Simulation of nitrous oxide peak emissions from a Dutch peat soil with SWAP-ANIMO

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ABSTRACT: Nitrous oxide (N\textsubscript{2}O) is a very strong greenhouse gas, with agricultural soils as its main anthropogenic source. Various management practices, like fertilization or tillage, can give rise to pulses of N\textsubscript{2}O emissions. In spite of their short duration, in the order of a couple of days to weeks, these pulses can constitute a major part of total annual N\textsubscript{2}O emission. Understanding, predicting and ultimately mitigating these pulses poses a considerable challenge. In this study the model combination SWAP-ANIMO is used to assess the sources of N\textsubscript{2}O peak emissions in a Dutch peat land. The results show that the simulation of highly dynamic N\textsubscript{2}O fluxes is possible, but requires accurate modelling of the hydrology, the carbon cycle and the nitrogen cycle. Failure in the simulation of peak emissions can be traced back to failures in the simulation of soil moisture content. In peat lands, including macropores is expected to improve the simulation of soil moisture, especially after dry periods. Peak emissions from peat land are the result of coupled nitrification-denitrification. Nitrification produces continuously nitrate, which is the substrate for peak emission of N\textsubscript{2}O produced by denitrification. Only after ammonium fertilization nitrification contributes directly to the peak emissions. The larger peaks occur just after soil saturation, when the groundwater level is decreasing. N\textsubscript{2}O production then takes place just above the groundwater level.

1 INTRODUCTION

Nitrous oxide (N\textsubscript{2}O) is one of the main contributors to the greenhouse effect causing global warming (e.g. Denman et al. 2007), with agricultural soils as its main anthropogenic source (Van der Maas et al. 2008). Various management practices, like fertilization or tillage, can give rise to peak emissions of N\textsubscript{2}O. In spite of their short duration, in the order of a couple of days to weeks, these peaks can constitute a major part of total annual N\textsubscript{2}O emission (e.g. Scheer et al. 2008; Yamulki et al. 1995). Measuring, understanding, predicting and ultimately mitigating these peaks poses a considerable challenge (Groffman et al. 2009).
Simulation models offer a promising tool to test and further develop process knowledge on the heterogeneous nature of N\(_2\)O production and emission. They can be applied to develop process understanding, integrate emissions over large temporal and spatial scales, predict future emissions or evaluate potential mitigation measures. Simulation of peak emissions is an essential part of this modeling. Considering the duration of peaks, a simulation model with a timestep of a day or shorter is required for proper simulation of N\(_2\)O peak emissions. Various simulation models for N\(_2\)O fluxes with a daily timestep on the field scale are available. A review on the history, application, strength and limitation of N\(_2\)O simulation models has been provided by Chen et al. (2008). However, very little statistics are found in literature on the performance of these models at a daily timestep.

Simulation of daily N\(_2\)O emissions requires simulation of the environmental drivers: soil temperature, soil moisture, organic matter and mineral nitrogen. The interactions between these dynamical drivers leads to peak emissions during rainfall events or agricultural management practices (Groffman et al. 2009). Accurate modelling of the hydrology is especially important, as it affects all N\(_2\)O-processes: production, transport and consumption (Heincke and Kaupenjohann 1999). The description of the soil hydrological processes varies widely among the various models and is potentially the main cause of differing model results (Groffman et al. 2009).

SWAP-ANIMO is a process oriented agrohydrological-biogeochemical model combination, originally developed for the simulation of nutrient leaching. It includes the simulation of transport of heat and water in the soil as well as the simulation of the carbon-cycle and the nitrogen-cycle. The model has recently been extended with a module to simulate N\(_2\)O emissions. In the present study the SWAP-ANIMO model is used to simulate daily N\(_2\)O fluxes on a Dutch peat land. The objective is to determine the sources of N\(_2\)O peak emissions and to assess the role of hydrology in the N\(_2\)O production.

## 2 MATERIAL AND METHODS

### 2.1 Model description SWAP-ANIMO

SWAP (Van Dam 2000; Kroes et al. 2008; Van Dam et al. 2008) is a multi-layered simulation model with output of soil moisture and soil temperature on a daily basis or shorter. Soil moisture transport calculations are based on the Richards equation and allows more complex processes like hysteresis, macroporous flow and water repellency. Top, bottom and lateral boundary conditions in SWAP allow runon and runoff, irrigation, lateral drainage to and infiltration from drains and surface water and seepage to or infiltration from deeper aquifers.

ANIMO (Rijtema and Kroes 1999; Groenendijk et al. 2005; Renaud et al. 2005) is a simulation model with a daily timestep for nutrients (N and P) and organic matter in the soil. Its layering is equal to SWAP and it uses the output from SWAP to prescribe water flow, soil moisture and soil temperature. Recently an N\(_2\)O module has been added (Hendriks et al., in prep.). Nitrogen components are N\(_2\)O, ammonia (NH\(_3\)), ammonium (NH\(_4\)) and nitrate (NO\(_3\)). Nitrogen inputs can occur via fertilization, incorporation of plant residues, root-exudates, atmospheric deposition and infiltration of nutrient rich water from ditches, infil-
tration drains or deeper aquifers. Nitrogen transformation processes include, mineralization, immobilization, nitrification and denitrification of NO$_3$ and N$_2$O. These processes are affected by the environmental parameters aeration, moisture deficit, temperature and acidity (pH). Transport of nitrogen components occurs both in the soil solution (NO$_3$, NH$_4$, N$_2$O) and in the gaseous phase (N$_2$O), both via diffusion and advection-dispersion. Output of nitrogen occurs via plant uptake (NH$_4$, NO$_3$), gaseous emissions (NH$_3$, N$_2$O) and leaching (NH$_4$, NO$_3$, N$_2$O).

2.2 Site description

The model was validated with observations from a site located in a polder in the west of the Netherlands near the village Stein (52° 01’ 15.09”N - 4° 46’31.53”E). The topsoil (< 30 cm) consists of peaty clay on a subsoil of eutrophic peat. It is classified as a Terric Histosol (FAO 1998). Originally the site was used for grass production, but it was taken out of production between 2000 and 2003. The site is now a meadow bird reserve and in use as hay field (Veenendaal et al., 2007).

The N$_2$O flux data was collected with two automatic chambers during 2006. The flux chambers were placed at about 2 m from a ditch. The chambers had a surface area of 0.6 m by 0.8 m and a height of 0.1 m. The chambers were closed for 60 minutes once every four hours. Gas concentrations were determined after 59 minutes. The outside concentration was determined after 4 minutes and was considered representative for the concentration inside the box at the time of closing. Gas concentration measurements were performed with a gas chromatograph (GC) located on the site. The GC was fitted with an electron capture detector (ECD) for N$_2$O. One calibration standard was applied to the GC once during every closure period. In 2006 the chambers received fertilization with ammonium-nitrate fertilizer on 21 September 2006 with 59 kg N ha$^{-1}$. There was no grazing.

Complementary measurements included soil moisture and soil temperature measured hourly at 5 cm and 30 cm. On 3 April and 31 July 2008, after removal of the chambers, soil samples were taken and analysed in the laboratory (see Table 1).

Table 1 Soil characteristics of Stein, average values.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>N-content (%)</th>
<th>C-content (%)</th>
<th>pH-KCl (-)</th>
<th>Bulk density (g cm$^{-3}$)</th>
<th>Clay (% of mineral parts)</th>
<th>Silt (%)</th>
<th>Sand (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>1.6</td>
<td>16.7</td>
<td>4.5</td>
<td>0.57</td>
<td>26</td>
<td>33</td>
<td>24</td>
</tr>
<tr>
<td>10-30</td>
<td>1.0</td>
<td>11.4</td>
<td>5.0</td>
<td>0.73</td>
<td>29</td>
<td>33</td>
<td>27</td>
</tr>
<tr>
<td>30-55</td>
<td>2.5</td>
<td>31.7</td>
<td>5.0</td>
<td>0.34</td>
<td>31</td>
<td>34</td>
<td>3</td>
</tr>
<tr>
<td>&gt; 55</td>
<td>2.9</td>
<td>43.7</td>
<td>4.9</td>
<td>0.17</td>
<td>18</td>
<td>20</td>
<td>18</td>
</tr>
</tbody>
</table>

2.3 Parameterization

SWAP and ANIMO were parameterized based on the soil analyses, the soil moisture observations and historical observations at this site (Veenendaal et al. 2007). Parameterization of the Mualem-Van Genuchten function for the water retention curve was based on the soil classification, following Wösten et al. (2001). Meteorological input was taken from the KNMI site of Cabauw, located near Stein. The resistance of the peat layer to vertical flow and the hydraulic head in the deeper aquifer were taken from the database of TNO (www.dinoloket.nl). Parameters for oxygen diffusion were based on the soil classification
following Groenendijk et al. (2005, p.77). For the N₂O module the default parameterization was used (Hendriks et al. in prep.).

Further parameterization for SWAP and ANIMO was taken from the corresponding plot in the nutrient emission modeling system STONE, version 2.3 (Wolf et al. 2003; Bakel et al. 2008). STONE is a chain of models developed for simulations on the regional and national scale in the Netherlands. Within STONE the hydrology and biogeochemistry are calculated with SWAP and ANIMO, respectively. The material definitions were slightly modified compared to STONE 2.3 based on measurements and expert judgement (Hendriks pers. comm.; see Table 2).

The initial conditions for the start of our modelling period on 1 January 2006 were determined via a start-up run with STONE from 1941 through 2005 for the selected STONE plot, using the modified material definitions. The output of organic matter in various fractions was scaled to match the measured organic matter content per layer in ANIMO. To prevent instabilities from the change in organic matter, additionally we ran ANIMO for one year (2006). The output of this run was used for the initial conditions. More work has to be done to improve the initial conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Present study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition rate constant high N-content eutrophic peat (a⁻¹)</td>
<td>0.0383</td>
</tr>
<tr>
<td>Decomposition rate constant low N-content eutrophic peat (a⁻¹)</td>
<td>0.001</td>
</tr>
<tr>
<td>N-content high N-content eutrophic peat (kg kg⁻¹)</td>
<td>0.0511</td>
</tr>
<tr>
<td>N-content low N-content eutrophic peat (kg kg⁻¹)</td>
<td>0.0333</td>
</tr>
<tr>
<td>C-content organic material (kg kg⁻¹)</td>
<td>0.58</td>
</tr>
</tbody>
</table>

2.4 Calibration

For SWAP a sensitivity analysis showed that the most sensitive parameters are the shape parameters alpha and n in the Mualem-Van Genuchten function in the layers 1 and 2 (Van Genuchten 1980), the saturated conductivity in the layers 1 and 2, and the drainage and infiltration resistance of the ditch. These parameters were roughly calibrated based on the observed soil moisture content. We included hysteresis to account for water repellency after a long dry spell in the summer. The parameter alpha for the wetting curve was estimated to be twice as large as alpha for the drying curve. In ANIMO, based on the calibration results, we decreased the decomposition rate for the fraction slow decomposing peat and humus.

Both for SWAP and ANIMO this is a first, rough calibration, still open for improvement.

2.5 Statistics

The goodness of fit for the simulation was expressed as the coefficient of determination $r^2$ (Spiegel, 1988) and the modeling efficiency $r^2_{eff}$ (Nash and Sutcliffe, 1970):

$$r^2 = \frac{\sum (P - \bar{P})(O - \bar{O})^2}{\sum (P - \bar{P})^2 \sum (O - \bar{O})^2}$$

(1)
\[ r^2_{\text{eff}} = 1 - \frac{\sum (P - O)^2}{\sum (O - \bar{O})^2} \]  

(2)

3 RESULTS AND DISCUSSION

3.1 Simulation results

Figure 1 and 2 show the observed and the simulated daily \( \text{N}_2\text{O} \) emissions and the observed and simulated soil moisture content, respectively. The observed \( \text{N}_2\text{O} \) emission shows seven peaks, around day 5, 50, 75, 240, 275, 300 and 320, respectively. All peak emissions occur after rainfall events. Fertilization took place at day 264.

The simulation results show a fair representation of the daily \( \text{N}_2\text{O} \) emissions, with \( r^2 = 0.42 \) and \( r^2_{\text{eff}} = 0.32 \). This is higher than the few values found in literature. The larger peaks around day 275 and 300 were simulated at the right time by the model, although the maximum emission levels are underestimated. The peak around day 240 was not simulated by the model. The smaller peaks around day 50 and 75 were captured by the simulation model, whereas the peaks around day 5 and 320 were not captured by the model.

Simulation of the soil moisture is good, with \( r^2 = 0.78 \) and \( r^2_{\text{eff}} = 0.74 \). Still, the simulation is too high from day 220 to 300. Field observations revealed that after the drought period before day 220 shrinkage cracks were present in the soil. These macropores can cause rapid drainage of precipitation to the ditches. They can stay open for prolonged time. In the hydrological model so far no shrinkage cracks were simulated.

![Figure 1 Observed and simulated N\(_2\)O emissions](image)

Figure 1 Observed and simulated \( \text{N}_2\text{O} \) emissions
3.2 Sources of $\text{N}_2\text{O}$ peak emission

Figure 3 shows the simulated production of $\text{N}_2\text{O}$ by denitrification in the soil profile throughout the year and the simulated groundwater level. Comparison of Figures 1 and 2 reveals that most peak emissions result from $\text{N}_2\text{O}$ production by denitrification. Only after the fertilization event, $\text{N}_2\text{O}$ produced by nitrification adds to the peak emission around day 275 (not shown). Denitrification mainly takes place in the upper 40 cm of the soil, where $\text{NO}_3$ is present. Here $\text{NO}_3$ is produced continuously by nitrification of $\text{NH}_4$, which on its turn is produced continuously by mineralisation during organic matter decomposition. This coupled nitrification-denitrification is typically for peat lands.

The results in Figures 1-3 also show that the simulated peaks around day 50, 75, 275 and 300 coincide with periods just after saturation of the soil profile. $\text{N}_2\text{O}$ production takes place just above the decreasing groundwater level. Smaller peaks occur after rainfall when the soil is not saturated. $\text{N}_2\text{O}$ is then produced just below the surface. Denitrification also takes place under the groundwater level, but this does not cause emissions to the atmosphere. Apparently, most $\text{N}_2\text{O}$ produced under the groundwater level is removed in another way, most probably by leaching.

Failures in the simulation of $\text{N}_2\text{O}$ emission coincide with failures in the simulation of the soil moisture content. Around day 5 the simulated soil moisture content was too low. Around days 240 and 320 the soil moisture content was too high and the model simulated a prolonged period of saturation. In the simulation the substrate was depleted by denitrification under the groundwater level (see Figure 3). The observations reveal that in reality saturation did not occur. As mentioned before, this is probably due to rapid drainage to shrinkage cracks. In future simulations we will test the hypothesis that implementation of shrinkage cracks in the hydrological model will further improve the simulation of both the soil moisture content and the $\text{N}_2\text{O}$ emissions.
Figure 3 Location of N$_2$O production by denitrification in the soil profile. The darker colours indicate the higher production rates up to 0.9 g N$_2$O-N m$^{-3}$d$^{-1}$.

4 CONCLUSION

The results of this study show that simulation of highly dynamic N$_2$O fluxes is possible, but requires accurate modelling of the hydrology, the carbon cycle and the nitrogen cycle in the soil. The carbon and nitrogen cycles are linked through the decomposition of organic matter that produces NH$_4$ through mineralization. Failure in the simulation of peak emissions can be traced back to failures in the simulation of soil moisture content. Accounting for effects of macropores on the soil water transport is expected to improve simulations of both soil moisture and N$_2$O emissions in peatlands after dry spells. Peak emissions from peatland are the result of coupled nitrification-denitrification. Nitrification produces almost continuously NO$_3$, giving small background emissions of N$_2$O at the same time. Denitrification of this NO$_3$ causes most peak emissions of N$_2$O. This system is typically for peatlands. The larger emission peaks occur just after soil saturation, when the groundwater level is decreasing. N$_2$O production then takes place just above the groundwater level. Peak emissions due to N$_2$O production directly by nitrification only occur after NH$_4$ fertilization.

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