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Technical Note: A diagnostic for ozone contributions of various NO_x emissions in multi-decadal chemistry-climate model simulations

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Abstract

Nitrogen oxide ($NO_x=NO+NO_2$) emissions from various sources contribute to the ozone budget. The identification of these contributions is important, e.g. for the assessment of emissions from traffic. The non-linear character of ozone chemistry complicates the online diagnosis during multi-decadal chemistry-climate simulations. A methodology is suggested, which is efficient enough to be incorporated in multi-decadal simulations. Eight types of NO_x emissions are included in the model. For each a NO_y (=all N components, except N_2 and N_2O) tracer and an ozone tracer is included in the model, which experience the same emissions and loss processes like the online chemistry fields. To calculate the ozone changes caused by an individual NO_x emission, the assumption is made that the NO_x contributions from various sources are identical to the NO_y contributions. To evaluate this method each NO_x emission has been increased by 5% and a detailed error analysis is given. In the regions of the main impact of individual sources the potential error of the calculated contribution is significantly smaller than the contribution. Moreover, the changes caused by an increase of the emissions of 5% were detected with a higher accuracy than the potential errror of the absolut contribution.

1. Introduction

The impact of NO_x emissions on the ozone budget has been discussed recently, e.g. for aircraft emissions (IPCC, 1999; Grewe et al., 2002a) as well as other emissions (e.g. Corbett et al., 1999; Granier and Brasseur, 2003, Grewe et al., 2001). In general, two different approaches were used to determine the effect of an individual NO_x source on the NO_x and ozone budget: (1) The difference of two model simulations one with and one without a (or with a reduced) distinct NO_x emission yields the contribution of that source to the individual budgets (e.g. Grewe et al., 2002a; Granier and Brasseur, 2003 and many others). (2) The tagging of emitted NO_x molecules yields directly the contribution to the NO_x or NO_y budget (e.g. Meijer et al., 2000).

The approaches differ in that (1) leads to a different composition of the atmosphere in either simulation, which in turn affects non-linearly also the NO_x and ozone concentration. For example, switching on lightning emissions can locally lead to a decrease of NO_x as well as NO_y. This occurs in regions far away from the source, where the emitted NO_x has already been washed-out (after conversion to HNO_3) but ozone increases are still present caused by its longer lifetime. This additional ozone leads to more OH and changes the NO_y partitioning in favor of HNO_3, leading to a decrease of NO_y by additional wash-out (Grewe et al., 2002b). Approach (1) also needs a number of simulations, to investigate all possible NO_x sources. Furthermore, the sum of all contributions from individual sources equals to 85% to 110% of the total NO_x (Grewe et al., 2001), because of the above mentioned non-linear effects. Approach (2) has the advantage that a correct mass budget can be calculated. However, for each individual emission the whole set of chemical species has to be chemically integrated and transported, which vastly increases computing time so that this approach has never been implemented in long-term simulations.

This paper describes a simplified methodology based on approach (2), which is efficient enough to be applied for climate-chemistry simulations. The methodology and its application for a climate-chemistry simulation are presented in Sect. 2. Section 3 concentrates on the analysis of the error caused by the simplification of the approach.

2. Methodology

Individual sources contribute differently to the NO_x and NO_y budgets. This is illustrated in Fig. 1. It shows the evolution of the contribution of a NO_x source (e.g. lightning) to the NO_x and NO_y concentration simulated with a simple two-box model. The model includes chemical conversion, temporally varying sources and sinks, and transport between the two boxes. The parameters are chosen to represent a situation, in which large deviations can be expected. Therefore the upper troposphere (300 hPa) with a slow chemistry (5 days lifetime for NO_x) was chosen. Sources and sinks include temporal variations. The simulation starts from highly non-steady state initial conditions (for details see appendix). During the first 12 h the NO_x and NO_y contributions converge to values within a 10% band. After that period they differ by 5%, although the sources and sinks differ significantly. The NO_y contributions can easiliy be diagnosed (see below Eq. 1) in coupled climate-chemistry simulations. On the other hand, the NO_x contributions, which determine the ozone production, are only correctly diagnosed by applying a chemical solver (chemical module) to every emission type, which would be too cost intensive for climate-chemistry simulations. This can be avoided by assuming that the contributions from an individual NO_x source to the NO_x contribution is equal to the NO_y contribution. The simple example above (Fig. 1) shows that this approach is justified, since even strong variations (temporal and between the two boxes, see appendix) in emissions, lead to relatively small (±5%) deviations between the NO_x and NO_y partitioning (Fig. 1, red vs. green line and blue vs. magenta line).

Based heron the following approach is suggested: For $i = 1, .., n$ given emission types, denote X_i, x_i, and Y_i the NO_y, NO_x and ozone mixing ratios at an arbitrary grid point caused by emission E_i (in mixing ratio per time); Y^{n+1} is the ozone mixing ratio resulting from stratospheric ozone production; X $(= \sum_i^n X_i)$, x $(= \sum_i^n x_i)$, Y $(= \sum_i^{n+1} Y_i)$ are the mixing ratios of NO_y, NO_x, and ozone simulated by a model and X_s, Y_p^x, Y_p, Y_s the NO_y loss, ozone production by NO_x, ozone production by oxygen photolysis and ozone loss, with loss and production terms in (mixing ratio per time).

The evolution of the NO_y and ozone mixing ratios caused by the emission i is then given by (transport/advection terms are omitted for simplicity)

$$\dot{X}_i = E_i - X_s \frac{X_i}{X}, \quad i = 1, \ldots, n. \tag{1}$$

$$\dot{Y}_i = Y_p^x \frac{x_i}{x} - Y_s \frac{Y_i}{Y}, \text{ for } i = 1, \ldots, n \text{ and} \tag{2}$$

$$\dot{Y}_{n+1} = Y_p - Y_s \frac{Y_{n+1}}{Y}. \tag{3}$$

Based on the box model calculation (Fig. 1), the simplification

$$\frac{x_i}{x} = \frac{X_i}{X}, i = 1, \ldots, n \tag{4}$$

can be applied and Eq. (2) gives

$$\dot{Y}_i = Y_p^x \frac{X_i}{X} - Y_s \frac{Y_i}{Y}, \quad \text{for} \quad i = 1, \ldots, n. \tag{5}$$

This analysis technique has been implemented into the climate-chemistry model E39/C (Hein et al., 2001) and applied to a model simulation, which is identical to Grewe et al. (2001), with the exception that emissions are adapted to the year 2000, ship $\mathrm{NO_x}$ emissions are included according to Corbett et al. (1999) and road traffic emissions are extracted from industry based on Matthes (2003). Figure 2 shows the ozone partitioning for January (other months give similar results). A comparison to earlier results (Grewe et al., 2001; Grewe et al., 2002a; Grewe et al., 2002b) shows a reasonable agreement. In the following a detailed error analysis is given.

3. Error analysis

To estimate the error of this methodology the exact ozone contributions from the individual sources have to be known. Since this is not possible, a second estimate is given: For each of the 8 nitrogen sources shown in Fig. 2, a simulation has been performed, where the emissions are increased slightly by 5%. The small change has been chosen to minimize non-linear effects as described above. In these simulations (denoted in the following with ${}^{i}\tilde{\cdot}$, where i indicates the increased emission type) $\mathrm{NO_y}$ (= ${}^{i}\tilde{X}$) is increasing and the ozone concentration (= ${}^{i}\tilde{Y}$) changes. Note that the index $\cdot_i$ always represents the diagnostic tracers defined in Eqs. (1) and (2), and that the index ${}^{i}\tilde{\cdot}$ indicates values of the simulation, where emission i is increased by 5%. For example, ${}^{i}\tilde{Y}_j$ denotes the mixing ratio of the ozone diagnostic for emission type j in the simulation, where the emission i is increased by 5%. In the following only the diagnostics for $i = j$ are mentioned.

From the ozone differences scaled with the NO_y changes a first estimate for the “true” ozone contributions from emission i ($= {}^i\bar{Y}^1$) to the ozone concentration (Y) can be derived (following the approach (1), see introduction):

$$ {}^i\bar{Y}^1 = ({}^i\tilde{Y} - Y)\,\frac{\sum\limits_{\text{model area}} (X_i\, m_{air})}{\sum\limits_{\text{model area}} (({}^i\tilde{X}_i - X_i)\, m_{air})}, \tag{6} $$

with m_{air} the mass in the model grid. The scaling factor is for all emission types between 20 and 23, mirroring the 5% increase. The quality of the estimate of the “true” ozone ${}^i\bar{Y}^1$ can be tested by comparing the sum of all contributions with the original ozone without any contributions from the stratospheric ozone production ($= \frac{Y - Y_{n+1} - \sum_{i=1}^{n} {}^i\bar{Y}^1}{Y - Y_{n+1}}$). Ideally, this fraction is 0%, i.e. $\sum_{i=1}^{n} {}^i\bar{Y}^1 = Y - Y_{n+1}$. However, because of the non-linearity of the ozone-chemistry maximum deviations in the order of −40% in the troposphere, 5% above the tropopause and −10% in the lower stratosphere can occur. This undererstimate of ozone contributions in the troposphere and overestimate in the lower-most stratosphere can be compensated for by scaling the individual ozone contributions, so that the sum of all leads to 100%:

$$ {}^i\bar{Y}^2 = \frac{Y - Y_{n+1}}{\sum\limits_{i}^{n} {}^i\bar{Y}^1}\, {}^i\bar{Y}^1. \tag{7} $$

This estimates ${}^i\bar{Y}^2$ for the ozone contributions from n individual NO_x emissions, which are derived from n simulations can than serve to derive an error estimate (F_a) for the simpler ozone diagnostic Y_i:

$$ F_a = \frac{{}^i\bar{Y}^2 - Y_i}{Y}. \tag{8} $$

It means that F_a gives an estimate on how much the relative contributions given in Fig. 2 can deviate from the estimate of the contributions based on the 5% emission increase simulations.

Figure 3 shows the estimated error of the ozone contributions (Fig. 2) for January (July shows similar results and are therefore not shown). The areas, where the approach of calculating ${}^{i}\bar{Y}^{2}$ obvisouly failed are omitted. Three conditions were applied: (1) The contributions ${}^{i}\bar{Y}^{2}$ get substantially below 0% (contributions should be strictly positive). (2) The scaling factor in Eq. (7) is more than a factor of two or less than a factor of −0.5 (highly non-linear behaviour in the ozone chemistry, caused by emission increase). (3) Chemistry is dominated by stratospheric ozone production by more than 85% (see Fig. 2).

The comparison of the two methodologies shows that the assumption Eq. (4) does not lead to dramatic differences to results obtained by the 5% increase of emissions. In the mid-troposphere ozone contributions are higher for lightning and air traffic, and smaller for biomass burning, soil, industry, land transportation. Lightning, air traffic and ships emit in a surrounding with smaller NO_x background values than the surface emissions in populated areas, which could lead to similar non-linear effects. In the case of lightning the calculated contribution of 40% (Fig. 2) in the tropics can be less by 15% (=25%) in the upper troposphere, or slightly more in the mid troposphere around 45%, when applying the 5% emissions increase diagnostic. In the case of aircraft emissions the maximum contribution is estimated to be 2.5% (Fig. 2) but can be more by approximatey 1%. In general the estimated difference between the two approaches in the troposphere is less than 3% for most of the emissions. However, clearly the 5% increase approach is also erroneous. So that the only conclusion, which can be drawn from this intercomparison is that both approaches are of the same quality and neither approach is superior.

The deviations of the partitioning (RMS) of the ozone contributions calculated by the two approaches is generally less than 1 to 2 % (Fig. 3, lower right). Taking into account that both approaches have their deficiencies, one can conclude from this analysis that the 5% increase estimation does not lead to significantly better results than the simple methodology, since the non-linear chemistry limits both appproaches.

A further possibility to evaluate the methodology is to concentrate on changes in emissions. This avoids all the problems with deriving the correct absoute contributions of individual NO_x sources to the ozone budget. The error of changes in the absolute contributions (= F_r) are given by

$$F_r = \frac{({}^i\tilde{Y} - Y) - ({}^i\tilde{Y}_i - Y_i)}{Y}. \tag{9}$$

Figure 4 shows the error F_r, which is the difference between the effect in the ozone concentration detected by the comparision of the ozone fields of both simulations and the effect in the ozone concentration detected by the new methodology. In principle the difference (error) is in the order of 0.1 to 0.3%. In the case of lightning it would mean that an increase of the lightning emissions in the order of 5% can be detected in the ozone contribution in the order of 0.2%. This shows both methodologies lead to similar results concerning trends in NO_x emissions and that the simple methodology can be used to determine trends in climate-chemistry simulations.

4. Conclusions

Multi-decadal climate-chemistry simulations are CPU-time and memory consuming. Diagnostics, which have to be carried out simultaneously with the simulation, are requested to be cheap in CPU-time and memory. One focus is the importance of NO_x emissions for the ozone budget. In principle two approaches were applied so far (see introduction). However, both are too CPU-time consuming for multi-decadal simulations. Here, a method is introduced, which is for practical use in such kind of simulations. The main assumption is that the contributions from various NO_x emissions to NO_x is identical to their contributions to NO_y (Eq. 4). In general this is not true. Using a two-box model simulation, it is shown that the deviations are only within 5% in a case, which highly varying emissions and a slow chemistry, representing a more extreme situation.

Several simulations have been performed to estimate the error of this assumption on the ozone budget: Each NO_x source has been increased by 5% to estimate its impact on the ozone partitioning. Caused by the non-linearity of the ozone chemistry, this turned out to be a difficult task, since the "true" ozone partitioning could not be calculated accurately. However, the best estimate lead to the result that the method, introduced here, is able to reproduce the individual ozone contributions within approximately 5% uncertainty, depending on the source strength. Moreover, the effect of the increased emissions were detected with a much higher accuracy of 0.2%. This makes the method valuable for transient simulations to detect climate change and emission change signals.

The method is probably not useful for high-resolution models, since there lokal emissions largely determine the NO_x concentrations at individual grid points. In this case the coarse resolution of chemistry-climate models (here T30, 300-400 km), which is normally a disadvantage in modelling, allows for a useful simplification leading to an effficient methodology to derive ozone contributions from various NO_x sources.

Appendix: Two-box model

The two-box model is used to illustrate the evolution of the NO_x and NO_y mixing ratios in a simple way, using typical values from a climate-chemistry model (here E39/C) for mid-latitudes at 300 hPa:

$$x_1 = P_1 - C_1 \frac{x_1}{x_1 + x_3} + T(x_1 - x_5) - D_1 x_1 \tag{10}$$

$$x_2 = P_2 + C_1 \frac{x_1}{x_1 + x_3} + T(x_2 - x_6) - D_2 x_2 \tag{11}$$

$$x_3 = P_3 - C_1 \frac{x_3}{x_1 + x_3} + T(x_3 - x_7) - D_1 x_3 \tag{12}$$

$$x_4 = P_4 + C_1 \frac{x_3}{x_1 + x_3} + T(x_4 - x_8) - D_2 x_4 \tag{13}$$

$$x_5 = P_5 + C_5 \frac{x_5}{x_5 + x_7} - T(x_1 - x_5) - D_5 x_5 \tag{14}$$

$$x_6 = P_6 - C_5 \frac{x_5}{x_5 + x_7} - T(x_2 - x_6) - D_6 x_6 \tag{15}$$

$$x_7 = P_7 + C_5 \frac{x_7}{x_5 + x_7} - T(x_3 - x_7) - D_5 x_7 \tag{16}$$

$$x_8 = P_8 - C_5 \frac{x_7}{x_5 + x_7} - T(x_4 - x_8) - D_6 x_8 . \tag{17}$$

Box 1 is described by indices 1 to 4, box 2 by 5 to 8; x_j describes NO_x mixing ratios for odd indices and the sum of all other nitrogen species for even indices (see Table 1 for more details).

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Table 1. Parameters for the box model simulations.

Volume	$6.05\ 10^{13}\ \mathrm{m}^3$
Mass	$2.77\ 10^{13}$ kg
Time step	30 min.
P_1	16.9 ngN m^{-3} every 2.5 h
P_5	3.94 ngN m^{-3} every 3.5 h
$P_j,\ j \neq 1,5$	0 ngN m^{-3}
C_1	$8.3\ 10^{-7}\mathrm{s}^{-1}$ (lifetime of 5 days)
C_5	$10.4\ 10^{-7}\mathrm{s}^{-1}$ (lifetime of 4 days)
T (exchage rate)	5% per timestep $2.8\ 10^{-5}\mathrm{s}^{-1}$
D_1	$0\ \mathrm{s}^{-1}$
D_2	15% every 13.5 h ($8.3\ 10^{-5}\mathrm{s}^{-1}$)
D_5	$0\ \mathrm{s}^{-1}$
D_6	15% every 11.0 h ($10.2\ 10^{-5}\mathrm{s}^{-1}$)

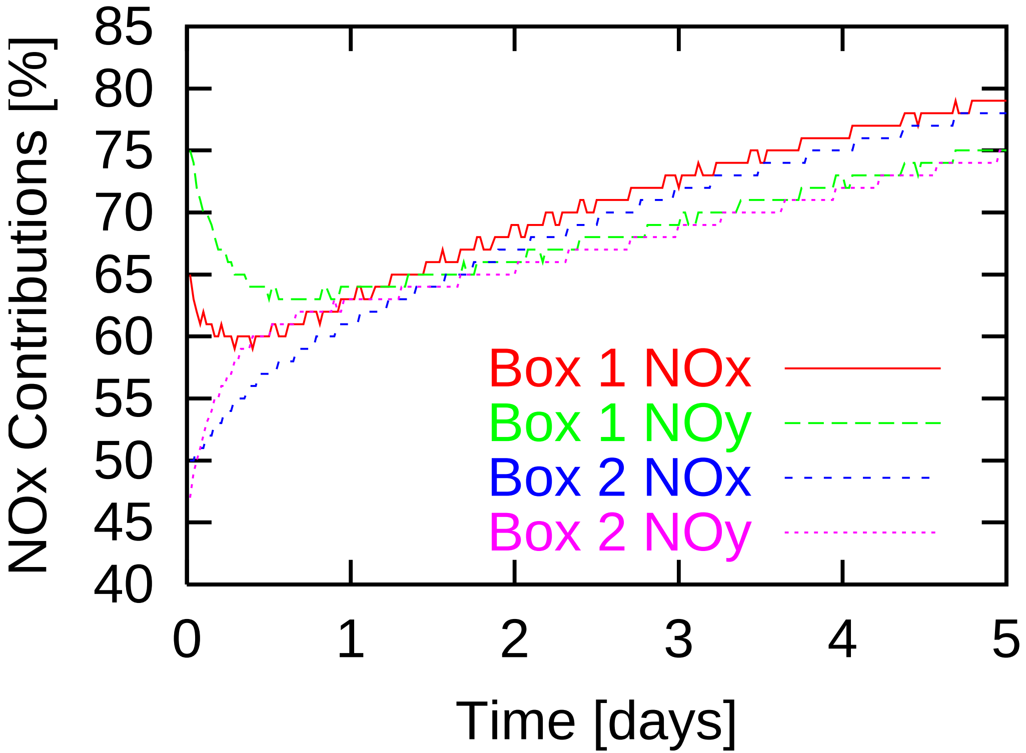

Fig. 1. Temporal development of the NO_x and NO_y contributions (%) from a NO_x source simulated with a two-box model with characteristics of a GCM simulation representing mid latitudes at 300 hPa (see text and appendix for details).

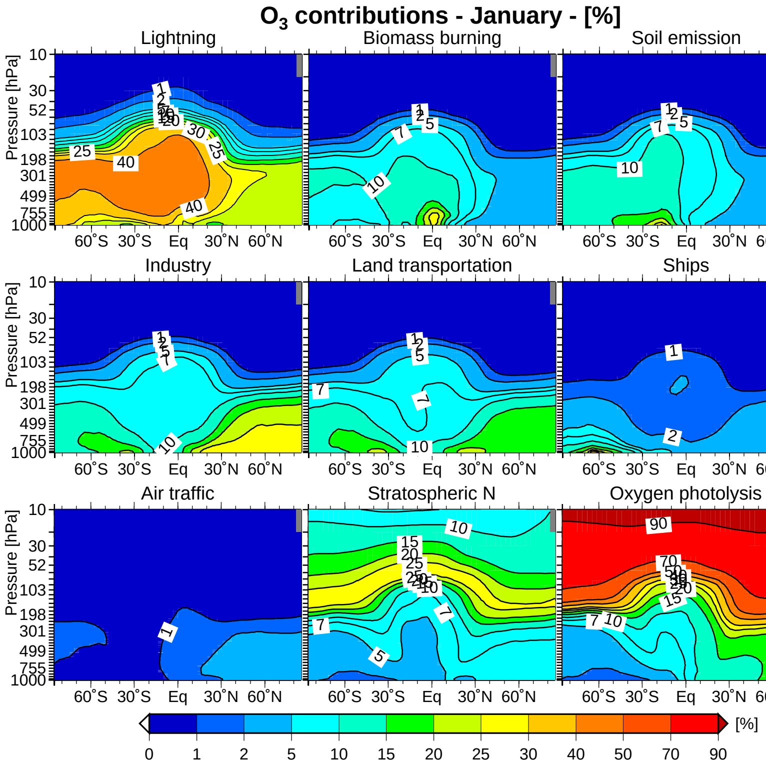

Fig. 2. Contributions of NO$_x$ sources to the ozone concentration derived with an online diagnostic for January (%).

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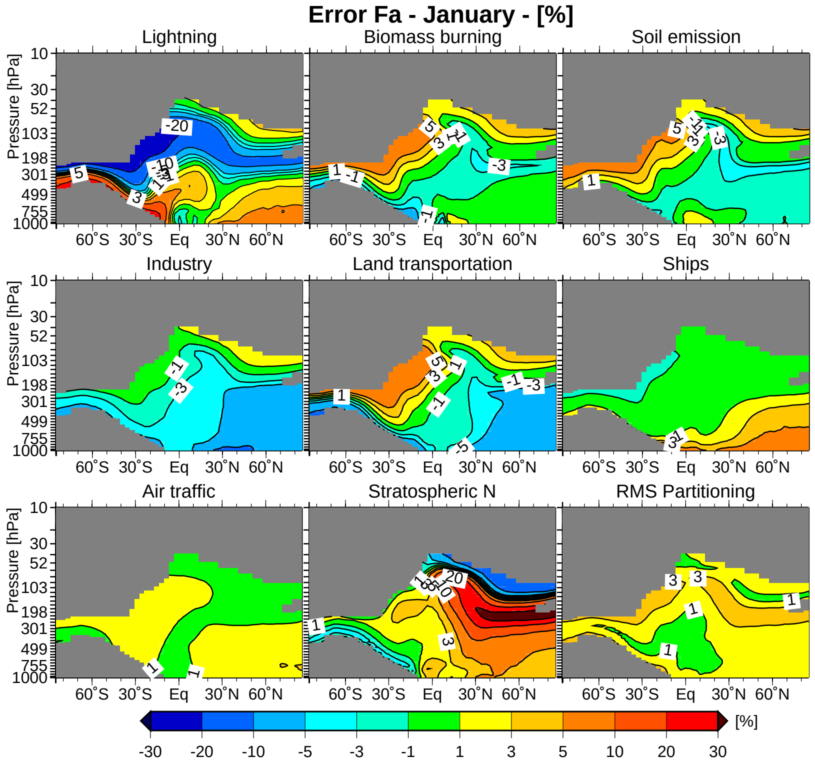

Fig. 3. Estimated error F_a (%) of the ozone contributions from various ozone sources relative to ozone concentration for January. Additionally (lower right) the RMS of the contributions is given relative to the ozone concentration, as an indicator of the deviations from the ozone partitioning (%). Shaded areas indicate regions, where the error estimate fails (see text).

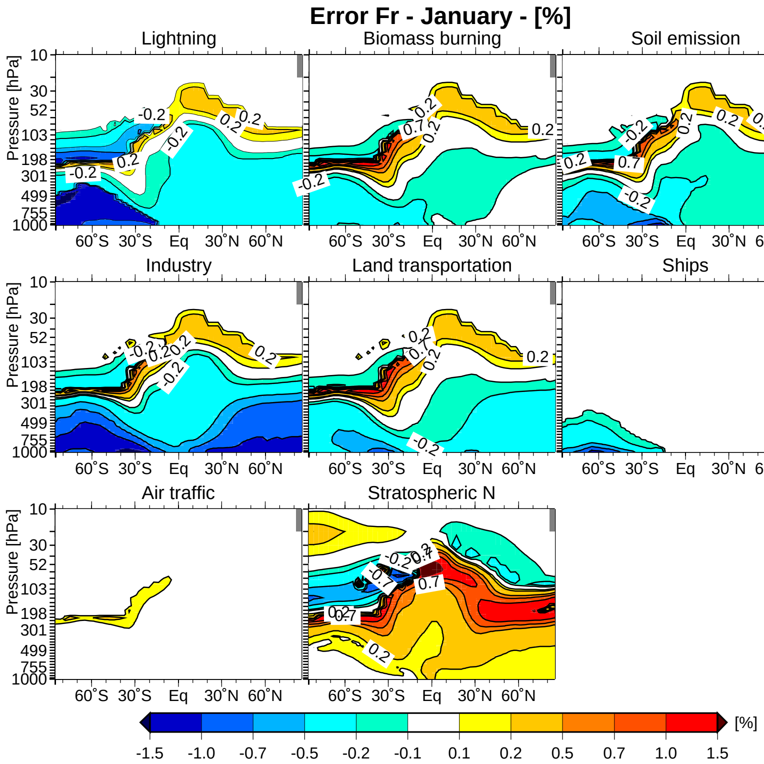

Fig. 4. Estimated error F_r (%) of the changes of ozone contributions from various ozone sources caused by a 5% increase in each emission relative to ozone concentration for January.

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