TAN) with increasing temperature (2-6°C increase) and decreases slightly (a few percent) with increasing rainfall (20% rainfall increase).
- The variability in these emission changes is however high because of the short duration of the emissions which are therefore more sensitive to variability in local meteorology.

## b) Site based estimates of the NO emissions with the LandscapeDNDC model for present and future environmental conditions

### Nitrification, denitrification and chemo-denitrification

Microbial nitrification and denitrification have been identified as major sources for NO and N<sub>2</sub>O whereas physicochemical processes such as chemodenitrification at soil pH values of < 5.0 for NO, occurring simultaneously in the soil.

Nitrification is an aerobic process usually referred to as the biological oxidation of ammonia (NH<sub>3</sub>) to nitrate (NO<sub>3</sub><sup>-</sup>) via the intermediate products ammonium (NH<sub>4</sub><sup>+</sup>), hydroxylamine (NH<sub>2</sub>OH) and nitrite (NO<sub>2</sub><sup>-</sup>):



During nitrification a certain amount of nitrogen is converted to NO and N<sub>2</sub>O by nitrifier denitrification. The model is based on the DNDC concept of nitrifier dynamics, which in turn is founded on the former work from. 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  $\mu_{mic}$ ,  $c_{mic}$  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 oneill equation (not shown).  $f_{NH_4}$  belongs to the available NH<sub>4</sub> in the soil. Finally  $\mu_{nit\_max}$  factor regulates the amount of NH<sub>4</sub> that will be transformed to NO<sub>2</sub> 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. Respective factors are adapted from the biochemistry of the DNDC modules. 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

$$N_2O_{NH_4-N_2O} = a_{NH_4} f_{tm} f_{pH} K_{N_2O}$$

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  $K_{N_2O}$  accounts 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 5, Figure 6).

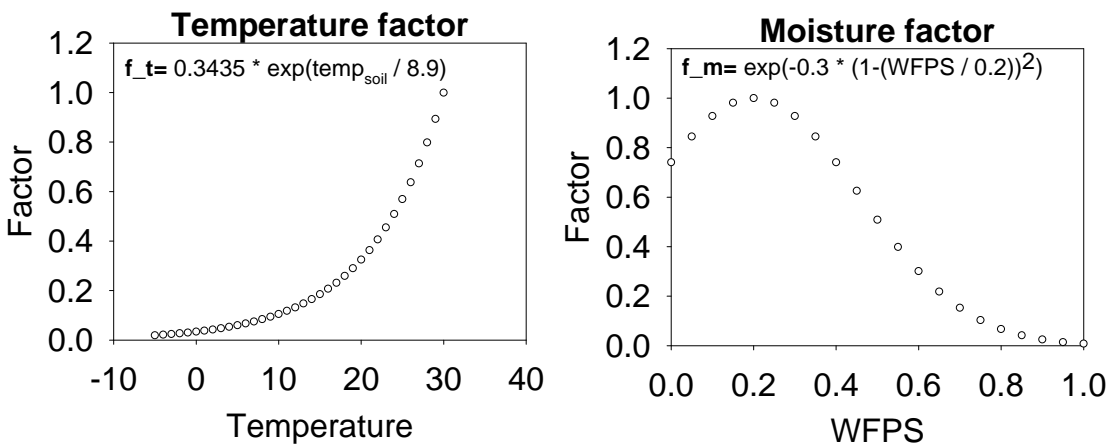


Figure 5 Temperature and moisture factors for  $NO$  emissions produced during nitrification

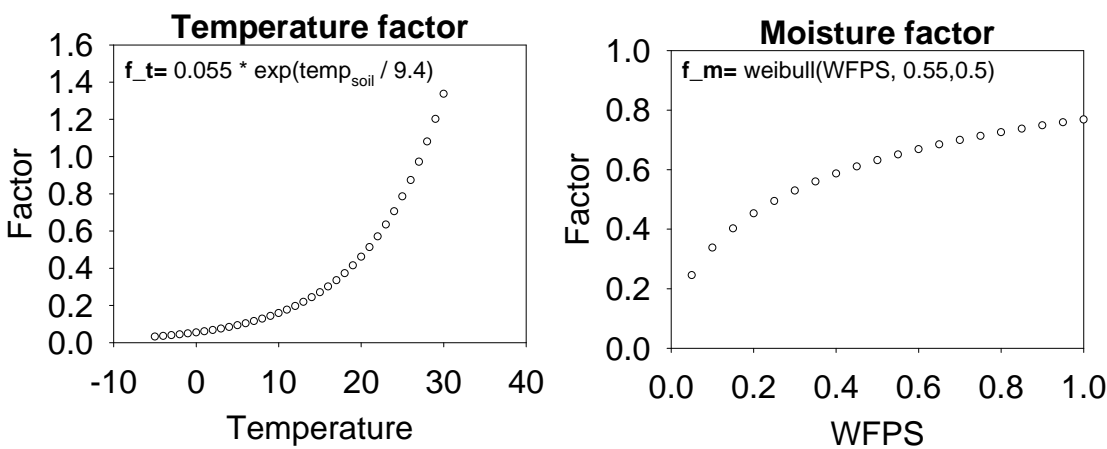
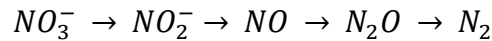


Figure 6 Temperature and moisture factor for  $N_2O$  emissions produced during nitrification step

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



To study the response of the simulated NO emissions to climate change conditions the LandscapeDNDC model was tested on a highly productive arable site which are expected to have the highest NO emissions. First NO emissions were simulated for observed present conditions for the Grignon site. When focusing on arable systems, the abrupt availability of ammonium and nitrate throughout fertilization is governing the budget of soil NO and N<sub>2</sub>O emissions, which can be demonstrated in Figure 7 and Figure 8. LandscapeDNDC is capable to predict the diurnal pattern of soil NO and N<sub>2</sub>O emissions with good agreement compared to the observations. The model captures the emission peaks well within the uncertainty of the observations. (Figures from the Deliverable 3.3)

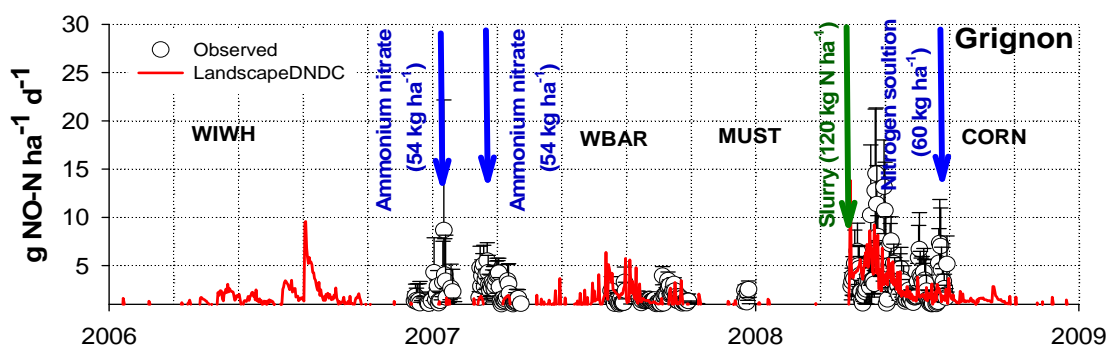


Figure 7 Daily NO emissions from arable soils at a research site close to Paris (Grignon, France)

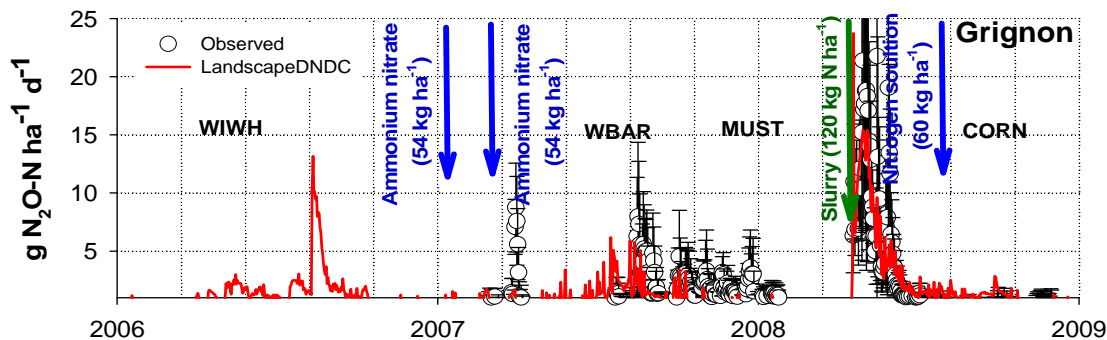


Figure 8 Daily N<sub>2</sub>O emissions from arable soils (Grignon, France)

To mimic environmental conditions of climate change the model input data was synthetically modified by alternating the temperature by +/- 1° and 2°C for temperature and by +/- 10 and 20% for precipitation. A combined dataset was constructed by simultaneously increasing/decreasing temperature and precipitation. The dataset was used to test the model response for NO emissions due to this climate change input. This is intended to show the sensitivity of the model to the input influenced by climate change and which will also have a known effect on the emission processes.

Indeed, NO emissions are directly influenced by temperature and moisture factors leading to a decrease/increase in the NO production. The interactions between rain and temperature were simulated but as the scenarios are selected arbitrarily, the final outcomes were assigned high uncertainties.



The model response based on the yearly average NO emissions was analysed for the altered climate input (Figure 9) resulted in linear responses of the modelled NO emissions to the temperature and precipitation input.

On the basis of yearly NO emission averages the response of the model to changes in yearly average temperature is linear by a factor of 0.0407 [kg NO – N / ha] per °C and a negative linear relationship of 0.0098 [kg NO – N / ha] per a change of 10% of annual average precipitation.

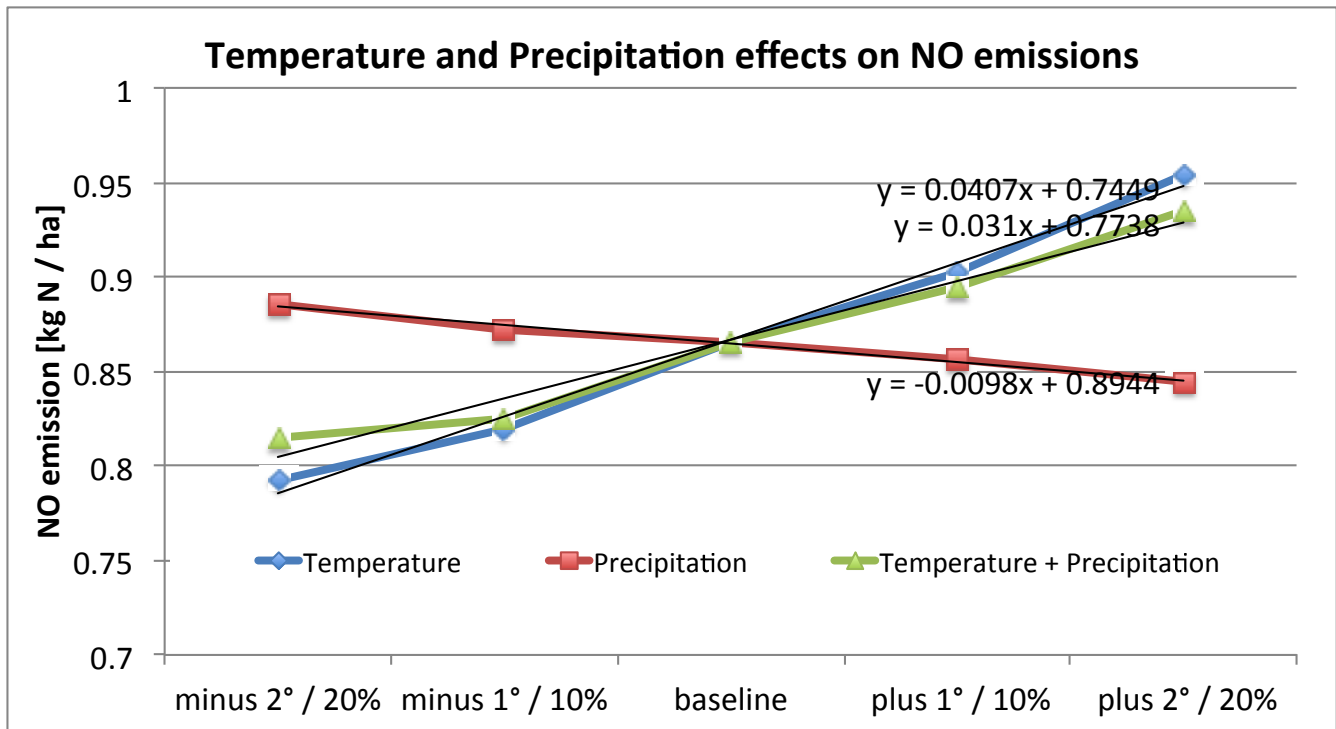


Figure 9 Temperature and Precipitation effects on NO emissions.

The findings have been validated for other ecosystems (Oensingen grassland site and Hoeglwald spruce forest) and could be confirmed but with different strengths of the resulting linear behaviour. This is due to the fact that each of the system is exposed to different nitrogen loads and is therefore in a different stage of nitrogen limitation. The study has also resulted in nonlinear response of the predicted NO emissions (data not shown) to changes in the agricultural management (mineral and organic fertilization rates) but this is not known for the future.

## Conclusion

- NO emissions following nitrogen fertilisation are mostly temperature dependent: They increases by approximately 4 % (of average yearly NO emissions) with an increase / decreases in temperature (per °C) and decrease slightly (below one percent) with increasing/decreasing rainfall (per change of 10% of the yearly average rainfall).
- The variability in these emission changes is however extremely high because of the pulsing nature of the NO emissions following fertilization which are therefore much more sensitive to variability in future management compared to local meteorology.

### 3) Publications

- Ferrara R.M., Loubet B., Decuq C., Palumbo A.D., Di Tommasi P., Magliulo V., Masson S., Personne E., Cellier P., Rana G., 2014. Ammonia volatilisation following urea fertilisation in an irrigated sorghum crop in Italy. *Agricultural and Forest Meteorology*, 195-196, 179-191.
- Flechard, C.R., Massad, R.-S., Loubet, B., Personne, E., Simpson, D., Bash, J.O., Cooter, E.J., Nemitz, E. and Sutton, M.A. 2013. Advances in understanding, models and parameterisations of biosphere-atmosphere ammonia exchange, *Biogeosciences* 10, 5183–5225.
- Personne, E., Tardy, F., Générumont, S., Decuq, C., Gueudet, J.-C., Mascher, N., Durand, B., Masson, S., Lauransot, M., Fléhard, C., Burkhardt, J. and Loubet, B., 2015. Investigating sources and sinks for ammonia exchanges between the atmosphere and a wheat canopy following slurry application with trailing hose. *Agric. For. Meteorol.*, 207: 11-23.
- Sutton, M.A.; Reis, S.; Riddick, S.N.; Dragosits, U.; Nemitz, E.; Theobald, M.R.; Tang, Y.S.; Braban, C.F.; Vieno, M.; Dore, A.J.; Mitchell, R.F.; Wanless, S.; Daunt, F.; Fowler, D.; Blackall, T.D.; Milford, C.; Flechard, C.R.; Loubet, B.; Massad, R.; Cellier, P.; Personne, E.; Coheur, P.F.; Clarisse, L.; Van Damme, M.; Ngadi, Y.; Clerbaux, C.; Skjoth, C.A.; Geels, C.; Hertel, O.; Wichink Kruit, R.J.; Pinder, R.W.; Bash, J.O.; Walker, J.T.; Simpson, D.; Horvath, L.; Misselbrook, T.H.; Bleeker, A.; Dentener, F.; de Vries, W. 2013. Towards a climate-dependent paradigm of ammonia emission and deposition. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences* 368 (1621) 10.1098/rstb.2013.0166.

### 4) References

- Générumont, S. and Cellier, P., 1997. A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil. *Agric. For. Meteorol.*, 88(1–4): 145-167.
- Sutton, M.A., Schjorring, J.K. and Wyers, G.P., 1995. Plant-atmosphere exchange of ammonia. *Philosophical Transactions of the Royal Society London serie A*, 351: 261-278.

### 5) Deviations and reasons:

This milestone was delayed because of the delayed development of the ESX model which was supposed to be used for such comparison. A different strategy was therefore developed in the last year of the project to revise parameterisation of the MNS-2010 model and develop meta-models out of existing CERES-EGC and Volt'air models.

No report on VOC models is included in this milestone due to delayed VOC emissions data from the ECLAIRE project.

### 6) List of Documents/Annexes:

None

