Influence of modelled soil biogenic NO emissions on related trace gases and the atmospheric oxidizing efficiency

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Abstract. The emission of nitric oxide (NO) by soils (SNOx) is an important source of oxides of nitrogen (NO\textsubscript{x}=NO+NO\textsubscript{2}) in the troposphere, with estimates ranging from 4 to 21 Tg of nitrogen per year. Previous studies have examined the influence of SNOx on ozone (O\textsubscript{3}) chemistry. We employ the ECHAM5/MESSy atmospheric chemistry model (EMAC) to go further in the reaction chain and investigate the influence of SNOx on lower tropospheric NO\textsubscript{x}, O\textsubscript{3}, peroxyacetyl nitrate (PAN), nitric acid (HNO\textsubscript{3}), the hydroxyl radical (OH) and the lifetime of methane (\textgreek{t}_{CH\textsubscript{4}}).

We show that SNOx is responsible for a significant contribution to the NO\textsubscript{x} mixing ratio in many regions, especially in the tropics. Furthermore, the concentration of OH is substantially increased due to SNOx, resulting in an enhanced oxidizing efficiency of the global troposphere, reflected in a \sim10\% decrease in \textgreek{t}_{CH\textsubscript{4}} due to soil NO emissions. On the other hand, in some regions SNOx has a negative feedback on the NO\textsubscript{x} emissions through O\textsubscript{3} and OH, which results in regional increases in the mixing ratio of NO\textsubscript{x} despite lower total emissions in a simulation without SNOx. In a sensitivity simulation in which we reduce the other surface NO\textsubscript{x} emissions by the same amount as SNOx, we find that they have a much weaker impact on OH and \textgreek{t}_{CH\textsubscript{4}} and do not result in an increase in the NO\textsubscript{x} mixing ratio anywhere.

1 Introduction

Nitric oxide (NO) in the soil is produced by the microbial processes of nitrification and denitrification (Firestone and Davidson, 1989). The NO emission originates from a natural pool of nitrogen and a fraction from fertilizer application (Yienger and Levy II, 1995; Stehfest and Bouwman, 2006). The estimates of NO emitted yearly by soils (hereafter called SNOx) ranges from 4 to 21 Tg(N) (Yienger and Levy II, 1995; Davidson and Kingerlee, 1997, and references therein). NO reacts rapidly with other atmospheric compounds, establishing an equilibrium between NO and nitric dioxide (NO\textsubscript{2}). These two species are frequently referred to as the oxides of nitrogen (NO\textsubscript{x}). Through reactions, deposition and stomatal uptake directly within the vegetation layer not all NO emitted by the soil escapes the canopy layer as NO\textsubscript{x} (Yienger and Levy II, 1995; Ganzeveld et al., 2002b).

SNOx is topped by the anthropogenic combustion of fossil fuels (20–24 Tg(N) yr\textsuperscript{-1}) (Denman et al., 2007) and is comparable to the production of NO\textsubscript{x} from lightning and biomass burning, but especially in remote continental regions of the mid- and low-latitudes SNOx is the dominant source of NO\textsubscript{x}. In this work SNOx refers to the flux from the canopy to the atmosphere.

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of methane (CH₄), another greenhouse gas. Beyond these climate related issues, high NOₓ and O₃ mixing ratios also have a direct impact on human health and on the vegetation (Sitch et al., 2007). NOₓ is removed from the atmosphere by reaction with hydroxyl radicals (OH) or oxidation to dinitrogen pentaoxide (N₂O₅) and subsequent deposition as nitric acid (HNO₃). It can also react with organic tracers to form peroxyl nitrates, mainly peroxyacetyl nitrate (PAN), which, once it is lifted to higher altitudes, can be transported over large distances releasing NOₓ when it is transported back downward again.

Previous model studies of the influence of SNOx on atmospheric chemistry mainly focused either on the NOₓ source itself, on O₃, mostly on a regional scale. Ganzeveld et al. (2002a,b) investigate two different modeling approaches of the role of canopy processes on the effective exchange of NOₓ between the canopy and atmosphere. They concluded that the application of the big leaf approach with a separate treatment of dry deposition and biogenic emissions, in which the canopy reduction factor accounts for the fraction of these emission that escapes the canopy, provides a reasonable first order estimate of NOₓ canopy top fluxes. Jaeglé et al. (2005) examined the global partitioning of NOₓ sources using inverse modelling and the space-based NO₂ column derived by GOME (Global Ozone Monitoring Experiment). Their a posteriori SNOx (8.9 Tg(N) yr⁻¹) is 68% greater than their a priori SNOx (5.3 Tg(N) yr⁻¹). Based on this, Jaeglé et al. (2005) suggest that the influence of SNOx on background O₃ could be underestimated in current chemistry transport models (CTMs). Bertram et al. (2005) come to a similar conclusion by inverse modelling using another satellite sensor (SCIAMACHY) above the Western United States, computing an underestimation of 60%. Delon et al. (2008) modelled higher O₃ concentrations with higher SNOx above Western Africa. For Europe, Simpson (1995) found that SNOx hardly has any influence on controlling the O₃ mixing ratio. Isaksson and Hov (1987) already investigated the influence of changes in the emission intensity of different relevant trace gases on the oxidizing efficiency through an increase in OH concentration with increased NOₓ emissions, but they did not consider SNOx separately in their assessment. Fuglestvedt et al. (1999) demonstrate the importance of the geographical region of NOₓ sources for the changes in the ozone concentration and the oxidizing efficiency.

In this study, we take these analysis a step further and follow the reaction chain from SNOx through O₃ and OH to its global influence on the oxidizing efficiency of the atmosphere. To do so, we compare two model runs with a state-of-the-art 3-D global chemistry climate model. One is a simulation with all relevant emissions and reactions (BASE), and the second simulation is without SNOx (NOBIONO = “No biogenic NO”). We expect a considerable influence of SNOx on the mixing ratios and distribution of related global tropospheric trace gases (NOₓ, PAN, HNO₃, O₃ and OH). Furthermore, the global oxidizing efficiency, indicated by the lifetime of CH₄ (tCH₄), is expected to decrease (tCH₄ increases) if we exclude NOₓ emission from soils. To investigate whether other surface NOₓ emissions result in similar effects, or if they differ due to differences in their distribution, we performed a third simulation (REDOOTHER) in which we reduced the NOₓ emission from all other sources by the same amount as is emitted by the soils.

In the following section we briefly describe the model setup. We then compare the relevant tracer mixing ratios from the BASE simulation versus the NOBIONO and REDOTHER simulations. In the final section we present our conclusions and outlook.

2 Model description and setup

2.1 General

For this study the Modular Earth Submodel System version 1.6 (MESSy) coupled to the general circulation model ECHAM5 is employed. MESSy connects, through a standardized interface, submodels for different processes with bidirectional feedbacks (Jöckel et al., 2005, 2006). The combined system is referred to as the ECHAM5/MESSy atmospheric chemistry (EMAC) model. The meteorology for these simulations is driven by sea surface temperature (SST) from the AMIPIIb dataset (Taylor et al., 2000). The calculation of SNOx in the BASE simulation is based on the algorithm of Yienger and Levy II (1995), which is the most widely used SNOx algorithm in CTMs (Ganzeveld et al., 2002a; Jaeglé et al., 2005; Delon et al., 2008). This calculation is performed in the submodel ONLEM (Kerkweg et al., 2006b). NOₓ produced by lightning is calculated in the submodel LNOX (1.6 Tg(N) yr⁻¹). The remaining sources of NOₓ (43.5 Tg(N) yr⁻¹) are read in from the offline EDGAR database (Olivier et al., 1994) by the submodel OFFLEM (Kerkweg et al., 2006b). NO emission from fossil fuel combustion, biomass and biofuel burning are combined and account for 43 Tg(N) yr⁻¹, while aircraft emit only 0.6 Tg(N) yr⁻¹. Other relevant emissions are calculated either by the ONLEM or OFFLEM submodel.

A model spinup time of eleven months (January–November 1994) was chosen and the data of the period December 1994–December 1995 is analyzed here. To achieve an identical meteorology of both simulations feedback through trace gases and water vapor is switched off. Table 1 recapitulates the setup of the two simulations.

In the BASE simulation a yearly emission flux of 9.7 Tg(N) was calculated. In the REDOTHER simulation the offshore surface NO emission (43 Tg(N) yr⁻¹) are reduced globally by 22.5%, which corresponds to 9.7 Tg(N) yr⁻¹.

2.2 Soil NO emission algorithm

The emission of NO from soils is calculated based on the algorithm developed by Yienger and Levy II (1995) and...
Table 1. Setup of the ECHAM5/MESSy model and applied submodels.

<table>
<thead>
<tr>
<th>Setup</th>
<th>Timestep of output</th>
<th>Literature ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horizontal resolution T42 (∼2.8°×2.8°)</td>
<td>20 min</td>
<td></td>
</tr>
<tr>
<td>Vertical resolution L31 (up to 10 hPa)</td>
<td>5 h</td>
<td></td>
</tr>
<tr>
<td>Internal timestep</td>
<td>1994–1995</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Used submodels</th>
<th>Calculation of</th>
<th>Literature ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLOUD</td>
<td>Clouds and precipitation</td>
<td>Jöckel et al. (2006)</td>
</tr>
<tr>
<td>CONVECT</td>
<td>Convection</td>
<td>Tost et al. (2006b)</td>
</tr>
<tr>
<td>CVTRANS</td>
<td>Convective tracer transport</td>
<td>Tost (2006)</td>
</tr>
<tr>
<td>DRYDEP</td>
<td>Dry deposition</td>
<td>Kerkweg et al. (2006a)</td>
</tr>
<tr>
<td>JVAL</td>
<td>Rates of photolysis</td>
<td>Jöckel et al. (2006)</td>
</tr>
<tr>
<td>LNOX</td>
<td>Lightning NOx</td>
<td>Tost et al. (2007)</td>
</tr>
<tr>
<td>MECCA</td>
<td>Chemical atmospheric reactions</td>
<td>Sander et al. (2005)</td>
</tr>
<tr>
<td>OFFLEMb</td>
<td>Offline emissions</td>
<td>Kerkweg et al. (2006b)</td>
</tr>
<tr>
<td>ONLEMc</td>
<td>Online emissions</td>
<td>Kerkweg et al. (2006b)</td>
</tr>
<tr>
<td>RAD4ALL</td>
<td>Radiation</td>
<td>Jöckel et al. (2006)</td>
</tr>
<tr>
<td>SCAV</td>
<td>Wet deposition</td>
<td>Tost et al. (2006a)</td>
</tr>
<tr>
<td>TNUDGE</td>
<td>Tracer nudging</td>
<td>Kerkweg et al. (2006b)</td>
</tr>
<tr>
<td>TROPOP</td>
<td>Calculation of the tropopause</td>
<td>Jöckel et al. (2006)</td>
</tr>
</tbody>
</table>

a Tropospheric reaction with NMHC and without halogens.
b Biomass burning and fossil fuel NO emission reduced in REDOTHER.
c Soil NO emissions switched off in NOBIONO simulation.

depends on ecosystem type, soil moisture state and the surface temperature. Our underlying ecosystem map is compiled from Olson (1992) (Ganzeveld et al., 2006), which 72 ecosystem classes have been reduced to the twelve ecosystems defined by Yienger and Levy II (1995), with corresponding dry and wet emission factors (Table 2). Agriculture and (tropical) rainforest is treated separately. In the original algorithm the precipitation history is used to distinguish between the dry and wet soil moisture state. In our implementation we define the dry state to be when the soil moisture is below 10% volumetric soil moisture and wet above 10%. The temperature dependence is calculated according to Eq. (1) for wet soil conditions and (2) for dry soil conditions.

\[
F_{NO}(T, A_w) = \begin{cases} 
0 & T > 30^\circ C \\
0.28\cdot T \cdot A_w & 0^\circ C < T \leq 10^\circ C \\
0.103\cdot T \cdot A_w & 10^\circ C < T \leq 30^\circ C \\
21.97 \cdot A_w & T > 30^\circ C 
\end{cases}
\] (1)

\[
F_{NO}(T, A_d) = \begin{cases} 
0 & T > 30^\circ C \\
0.03\cdot T \cdot A_d & 0^\circ C < T \leq 30^\circ C \\
0.03 & T > 30^\circ C 
\end{cases}
\] (2)

In the rainforest Yienger and Levy II (1995) assumed SNOx to be constant: a dry emission factor is applied for the five driest months (Northern Hemisphere: May–September, Southern Hemisphere: November–March) and a wet emission factor for the remaining seven months. For agricultural areas wet grassland conditions are assumed for the whole year. On top of that, fertilizer induced emission based on Bouwman and Boumans (2002) is added.

Table 2. Ecosystems and emission factors according to Yienger and Levy II (1995).

<table>
<thead>
<tr>
<th>Ecosystem</th>
<th>wet $A_{w,e}$</th>
<th>dry $A_{d,e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 water</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2 ice</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3 desert</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4 scrubland</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5 tundra</td>
<td>0.05</td>
<td>0.37</td>
</tr>
<tr>
<td>6 grassland</td>
<td>0.36</td>
<td>2.65</td>
</tr>
<tr>
<td>7 woodland</td>
<td>0.17</td>
<td>1.44</td>
</tr>
<tr>
<td>8 deciduous forest</td>
<td>0.03</td>
<td>0.22</td>
</tr>
<tr>
<td>9 coniferous forest</td>
<td>0.03</td>
<td>0.22</td>
</tr>
<tr>
<td>10 dry deciduous forest</td>
<td>0.06</td>
<td>0.4</td>
</tr>
<tr>
<td>11 rainforest</td>
<td>2.6</td>
<td>8.6</td>
</tr>
<tr>
<td>12 agriculture</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

If, after a certain period of dryness, the soil receives a sufficient amount of precipitation a burst of NO emission occurs. Based on the precipitation history of the last 14 days and if the soil moisture state is defined as dry, this burst is implemented as pulsing factor, depending on the amount of precipitation during the last day (Eq. 3) and lasting for $d$ days.
shows an overview of these comparisons. We found

\[ \text{flux} = \text{CRF} \times \text{pulse} \times F_{NO}(T, A_{d/w}) \] (4)

We have made a preliminary comparison of the model simulated soil NO emissions versus measurements for the period 1990 to 2000 without canopy reduction (Steinkamp, 2007). Figure 1 shows an overview of these comparisons. We found that the yearly averaged flux in the tropics compares well with measurements, whereas the fluxes in temperate regions seem to be underestimated. Since the applied algorithm is

empirically based, comparison on a point by point basis are not appropriate, but the overall distribution can be compared, in general the emission flux tends to be underestimated in all ecosystems, except for the rainforest.

### 3 Results and discussion

The emissions of NO from soils in the BASE simulation accounts for 18% of the total annual global NO emissions (Table 3). The interannual variability of SNOx is low in the model (Steinkamp, 2007). The largest SNOx emissions are calculated for tropical regions. During JJA there are some exceptions further north in Northern America, Europe and North-Eastern China. These are fertilizer induced emissions in agricultural regions (Fig. 2 and Table 3).

The data is analyzed by season with a focus on the winter and summer season. There is a notable seasonal variation with larger SNOx in the summer period of each hemisphere and with a larger contribution of SNOx to the total NO emissions during the northern hemispheric spring and summer (Table 3). The first point can be explained by the temperature dependence of SNOx and the second one by the greater landmasses in the Northern Hemisphere. In the

![Figure 1](https://example.com/figure1.png)
Table 3. Simulated total NOx emissions, SNOx in Tg(N) in the BASE simulation and in brackets relative contribution of SNOx to the total NO emissions for different regions and periods.

<table>
<thead>
<tr>
<th>Season</th>
<th>Global</th>
<th>Low-latitudes (30° N–30° S)</th>
<th>Mid-latitudes (30°–60° S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total</td>
<td>soil</td>
<td>total</td>
</tr>
<tr>
<td>DJF</td>
<td>13.08</td>
<td>1.78 (14%)</td>
<td>7.64 (21%)</td>
</tr>
<tr>
<td>MAM</td>
<td>13.42</td>
<td>2.38 (18%)</td>
<td>7.27 (24%)</td>
</tr>
<tr>
<td>JJA</td>
<td>15.26</td>
<td>3.35 (23%)</td>
<td>7.72 (23%)</td>
</tr>
<tr>
<td>SON</td>
<td>14.84</td>
<td>2.13 (14%)</td>
<td>8.75 (19%)</td>
</tr>
<tr>
<td>All</td>
<td>54.79</td>
<td>9.74 (18%)</td>
<td>29.90 (23%)</td>
</tr>
</tbody>
</table>

a) DJF = December 1994, January, February 1995; MAM = March, April, May 1995; JJA = June, July, August 1995; SON = September, October, November 1995

northern mid-latitudes SNOx plays a less important role relative to other NOx emissions, except during the JJA period.

3.1 Influence of NO emissions on related trace gases

The column mean mixing ratios of NOx, PAN, HNO3 and O3 and the column mean concentration of OH in the gridcells (weighted by the air mass in the gridcells) in the lower troposphere (below 500 hPa; hereafter “LT”) from the BASE simulation are compared with the values from the NOBIONO and REDOTHER simulations in this section. Here we first consider the overall correlations between the changes in the trace gas columns and the SNOx distribution (Table 4), then we discuss the changes in the individual gases in the following subsections.

As expected, in the surface layer (hereafter “SL”) as well as in the LT the difference between the NOx column mean mixing ratio in the NOBIONO simulation versus the BASE simulation is well-correlated with SNOx in all regions (Table 4; scatterplots are included in the supplement http://www.atmos-chem-phys.net/9/2663/2009/ACP-9-2663-2009-supplement.pdf). A low correlation is computed for the Northern Hemisphere LT during DJF, as expected due to the small SNOx compared to the anthropogenic emissions.

There is hardly any correlation in the low-latitudes and in the northern mid-latitudes of SNOx and the difference in the column mean mixing ratio of PAN in the two simulations (Table 4). In contrast, there is a better correlation in the southern mid-latitudes between the difference in the LT PAN column mixing ratio and SNOx. This suggests a dominating role of SNOx in the formation of PAN in the mid-latitudes of the Southern Hemisphere. The other precursor of PAN, peroxycetyl radicals, depend on the photooxidation of VOCs, which in turn depends on O3 and OH (Roberts et al., 2001; Cleary et al., 2007). At low latitudes, convective updrafts and subsiding airmasses, combined with the strong temperature dependence of the decomposition of PAN decreases the correlation.

The correlation between SNOx and the difference in the LT O3 column mean mixing ratio is lower than for NOx. This is partly due to the longer lifetime of O3, which is better mixed in the LT. Furthermore the production of O3 is not only determined by the NOx mixing ratio, but also by the concentration of VOC. The correlation of the OH column mean concentration difference in the LT with SNOx is similar to O3. OH is a very short lived tracer, whose production depends mainly on: 1.) the photolysis of O3 and the water vapor concentration in the lower troposphere, 2.) the reaction of NO with HO2 in the upper troposphere and 3.) the reaction of O3 with HO2 (Fig. 3). This results, depending on the dominating reaction, in a higher or lower correlation of the OH column concentration difference versus SNOx than the
Table 4. Correlation coefficient ($R^2$) between surface SNOx flux values and the difference (NOBIONO-BASE) of the tracer burden in the overlying model surface layer (SL) lower troposphere (LT; >500 hPa) by gridcell, averaged over the corresponding period; only gridcells with a land surface fraction of at least 75% were included.

<table>
<thead>
<tr>
<th>Season</th>
<th>NOx</th>
<th>PAN</th>
<th>HNO3</th>
<th>O3</th>
<th>OH</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>SL</td>
<td>LT</td>
<td>SL</td>
<td>LT</td>
<td>SL</td>
</tr>
<tr>
<td>Global (N=2462)</td>
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<tr>
<td>DJF</td>
<td>0.82</td>
<td>0.83</td>
<td>0.54</td>
<td>0.43</td>
<td>0.41</td>
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<tr>
<td>MAM</td>
<td>0.90</td>
<td>0.88</td>
<td>0.42</td>
<td>0.34</td>
<td>0.56</td>
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<tr>
<td>JJA</td>
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<td>0.87</td>
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<td>0.22</td>
<td>0.50</td>
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<tr>
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<td>0.89</td>
<td>0.54</td>
<td>0.42</td>
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<tr>
<td>Year</td>
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<td>0.48</td>
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<td>0.56</td>
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<td>Low-latitudes, 30°N–30°S (N=646)</td>
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<tr>
<td>DJF</td>
<td>0.68</td>
<td>0.66</td>
<td>0.19</td>
<td>0.14</td>
<td>0.15</td>
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<tr>
<td>MAM</td>
<td>0.79</td>
<td>0.75</td>
<td>0.16</td>
<td>0.05</td>
<td>0.41</td>
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<tr>
<td>JJA</td>
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<td>0.77</td>
<td>0.28</td>
<td>0.18</td>
<td>0.16</td>
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<tr>
<td>SON</td>
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<td>0.26</td>
<td>0.15</td>
<td>0.18</td>
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<tr>
<td>Year</td>
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<td>0.78</td>
<td>0.25</td>
<td>0.15</td>
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<td>Northern mid-latitudes, 30°N–60°N (N=637)</td>
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</tr>
<tr>
<td>DJF</td>
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<td>0.30</td>
<td>0.03</td>
<td>0.01</td>
<td>0.51</td>
</tr>
<tr>
<td>MAM</td>
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<td>0.90</td>
<td>0.03</td>
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<tr>
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<tr>
<td>Year</td>
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<td>0.89</td>
<td>0.04</td>
<td>0.04</td>
<td>0.44</td>
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<td>Southern mid-latitudes, 30°S–60°S (N=46)</td>
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<td>0.36</td>
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<td>0.71</td>
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</tr>
<tr>
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<td>0.90</td>
<td>0.74</td>
<td>0.73</td>
<td>0.69</td>
</tr>
</tbody>
</table>

a See Table 3 for abbreviations.

The global mean mixing ratio of NOx in the LT during DJF decreases by 7% in the NOBIONO simulation compared to the BASE simulation. During JJA it decreases by 17%. In both cases the decrease in the mixing ratio is less than the contribution of SNOx (14% and 23%, respectively). The maximum decrease is 81% in DJF and 78% in JJA, while the maximum absolute decreases in the DJF and JJA periods are 365 and 319 pmol mol$^{-1}$, respectively (figures with absolute differences can be found in the supplement http://www.atmos-chem-phys.net/9/2663/2009/acp-9-2663-2009-supplement.pdf). Interestingly, during DJF the mixing ratio above large parts of the Northern Hemisphere increases, by up to 7% (Fig. 4a) in the NOBIONO simulation, with the largest absolute increase of 12.3 pmol mol$^{-1}$ above Europe. In the JJA period the maximum relative increase of 7.6% is larger than in the DJF period, but the maximum absolute difference is only 7.0 pmol mol$^{-1}$ (Fig. 4b).

A similar result has been noted for model sensitivity simulations with and without NOx from lightning (Stockwell et al., 1999; Labrador et al., 2005), in which a decrease in near-surface NOx mixing ratios was computed for similar regions with increasing production of NOx by lightning. Although NOx produced by lightning is formed in the free troposphere and SNOx originates from the surface, we achieve comparable results with SNOx as with lightning NOx by
Steinkamp et al.: Modelled NO soil emissions, related trace gases and oxidizing efficiency

Labrador et al. (2005). To explain why the NOx mixing ratio decreases less than the relative decrease in the emission of the NOBIONO simulation compared to the BASE simulation, and why it even increases during the DJF period in large areas in the Northern Hemisphere, the feedback through O3 and OH has to be taken into account. Stockwell et al. (1999) assumed that the general increase in O3 with lightning NOx causes an increase in OH. This OH reduces the lifetime of NOx (τNOx) through Reaction (R1) above regions with high non-lightning NOx sources. Labrador et al. (2005) showed that the conversion to HNO3 via N2O5 also contributes to the shorter τNOx, (Reaction R2) with higher NOx emissions.

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \quad \text{(R1)}
\]

\[
\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5
\]

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \quad \text{(R2)}
\]

Similarly we find that without SNOx, O3 and OH levels decrease over large regions due to the longer O3 lifetime, resulting in enhanced τNOx, and due to Reactions (R1) and (R2) the NOx mixing ratio increases in some regions with low SNOx. The changes in HNO3, O3 and OH related to this are discussed in the following sections.

Fig. 3. Zonal mean relative contribution of the eight major OH producing reactions in the BASE simulation integrated over one year.

\[
\text{H}_2\text{O} + \text{O}^1\text{D} \rightarrow 2 \text{OH}
\]

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}
\]

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2 \text{O}_2
\]

\[
\text{H}_2\text{O}_2 \rightarrow 2 \text{OH}
\]

\[
\text{HONO} \rightarrow \text{NO} + \text{OH}
\]

\[
\text{HNO}_3 \rightarrow \text{NO}_2 + \text{OH}
\]

\[
\text{HNO}_4 \rightarrow .667 (\text{NO}_2 + \text{HO}_2) + .333 (\text{NO}_3 + \text{OH})
\]

\[
\text{H}_2\text{O} \rightarrow 2 \text{OH}
\]

\[
\text{CH}_3\text{OOH} \rightarrow \text{HCHO} + \text{OH} + \text{HO}_2
\]
In the vertical direction the strongest effects of SNOx are simulated near the surface (DJF: 59%, JJA: 55%), and a decrease of up to 10 to 25% at higher altitudes in the zonal mean is calculated when SNOx is switched off (Fig. 5). The effect of convective transport to higher altitudes has a stronger influence on the difference in the total burden between 500 and 250 hPa during DJF (relative: 11.3%, absolute: 1.6 Gg) than during JJA (relative: 9.0%, absolute: 1.1 Gg). This is because the main regions where the convective transport is most effective are in the Southern Hemisphere, especially the Amazon Basin and the southern tropics of Africa (not shown). In the REDOTHER simulation the relative decrease between 500 and 250 hPa is much smaller (DJF: 5.2%, JJA: 2.9%).

The reduction of all remaining surface emissions in the REDOTHER simulation leads to a decrease in the LT NOx mixing ratio of 19% during DJF and 12% during JJA compared to the BASE simulation. A small relative increase, by less than 1%, occurs only in oceanic regions where the absolute mixing ratio is below 30 pmol mol\(^{-1}\). The main decreases are located above the (northern hemispheric) land surfaces (Fig. 6). In the zonal mean the maximum extent of the relative decrease is located closer to the surface, because the major changes are outside the tropics and are not lifted as effectively by deep convection (Fig. 7).

**3.1.2 PAN**

The LT PAN mixing ratio decreases globally by 4% during DJF and 10% during JJA without SNOx. In both periods the PAN mixing ratio decreases nearly everywhere above the continents (Fig. 8). Above the tropical oceans, especially during JJA, there is a high relative but a negligible absolute increase in the PAN mixing ratio associated with a decrease in SNOx. As mentioned above, the formation of PAN in the northern mid- and low latitudes relies more on other trace gases than on SNOx, but more on SNOx in the southern mid-latitudes. This explains the larger decrease during DJF than during JJA. There is also no increase of PAN in the Northern Hemisphere during DJF despite higher NOx mixing ratios, which confirms a dominating role of VOC in PAN formation.

Interestingly, in the upper troposphere between 500 hPa and 250 hPa the largest decrease in the PAN mixing ratio is during DJF (6.5%), whereas it is 5.1% during JJA. In the zonal mean of the relative difference in PAN mixing ratio with and without SNOx (Fig. 9), the effect of convective transport in the lower latitudes is more effective during DJF than during JJA. At the higher altitudes PAN does not increase anymore, due to its longer lifetime resulting in better mixing. In the REDOTHER simulation the decrease (DJF: 4.1%, JJA: 1.4%) is smaller between 500 and 250 hPa.
The differences in the PAN mixing ratio should be interpreted with caution, because the model generally overestimates its levels compared to observations (Jöckel et al., 2006), though this may improve with a new isoprene oxidation scheme (Taraborrelli et al., 2008).

3.1.3 HNO$_3$

The global LT mean mixing ratio of HNO$_3$ decreases by 15% (DJF) and 19% (JJA) without SNOx. The greatest decrease occurs above continental regions of the low-latitudes and in the summer months in the Northern Hemisphere (Fig. 10). The amplified decrease in the mixing ratio of HNO$_3$ compared to the decrease of NO$_x$ mixing ratio is because the formation of HNO$_3$ is not only determined by the NO$_x$ mixing ratio, but also relies on the mixing ratios of O$_3$ and OH, which also decrease, as discussed in the following sections.

Nitric acid is mainly deposited on aerosol particles, taken up by cloud water or directly deposited on the earth’s surface. The deposition of HNO$_3$ is decreased by 18% throughout the year without SNOx. During DJF the decrease is 15% and during JJA it is 25%. In the REDOTHER simulation the deposition decrease does not substantially change during the year (18%, DJF: 19%, JJA: 17%).
3.1.4 O$_3$

The mixing ratio of O$_3$ in the NOBIONO simulation compared to the BASE simulation decreases by 5% in the LT during both seasons, with the greatest decline above the continents (Fig. 11). The maximum relative decrease during DJF is 38% and during JJA it is 33%. The maximum absolute decrease (16.2 nmol mol$^{-1}$) occurs during DJF above Australia (Fig. 11a). In contrast to what was found for NO$_x$, there is no region with increasing O$_3$ mixing ratios. The removal of SNO$_x$ is less effective in reducing the O$_3$ mixing ratio during JJA (17%) than during DJF (7%). This is because the formation of O$_3$ through SNO$_x$ competes with other strong sources of NO$_x$ during JJA in the Northern Hemisphere, whereas SNO$_x$ is relatively much more important the formation of O$_3$ during DJF in the Southern Hemisphere. Furthermore, as was noted above for the PAN formation in the Northern Hemisphere the simulated O$_3$ production depends more on VOC and other NO$_x$ sources than SNO$_x$, Beekmann and Vautard (2009) show for example different photochemical regimes in Europe.

In the zonal mean distribution (not shown) a similar pattern of the influence of convection can be seen as already discussed for NO$_x$ and PAN. But due to the longer lifetime of O$_3$ the relative change is a maximum decrease of 13% (DJF) and 10% (JJA), which is not as strong and is more evenly distributed above all latitudes, as well as in the vertical direction. In the zonal mean there is, as with the horizontal, no region in which the mean O$_3$ mixing ratio increases.
Interestingly, in contrast to these results for SNOx, in the REDOTHER simulation the mean LT $O_3$ mixing ratio only decreases by 2.7% (DJF) and 1.8% (JJA). In the zonal mean the increase does not exceed 5%.

### 3.1.5 OH

When we exclude the contribution of SNOx, the mean LT OH concentration decreases by 10% during DJF and 9% during JJA. The largest relative decrease is 65% during DJF and 62% during JJA above the tropical land regions. During DJF the decrease is shifted to the southern tropics and to the northern tropics during JJA (Fig. 12). Note that during JJA an absolute increase above the Antarctic region is calculated, but the OH concentration here is less than $1 \times 10^4$ molec cm$^{-3}$.

The decrease is in part induced directly by NOx through Eq. (R3), and in part indirectly by the lower $O_3$ mixing ratio, leading to less primary OH production, and therefore to a decrease of the OH concentration in the LT.

$$\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R3)}$$

The largest relative decrease in the zonal mean concentration of OH is 19% during DJF and 16% during JJA. This maximum of the relative decrease in the OH concentration without SNOx is nearly detached from the surface, despite the surface source of SNOx (Fig. 13). At the surface OH production is mainly related to the reaction of O($^1D$) with water, while at higher altitudes it depends more on the reaction of NO with HO$_2$ (Eq. R3, see also Fig. 3). In the zonal mean the shift to the Southern Hemisphere during DJF is stronger than the shift during JJA to the Northern Hemisphere. The major driving reactions for the absolute decrease are the reaction of $H_2O$ with O($^1D$), reaction R3, and HO$_2$ with $O_3$ and photolysis of $H_2O_2$. The relative contribution of the four major OH producing reactions shows their strongest decrease in the
lower latitudes throughout the year for the NOBIONO simulation (Fig. 14), whereas the largest changes in the REDOTHER simulation are located much closer to the surface (Fig. 15) and are not as large as in the NOBIONO simulation.

In the REDOTHER simulation, with a 4% decrease during both seasons in the LT, the region with the strongest decrease is always located over the Northern Hemisphere and the maximum relative decreases are only 15% and 11%, respectively.

### 3.1.6 Summary for the trace gases

By following the reaction chain from NO\textsubscript{x} through O\textsubscript{3} and OH, including the branches of HNO\textsubscript{3} and PAN, the correlation of the change in the mixing ratio between the BASE and NOBIONO simulation with the SNO\textsubscript{x} source declines. The strongest correlations can be found in the southern hemispheric mid-latitudes, which indicates an important role of SNO\textsubscript{x} in that region.

Although the total NO\textsubscript{x} emission decreases in the NOBIONO simulation, we simulate an increase in the LT NO\textsubscript{x} mixing ratio during DJF in the Northern Hemisphere. When reducing the other surface NO\textsubscript{x} emissions in the REDOTHER simulation, we did not see an increase in the mixing ratio. This is because the influence on the O\textsubscript{3} and OH mixing ratios in the NOBIONO simulation is stronger than for the REDOTHER simulation and the feedback on \( \tau_{NO_x} \) is not strong enough in the REDOTHER simulation to increase the mixing ratio with reduced surface NO\textsubscript{x} emissions. Our results suggest that SNO\textsubscript{x} has a stronger influence on the related chemical processes than the remaining NO\textsubscript{x} sources due to the geographical distribution.

### 3.2 Influence of SNO\textsubscript{x} on the oxidizing efficiency

The oxidation of CO and VOC in the atmosphere is mainly driven by OH. As a measure for the oxidizing efficiency of the atmosphere, \( \tau_{CH4} \) is calculated for all simulations according to Lawrence et al. (2001). The trend of monthly mean values is depicted in Fig. 16. The mean \( \tau_{CH4} \) averaged for one year (December 1994 to November 1995) for the BASE simulation is 7.25 years. It is 7.96 years in the NOBIONO simulation, a 9.8% increase without SNO\textsubscript{x} and 7.6 years (a 4% increase) for the REDOTHER simulation. The maximum prolongation of 0.97 years (12%) occurs in February 1995 for the NOBIONO simulation and 0.38 years (4%) in December 1995 for the REDOTHER simulation.

Fig. 17. Relative increase of \( \tau_{CH4} \left( \frac{\tau_{CH4, \text{simulation}} - \tau_{CH4, \text{BASE}}}{\tau_{CH4, \text{BASE}}} \times 100\% \right) \) for the NOBIONO (red) and REDOTHER (blue) simulation in various zonal subdomains of the atmosphere (calculated according to Lawrence et al., 2001).
latitudes for the NOBIONO simulation (Fig. 17). This agrees with the smaller relative change in the OH concentration in the northern latitudes (Fig. 12). In the zonal mean, the relative changes are slightly larger above 500 hPa for the NOBIONO simulation, despite the origin of SNOx at the surface. Beginning from the surface source of SNOx and following the reaction chain from NOx over O3 and OH in each step, the relative difference of our two simulations becomes smaller near the surface and larger at higher altitudes. This trend corroborates the larger relative change of the oxidizing efficiency at higher altitudes. However, only ~15% of the absolute amount of CH4 in the troposphere is oxidized above 500 hPa (Lawrence et al., 2001).

Labrador et al. (2004) modelled a decrease of 15% in $\tau_{CH_4}$ in a simulation with 5 Tg(N) NOx produced by lightning relative to one with no lightning NOx. Compared to this, SNOx is somewhat less effective in altering the oxidizing efficiency of the atmosphere, which is interesting, given that CH4 oxidation is more effective near the surface where SNOx is emitted, due to the strong temperature dependence of the reaction of OH with CH4. The change in the oxidizing efficiency due to lightning NOx is larger than due to SNOx, even though the total emission rate is lower. This is because at higher altitudes the NO:NOx ratio is greater, so that with more NO the NOx lifetime is not diminished as strongly as near the surface. Furthermore at higher altitudes more NO results in higher OH yields by reaction with HO2.

4 Conclusions and outlook

The emission of NO from soils plays an important role for chemical reactions in the atmosphere in our simulations. Lower global mean NOx mixing ratios without SNOx lead to lower global O3 mixing ratios in the LT. The lower O3 mixing ratios result in lower OH concentrations. This results in an enhanced lifetime of NOx in regions with other dominating sources of NOx. Hence the NOx mixing ratios increases in some regions, despite lower emissions when NOx is neglected in our NOBIONO simulation. This effect did not occur in the REDOTHER simulation, in which we comparatively reduced the remaining surface NO emissions. From this it follows that although NOx is a short-lived tracer it indirectly influences chemical processes in regions with low SNOx through feedback with O3 and OH. By following the reaction chain up to PAN and HNO3, we detected a dominating role of SNOx compared to VOC in the mid-latitudes of the Southern Hemisphere. Also by following the reaction chain (SNOx→NOx→O3→OH), the magnitude of relative effects are shifted step by step to higher altitudes in the troposphere.

Through reaction of NO with HO2, SNOx is directly involved in the production of OH. SNOx also has, through O3, an indirect influence on OH production. With OH formed by SNOx through these pathways, $\tau_{CH_4}$ is decreased considerably, and the influence of SNOx on the tropospheric oxidizing efficiency is considerable, approximately 10%. Reducing the other surface NO emissions by the same amount only lead to an increase of 4% in $\tau_{CH_4}$.

The notable modelled influence of SNOx on directly and indirectly related trace gases shown in this work supports further efforts to improve the parameterization of SNOx in CTMs, as also proposed by Jaeglé et al. (2005).

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Steinkamp et al.: Modelled NO soil emissions, related trace gases and oxidizing efficiency


