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The effects of lightning-produced NO_x and its vertical distribution on atmospheric chemistry: sensitivity simulations with MATCH-MPIC

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Abstract

The impact of different assumptions concerning the source magnitude as well as the vertical placement of lightning-produced nitrogen oxides is studied using the global chemistry transport model MATCH-MPIC. The responses of NO_x, O_3, OH, HNO_3 and peroxyacetyl-nitrate (PAN) are investigated. A marked sensitivity to both parameters was found. NO_x burdens globally can be enhanced up to 100% depending on the vertical placement and source magnitude strength. In all cases, the largest enhancements occur in the tropical upper troposphere, where lifetimes of most trace gases are longer and where they thus become more susceptible to long-range transport by long-range circulation patterns. Comparison with observations indicate that the 0 and 20 Tg/yr(N) production rates of NO_x from lightning are too low and too high a source magnitude, respectively. However, no single intermediate production rate or vertical distribution can be singled out as best fitting the observations due to the large scatter in the datasets. This underscores the need for further measurement campaigns in key regions. The vertical profiles of Pickering et al. (1998) have been implemented in MATCH-MPIC for this study.

1. Introduction

Nitrogen oxides (NO_x=NO+NO_2) play an important role in tropospheric chemistry. They are catalytic precursors of ozone (O_3) and also have a strong influence on the hydroxyl radical (OH) concentration. Lightning-produced nitrogen oxides constitute an important part of the total NO_x budget and are one of the sources with the largest uncertainty, with estimates ranging from 1–20 Tg(N)/yr (Lawrence et al., 1995; Price et al., 1997a). Produced mostly in and around active thunderstorms, lightning-produced NO_x (ltNO_x hereafter) is readily carried to the upper levels of the troposphere by convection, where its lifetime is considerably longer than in the lower troposphere (LT). The link between lightning and nitrogen oxides was probably first recognized in 1827 by J. von

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Liebig (von Liebig, 1827), although it was not until the 1970s that further studies started to be conducted to determine its role in the photochemistry of the LT, primarily in controlling ozone concentrations. LtNO_x is also closely linked with OH radical production and hence has the potential to affect the atmosphere's oxidizing efficiency (Labrador et al., 2004). In order to determine an accurate budget for tropospheric ozone, it is crucial to determine an accurate budget for LtNO_x. The large uncertainty in LtNO_x production estimates is reflected in Table 1. From early estimates of the production range exceeding 100 Tg(N)/yr, only in the last decade do we see the estimates in different studies settling within the 1–20 Tg(N) range. The reasons for these uncertainties are many-fold; among them, on the one hand, the relatively poorly understood aspects of the lightning phenomenon itself, including the charge separation process, the amount of energy deposited per flash, the partitioning among cloud-to-ground, intracloud and intercloud flashes, and on the other hand, those aspects related to the production of NO_x, such as the amount of NO molecules produced per flash or per unit energy. While a number of laboratory studies have been carried out to determine these parameters, issues such as the similarity of simulated sparks to real flashes and the scalability of laboratory measurements to the characteristic dimensions of the atmosphere may be a source of error. The global distribution of lightning, and the total global flash rate continue to be a source of uncertainty, although this has been improved substantially by the recent advent of dedicated space-borne observation platforms such as the Optical Transient Detector (OTD) and Lightning Imaging Sensor (LIS) (Christian et al., 2003). Airborne observation campaigns provide critically-needed data to help validate model results. As will be discussed later, there is a definite need for further measurements of NO_x enhancements in storm areas, particularly in the tropics.

3-D global chemistry transport models also constitute useful and powerful tools to study the production of LtNO_x and its potential effects on atmospheric chemistry. In this paper, we study the sensitivity of tropospheric chemistry to various assumptions concerning the vertical placement and source magnitude of LtNO_x using a 3-D chemistry transport model. Given the uncertainties mentioned above, it is currently difficult

to arrive at definitive conclusions on the effects of these two parameters on the overall lightning NO_x issue. In the light of this, our main objective with this study is to add to the groundwork of knowledge on the issue of lightning-produced NO_x with the help of a modeling tool.

This study is broken down as follows; in Sect. 2 a brief description of our modeling tool, as well as our approach to modeling the vertical distribution of $LtNO_x$, is laid out. In Sect. 3, the results of model runs with 3 different assumptions concerning the vertical placement of $LtNO_x$ and 5 different total amounts are considered. In Sect. 4 the sensitivity of a number of tropospheric trace gases to different $LtNO_x$ source magnitudes is discussed. In Sect. 5 the results of our different runs are compared with a set of observations for NO_x. Section 6 gives our conclusions.

2. Approach to modeling $LtNO_x$

The model used for this study is the Model of Atmospheric Transport and Chemistry, Max-Planck Institute for Chemistry version, or MATCH-MPIC, an off-line chemistry and transport model based on the NCAR CCM (Community Climate Model) that consists of two main parts, a meteorology module and a chemistry module. The chemistry module comprises a suite of 140 gas phase reactions plus one heterogeneous reaction, including the major known sources and sinks of ozone and its associated chemistry as described in detail in von Kuhlmann et al. (2003a). MATCH-MPIC is an off-line model, and therefore needs basic meteorological data as input (temperature, zonal and meridional winds, surface pressure, latent and sensible heat fluxes) to calculate the remaining meteorological parameters, namely vertical wind velocity, convective mass fluxes, cloud fraction and precipitation and vertical turbulence. Two schemes are used to parameterize moist convection; the penetrative deep convection scheme by Zhang and McFarlane (1995), plus the convective adjustment scheme by Hack (1994). The runs for this study were done with input data from the NCEP/NCAR reanalysis at a reduced horizontal resolution of T21 (approximately $5.6^\circ \times 5.6^\circ$) and an unchanged ver-

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tical resolution which comprises 28 levels, from the surface to 0.2 hPa, in sigma coordinates. The runs were carried out for the year 1997 with a spin-up time of four months, and a timestep of 30 min was used. Further details on MATCH-MPIC are in von Kuhlmann et al. (2003a), Lawrence et al. (1999, 2003a), Rasch et al. (1997) and references therein.

2.1. Lightning parameterization

The parameterization for the horizontal distribution of lightning used in MATCH-MPIC is based on Price and Rind (1992)(PR92 hereafter). PR92 developed a simple lightning parameterization based on cloud top height as a predictor of lightning activity. It has been shown that efficient charge buildup and separation processes are strongly dependent on updraft velocity. Cloud top height has in turn been shown to correlate positively with updraft velocity. This, plus the possibility to readily determine cloud top height from direct satellite measurements, was the basis for choosing it as a first suitable predictor of lightning activity. The parameterized relationship between cloud top height and flash frequency is: $F=3.44\times10^{5}\ H^{4.9}$ for continental convective clouds, and $F=6.4\times10^{4}\ H^{1.73}$ for marine clouds, where F is the flash frequency (in flashes/min/8°×10° box) and H is the modeled cloud top height (in km). Figure 1 shows the averaged global lightning distribution using PR92 in MATCH-MPIC for the year 1997 and as observed by the OTD and LIS for the the period from mid 1997 to early 2003. The model captures the main features and the general pattern of the observed flash distribution well. The flash activity over the South Eastern United States is well reproduced, as is the overall pattern over India and South East Asia. However, an overestimation of the flash activity is apparent over the tropics, particularly over northern and central South America, Central America, South-East Asia, eastern India, eastern Borneo, Papua-New Guinea and northern Australia. On the other hand, flash activity is underestimated mostly over the extratropics, particularly over the Western and South Western United States, the Mediterranean basin, parts of central Europe and the Caucasus range, the Middle East, Central and South-Central Asia, north-eastern China and southern Australia.

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Most of the activity over Indonesia is underestimated, except for easternmost Borneo. The strong signal over the congo basin is well reproduced except for some underestimation at the center of the feature. Coastal lightning is mostly underestimated by the model as is marine lightning, particulalrly over the North and South Atlantic and the north-western Pacific. While these discrepancies might be a result of the parameterization itself, other factors, such as the convection parameterization used and the model's failure to reproduce off-shore transport of lightning-active convective clouds, may also play a role. In the last few years, other lightning parameterizations have been proposed, particularly focusing on using convective mass fluxes (Allen and Pickering, 2002); the use of these in MATCH-MPIC is being examined in a parallel study.

2.2. Vertical distribution of $LtNO_x$ in MATCH-MPIC

In previous versions of MATCH-MPIC, $LtNO_x$ was input as a uniform volume mixing ratio throughout the vertical convective column. This was chosen based on three assumptions; first, intracloud flashes are much more frequent than cloud to ground flashes (Price and Rind, 1994). Second, cloud to ground discharges are much more energetic than intracloud discharges (Turman, 1978; Kowalczyk and Bauer, 1982) and third, NO_x production by lightning apparently exhibits a strong dependence on the ambient air density, being less for lower densities (Goldenbaum and Dickerson, 1993). The first two can be regarded as canceling each other out to an extent. The third assumption results in a an approximately even mixing ratio (i.e. density-weighted) distribution of the emissions in the vertical. While these assumption are hard to prove or disprove, there is recent evidence that the vertical distribution of $LtNO_x$ in deep-convective clouds is likely to be quite different than an even mixing ratio in the vertical. Pickering et al. (1998) (subsequently P98) used a cloud-resolving model to develop a set of profiles to typify the vertical distribution of $LtNO_x$ after a convective storm for use in specifying the effective lightning NO_x source in global and regional chemistry models. Profiles were computed for three different regimes: tropical continental, marine continental and mid-latitude continental. We have implemented all three profiles

from P98 in MATCH-MPIC and, since a midlatitude marine profile was not developed in P98, we adopted the midlatitude continental profile for all midlatitude areas, marine areas included. The profiles were scaled (stretched or squeezed in the vertical) to fit the depth of convection in each model column.

A recent study by Zhang et al. (2003) has shown that simulations of different storms can lead to qualitatively similar but quantitatively different profiles from P98. Thus, more work is needed to determine the most appropriate assumptions for use in global models. Here we examine the basic sensitivity of the simulated tropospheric chemistry to various assumed profiles of $LtNO_x$, which provides an indication of the degree of importance of refining the knowledge and parameterizations of its vertical placement.

2.3. Sensitivity studies

In order to assess the impact of $LtNO_x$ and its vertical placement on tropospheric chemistry, a set of sensitivity runs was carried out where a number of different assumptions concerning the source strength and the vertical distribution of the lightning NO_x source were implemented, as summarized in Table 2.

First, a run in which the lightning NO_x source was turned off ($NoLtNO_x$ run) was carried out. Although a zero $ltNO_x$ production rate is not realistic, this run serves as a "Gedankenexperiment" against which to compare other runs, in order to be able to assess the net impact of the lightning NO_x source on the model's NO_x distribution and budget.

Second, a series of runs with various $LtNO_x$ source magnitudes was done with 3 vertical distributions: 1) a density-weighted distribution as in previous versions of MATCH-MPIC, from cloud top to ground (or cloud bottom over the oceans), which we will refer to as the EVEN distribution; 2) the distribution according to the vertical profiles developed by Pickering et al. (1998), hereafter referred to as the PICK distribution; 3) a distribution in which all of the $LtNO_x$ is deposited in the five top-most layers of the convective column, intended to represent the upper limit of upward transport of $LtNO_x$ by convective updrafts which we will call the ANVIL distribution.

The mean vertical profiles of the lightning NO_x source in MATCH-MPIC based on these three assumptions are plotted in Fig. 2. The EVEN distribution simulates an even-mixing ratio profile in the vertical, which means decreasing fluxes with altitude, as plotted in all 3 cases. The PICK midlatitude continental distribution deposits the largest amount of $LtNO_x$ in the LT, more than 100% greater than the EVEN distribution. Interestingly, in this profile, the maximum fluxes at the surface are nearly twice as large as those at high altitude. In the tropical continental and tropical marine cases, while the PICK distribution still simulates relatively large fluxes at the lower levels, those are ∼15% and ∼60% lower, respectively, than those of the EVEN distribution at the same levels. The ANVIL distribution simulates, as expected, little or no fluxes at the lower levels and peaks at ∼400 hPa in all three cases. Due to this and the large fluxes of the PICK continental distributions in the LT, the ANVIL distribution values are higher, by over 10%, than the PICK values at high altitudes in these two cases.

Different $LtNO_x$ source magnitudes, spanning the currently accepted range of uncertainties in the source, were used for these distributions. A series of runs with a 2, 5, and 10 Tg(N)/yr $LtNO_x$ production rate using the EVEN distribution were carried out (hereafter EVEN2, EVEN5 and EVEN10). Similarly, runs with a 2, 5, 10 and 20 Tg(N)/yr $LtNO_x$ production rate using the PICK distribution (hereafter PICK2, PICK5, PICK10 and PICK 20 runs) and a 2 and 5 Tg(N)/yr production rate using the ANVIL distribution (ANVIL2 and ANVIL5 runs) were made. The largest source (20 Tg(N)/yr), which we consider to be relatively unlikely, was only examined for the "best" vertical distribution (i.e. PICK20). In this study, we will analyze the effects of these different vertical distributions and source magnitudes on NO_x, O_3, OH, HNO_3 and peroxyacetyl nitrate (PAN, hereafter). We will focus our discussion on the PICK5 run, since it best reflects the currently accepted estimate for $LtNO_x$ and the most physically-based vertical distribution in the literature.

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3. Significance of $LtNO_x$ for tropospheric NO_x concentrations

In this section, we will analyze the significance of the source of NO_x from lightning on total NO_x concentrations. To that end, we will compare the results of the PICK5 run (i.e. our reference run) against the $NoLtNO_x$ run. Figure 3a and b depict the ratio of the annual zonal means of the the PICK5 vs $NoLtNO_x$ runs, and the ratio of the horizontal NO_x distributions at 300 hPa, respectively. Most of the enhancement due to $LtNO_x$ takes place in the tropical mid- and upper troposphere, mainly between 40° north and south latitude and between 800 and 200 hPa. A 20% enhancement in the zonal mean mid- and upper troposphere is evident at 700 hPa, peaking at approximately 300 hPa over the equator, where a factor of 3.4 more NO_x is present compared to the $NoLtNO_x$ run. The largest enhancements in the tropical upper troposphere (UT) are consistent with lightning activity, which is predominant over the tropics and continental regions (Christian et al., 2003), especially over equatorial South America, central Africa, and Indonesia. However, based on the preliminary evaluation discussed above, comparisons with OTD data indicate that the enhancements in NO_x might be biased high due to a tendency of the lightning parameterization to overestimate flash activity in the tropics. We see that, despite the fact that the PICK5 vertical distribution of $LtNO_x$ prescribes around 20% of the total $LtNO_x$ to be released in the first 2 km above the continental landmasses, the enhancement there is relatively small. This is mainly due to the fact that, at surface levels, $LtNO_x$ must compete against other surface sources, such as soils, biomass burning and urban and industrial fossil fuel burning emissions.

Interestingly, the addition of $LtNO_x$ causes surface total NO_x mixing ratios to decrease by ~5%, particularly over the extratropical LT (Fig. 4a). Stockwell et al. (1999) found the same result, particularly over Europe and North America, and attributed it to increases in OH due to the general increase in O_3 when lightning is included in their model simulations. There are two mechanisms to account for the computed NO_x losses, namely the reaction of OH with NO_2 to form HNO_3 and the conversion of N_2O_5 into HNO_3 via hydrolysis on aerosols. Figure 4b shows the annual mean surface ratio of

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OH for the PICK5 and the NoLtNO$_x$ runs. A general decrease of ~2% in surface OH is simulated over most midlatitude and some tropical landmasses when LtNO$_x$ is included in our simulations, mainly between 50° north and 40° south, rendering the firts mechanism unsuitable to explain the loss (NO_2 levels do increase slightly but not enough to compensate for the decrease in OH). Stockwell et al. (1999)'s explanation can be used to interpret our results outside of that latitude range where, in our simulations, surface OH increases when adding LtNO$_x$. However, wherever there is a decrease in surface OH, the negative NO$_x$ feedback can only be explained by an increase in the NO$_x$ loss rate via the second loss reaction. This mechanism depends partly on O_3 levels, which control the formation of NO_3 and therefore N_2O_5. We compute an increase in surface O_3 concentration of ~ 3% for the midlatitude continental areas (not shown), largely due to downward convective mixing of O_3 produced by LtNO$_x$ aloft (Lawrence et al., 2003b). This enhances the loss of NO$_y$ via hydrolysis of N_2O_5, and ultimately leads to the computed reduction in NO$_x$ levels.

4. Effects of the different assumptions of vertical placement of ltNO$_x$ on the vertical distribution of different trace gases

What is the impact of the different assumed vertical distributions of LtNO$_x$ on atmospheric chemistry? In order to answer this question, we compare the effects of the three main vertical distributions tested in this study for the 5 Tg(N)/yr source, i.e. EVEN5, PICK5, and ANVIL5, against the NoLtNO$_x$. We consider NO$_x$ as well as O_3, OH, HNO_3 and PAN. Common to all three distributions is that the largest enhancement in all of these species occurs in the tropical UT, between approximately 500 and 300 hPa, with the main differences being in the magnitude and the vertical extent of the enhancement.

The EVEN5 distribution (Fig. 5b) results in a gradual enhancement in NO$_x$ with altitude, consistent with a density-weighted distribution, reaching a maximum of a factor of 2 higher than the NoLtNO$_x$ run between approximately 300 and 400 hPa above the

equator. This is quite different than the PICK5 and ANVIL5 runs (Figs. 3a and 5a, respectively), which simulate very similar enhancements to each other, although the ANVIL5 run, more weighted toward the UT, simulates a reduction below 900 hPa at all latitudes and no evident enhancement below 800 hPa. The maximum enhancement in these two runs is about a factor of 3 higher than the mixing ratio of the NoLtNO$_x$ run at 300–400 hPa and represents a 100% larger enhancement than computed for the EVEN5 distribution. Considering that all three runs were done with the same 5 Tg(N)/yr LtNO$_x$ production rate, this is a significant result, since accounting for the uplifting by convection in the PICK5 and ANVIL5 runs results in twice the enhancement of NO$_x$ in the UT compared to the EVEN distribution. In all three runs, decreases in total NO$_x$ are computed at the surface in the extratropics and even in the tropics in the ANVIL5 run. As discussed before, this is mainly due to downward transport of ozone produced by enhanced NO$_x$ in the UT, reducing the near-surface NO$_x$ lifetime

Much like with NO$_x$, a gradual vertical enhancement of O$_3$ is simulated in the EVEN5 run (Fig. 6c), with the largest enhancements occurring at the tropical latitudes. Surface enhancements range from 12% within the tropics to ~4% at high latitudes. The peak enhancement is approximately 30% between 200 and 700 hPa in the tropics. Again, the PICK5 and ANVIL5 runs (Figs. 6a and b, respectively) simulate very similar profiles except at the surface, where the PICK5 run results in an enhancement of up to 15% close to the equator and ~10% in the tropical regions, compared to a maximum zonal mean surface layer enhancement of 10% in the ANVIL5 run for most of the tropics. The largest enhancements in both runs are simulated between 200 and 400 hPa over the tropics with 45% more O$_3$ compared to the NoLtNO$_x$ run. The general differences in tropospheric O$_3$ as a result of the different vertical placements emphasize the role of NO$_x$ in controlling the O$_3$ budget, and underscores the need not only to determine an accurate estimates of the LtNO$_x$ source magnitude, but also to correctly assess its post-storm vertical distribution.

There is a significant impact on OH by LtNO$_x$. In the EVEN5 run (Fig. 7c), enhancements of up to 60% with respect to the NoLtNO$_x$ run are simulated in the tropical UT,

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mainly in the altitude band between 300 and 100 hPa. Again the PICK5 and ANVIL5 runs (Figs. 7a and b, respectively) show very similar profiles for OH, with enhancements of approximately 100% between 100 and 200 hPa. All three runs also simulate enhancements of about 10% near surface levels in the tropics. The enhancements in the cold and dry tropical UT are because there production of OH via $O(^1D)+H_2O$ is slow, while secondary sources, such as enhancements in HO_x recycling efficiency due to NO_x increases, take on a more important role. Despite the strong temperature dependency of the oxidation reactions of long-lived trace gas such as methane and methylchloroform, this result has an important effect on the oxidizing efficiency of the troposphere, and increases in the source magnitude of $LtNO_x$ can lead to a substantial reduction in the computed lifetimes of these trace gases (Labrador et al., 2004).

There is a very sensitive response of nitric acid, one of the main reservoirs through which reactive nitrogen is lost (via dry and wet deposition), to $LtNO_x$. All three distributions simulate enhancements greater than a factor of 2 with respect to the $NoLtNO_x$ run, as can be seen in Figs. 8 a, b and c. The particularly sensitive response is due to the fact that, on adding $LtNO_x$, a direct precursor of nitric acid, another precursor, OH, is also enhanced. From all three distributions, it can be observed that, compared to most other trace gases discussed, the maximum enhancements in nitric acid occur at a somewhat lower altitude i.e. between 400 and 500 hPa. Two main reasons could account for this fact: first, while the largest relative increase in OH by adding $LtNO_x$ occurs in the UT, the largest absolute enhancement occurs at a lower altitude (Labrador et al., 2004), coinciding with the maximum enhancement in nitric acid. Furthermore, in the UT, there is a buffering effect of PAN, which is enhanced at the expense of nitric acid. The PICK5 and ANVIL5 runs (Figs. 8a and b, respectively) are very similar, although the enhancement in the UT at higher latitudes is greater in the ANVIL5 run and the PICK5 run simulates larger enhancements than the ANVIL5 run in the lowermost levels.

The importance of the NO_x reservoir species peroxyacetyl nitrate (PAN) lies in its high stability at low temperatures. Once produced, it can be transported long dis-

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tances and, through thermal degradation, it can introduce NO_x into remote regions, where background levels are generally low. As shown in Figure 9a, the burden of PAN is doubled in the tropical UT by assuming the PICK5 lightning NO_x vertical distribution. The EVEN5 run (Fig. 9c) simulates increases of over 50% from 500 hPa up to tropopause level over the tropics, where values peak at a factor of 1.6 larger than the $NoLtNO_x$ run. The PICK5 and ANVIL5 runs (Figs. 9a and b, respectively) show again a very similar pattern. Maximum enhancements are of the order of 100% between ~300 and 200 hPa in both distributions, with enhancements decreasing rapidly outside of the tropical latitudes. All three distribution simulate enhancements in PAN in the UT, as a result of increases in total NO_x in the same region. The ANVIL5 run simulates no notable enhancement at the surface, whereas the PICK5 run shows a 10% enhancement, consistent with the placement of NO_x by the PICK98 profiles in the lowermost troposphere.

5. Sensitivity of tropospheric trace gas burdens to the increase in the source of NO_x from lightning

In this section, we analyze the responses of NO_x, as well as O_3, OH, HNO_3 and PAN to increases in the source magnitude of $LtNO_x$. We calculated the burdens of these trace gases for the whole globe (90° north to 90° south), the tropics (between 25° north and south), and the extratropics (90° to 25° north and 25° south to 90° south), for the EVEN2, 5 and 10 and PICK2, 5, 10 and 20 runs. Since the PICK and ANVIL runs produce mostly similar results, we will limit our comparison to the EVEN and PICK set of runs.

Fig. 10a–e show the burdens for the EVEN and PICK runs as a function of the $LtNO_x$ source magnitude. A consistent tendency was for the PICK runs to result in higher burdens for all trace gases than the EVEN runs, due to their lifetimes generally being longer in the UT, where most of the NO_x in the PICK runs is released.

Globally, adding $LtNO_x$ produces a tendency towards saturation, already seen from

2 Tg(N)/yr–5 Tg(N)/yr and which becomes very clear in the 20 Tg(N)/yr production rate. The response of the EVEN set of runs is similar to the PICK runs, although the magnitude of the absolute increase in total NO_x is not as marked as that of the PICK runs. Interestingly, the difference in the total NO_x burden for equivalent production rates between the PICK and EVEN runs increases with increasing $LtNO_x$: relative to the NO $LtNO_x$ run, the PICK2 run simulates a total NO_x burden 2.5% larger than the EVEN2 run. For the 5 and 10 Tg(N)/yr production rates, these differences are 4.3 and 5.3%, respectively. This is as a consequence of the weighting of the PICK distribution towards the higher altitudes, as opposed to the even (density-weighted) EVEN distribution.

The tropical regions simulate a more sensitive response, due in large part to the fact that most of the lightning activity in the model is concentrated there (Fig. 1) and because the other competing sources (especially fossil-fuel burning) tend to be smaller in the tropics than in the extratropics. Though the same non-linear response as in the whole globe is also present, increases in total NO_x are larger. The differences in burden growth with respect to the $NoLtNO_x$ run between the PICK and EVEN runs are also larger than in the whole globe: 4%, 6.7% and 7.9% for the 2, 5 and 10 Tg(N)/yr production rates, respectively.

As with NO_x, O_3 shows a non-linear response to increases in $LtNO_x$, tending towards saturation at the highest end of the range in both sets of runs. The PICK runs simulate larger enhancements throughout the entire production range, particularly in the tropical regions (Fig. 10b and Table 3). Globally, the PICK20 run simulates increases of up to 30% with respect to the $NoLtNO_x$ run, while in the tropics O_3 is enhanced by 45% for the same run. These enhancements are all the more important considering that they take place in the UT, where longer lifetimes and the Hadley circulation can transport this ozone to higher latitudes and because O_3 is more efficient as a greenhouse gas at higher altitudes. This increase of O_3 at higher altitudes is responsible for the reduction of surface NO_x levels simulated at high latitudes in Figs 2a and 4a.

Figure 10c shows that the relative change in global enhancement of the OH burden is greater than that of O_3 and is close to that of NO_x. Table 4 shows the regional annual

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mass-weighted OH mean concentrations, as suggested by Lawrence et al. (2001), for the different vertical distributions with a 5 Tg(N)/yr $LtNO_x$ production rate, as well as the relative increases of the two vertical distributions versus the $NoLtNO_x$ run. The largest OH increases in all three distributions are in the southern hemisphere, despite the lightning activity being dominant over the northern hemisphere (Christian et al., 2003). For instance, in the EVEN5 distribution, the enhancements in the 90° S–30° S domains at all altitudes are about a factor of two larger than those in the equivalent domains in the northern hemisphere, whereas in the in the 30° S–0° domains, they are about 50% larger than in the 0°–30° N ones. In the PICK distribution the enhancements in the 90° S–30° S regions below 750 hPa are a factor of three larger, and in the 750–500 hPa and 500–250 hPa domains approximately a factor of two larger than the equivalent northern hemisphere domains. In the 30° S–0° domains, the enhancements are about 50% larger than in the 0°–30° N domains. This marked sensitivity of the southern hemisphere to $LtNO_x$ is a result of smaller total NO_x emissions from other sources, which makes OH more sensitive to increases in NO_x there. The PICK distribution simulates larger relative increases vs. the $NoLtNO_x$ run in the uppermost domains than the EVEN distribution, particularly in the tropics, consistent with the larger amounts of $LtNO_x$ deposited in the upper levels by the former.

Nitric acid (HNO_3) (Fig. 10d) shows a marked sensitivity to increases in $LtNO_x$ which is different from the other gases. There is more than a doubling in its burden between the 2 and 5 Tg(N)/yr runs in both the PICK and EVEN distributions over the whole globe as well as in the tropics. For higher production rates, the approximately linear response continues without abatement until the top of the production range for both sets of runs, with enhancements of over 100% and 200% over the whole globe and tropics, respectively, in the PICK20 run. This sensitivity increases with the magnitude of the source of NO_x from lightning (Table 3) and is due to the increase in its two main precursors, NO_2 and OH. From Fig. 10d, it is readily apparent that the burdens for the tropical and extratropical regions are very approximately the same; this is in part accounted for by the fact that the OH radical is more abundant in the tropics (see

Table 4), while NO_2 is more abundant in the extratropics.

Figure 10e shows that the burden of PAN can be doubled versus the NoLtNO_x run in the tropical UT by assuming the PICK vertical distribution. For every 5 Tg(N)/yr of NO_x from lightning, PAN is enhanced by almost 52% between the NoLtNO_x and PICK5 runs, or about 14% more than NO_x (Table 3). Then, for every additional 5 Tg(N)/yr, PAN is enhanced by 17% between the PICK10 and 20 runs, or about half the increase in NO_x for the same range; thus, the tendency towards saturation is much stronger for PAN than for other trace gases. The strong response at the lower end of the LtNO_x production range in the tropics can be accounted for by the very strong emissions of isoprene in MATCH-MPIC runs in the tropics (von Kuhlmann et al., 2004). The formation of PAN depends, among other factors, on the availability of the peroxyacetyl radical, the dominant producer of which in our runs in the tropical regions is isoprene. As LtNO_x is further increased, however, one moves into a hydrocarbon-limited PAN formation regime. While NO_x is increased through LtNO_x, isoprene emissions, and other PAN precursors are kept constant in our runs, leading to the rapid saturation signal.

6. Comparisons with observations

In this section we compare the model output from the sensitivity runs with the composites of airborne field campaign observations of Emmons et al. (2000). Table 5 and Fig. 11 show the selected set of observation campaign regions for comparison with our model results. Six regions were selected for their location within the tropics, which are representative of both maritime (regions 2, 8 and 9 in Fig. 11), continental (regions 1 and 4) as well as coastal areas (region 3). Regions 2 and 3 are of particular importance since they are located downwind of NO_x sources such as LtNO_x and biomass burning from the African continent. Four regions were selected in the extratropics, of which two in coastal areas (region 5 and 10), and two in continental areas (region 6 and 7). It bears keeping in mind that the years of the campaigns generally do not co-

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incide with the year of our simulation; this introduces a further element of uncertainty which may need to be assessed in the future in the light of interannual variability of lightning. Figure 12 shows the vertical profiles of NO_x for the measurements of each campaign region plotted (box-whiskers plots) as well as those of the model output for the NoLtNO_x, EVEN5, PICK5 and PICK20 runs for the selected regions.

In all but one case, the PICK20 run overestimates the observed NO_x profiles, particularly over the tropical sites. In the case of regions 3 and 4, the modeled concentrations can be up to a factor of 3 higher than those of the observations at the higher altitudes. While the trend is not as strong over the tropical marine sites (regions 8 and 9), it is still evident. Over the midlatitudes, where measurements were available (region 10), the same tendency is again observed, with the PICK20 modeled concentrations about 50% higher than observed ones. Although more observations are needed, our results give a strong indication that the 20 Tg(N)/yr production of NO_x from lightning is too high a source magnitude.

Other than with for PICK20 run, it is difficult to discern any particular trend of over- or underestimation of the model results, even when dividing the comparison between tropics and extratropics. Over the tropical continental landmasses, there is generally good agreement between modeled results and observations in the first 4 km for all 4 areas (regions 1, 3, 4 and 5) considered. However, there is also little difference between the different model profiles up to that height, which underscores the fact that the largest differences in NO_x mixing ratios are found in the UT (see Fig. 2a). The runs start to exhibit larger differences among them above about 4 km. In region 4, the PICK20 run shows a clear tendency to overestimate above ~3 km as do, to a much lesser extent, the two runs with 5 Tg(N)/yr production rate. In South Africa (region 1), the model results tend to underestimate NO_x in the LT, probably as result of underestimated biomass-burning emissions in the model, but there is a slightly better agreement in the free and upper troposphere. The overall low mixing ratios in the UT for both measurements and model results indicate low lightning activity over the campaign region at that time. Even then, the PICK20 run clearly overestimates NO_x in the UT. NO_x mea-

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surement above Natal, Brazil (region 3) were only made for the first 5 km and, up to that height, the PICK5 run shows the best agreement with the observations. Over the two maritime regions in the tropical Pacific Ocean (regions 8 and 9), all 4 runs plotted tend to clearly overestimate NO_x mixing ratios in the first 4–6 km, probably as a result of excessive downward transport of NO_x-rich air into the lower reaches of the marine troposphere on the part of the model. Above that, there is a better agreement between the runs and the measurements, with the exception of PICK20 run clearly being on the higher end (when not outside) of the measured values. However, since in the UT the range of measured values is wide and includes the values for most of the model runs, is it not possible to single out any run as having the best agreement. Region 2, in the tropical south Atlantic, shows a much clearer separation of the profiles for the different runs. Since one would not expect much lightning activity there, this is an indication of transport of NO_x-rich air form the African continent and underscores the importance of long-range transport of trace gases. In the lowermost troposphere and up to 4 km, most runs overestimate measured values, a probable result of excessive PAN in the model as diagnosed before (von Kuhlmann et al., 2003b). The $NoLtNO_x$ run clearly underestimates the measured values in the UT and, while the EVEN5 and PICK20 runs are still within the observed range there, it is the PICK5 run that more closely reproduces observed values. In the middle troposphere, between 4 and 8 km, most runs tend to underestimate measured values.

Over the extratropical continental areas (regions 6 and 7), measurements were not carried out above 6 km, where the simulated values start to spread. Over region 6, all runs overestimate NO_x in the first 2 km, as does the PICK20 run for the entire altitude range. The rest of the runs show a better agreement in the free troposphere but, again, no particular run shows better agreement with measured values than the rest. The NO_x profile over Japan (region 10) shows most runs overestimating NO_x, particularly in the lower and middle troposphere. All 4 runs show very little differences among them at that height, which indicated low flash activity over the region and might point towards other sources than $LtNO_x$, such as excessive PAN decomposition (von

Kuhlmann et al., 2003b), that could be responsible for the disagreement. The coastal area of Brazil (region 5) shows a clearer separation between all modeled NO_x profiles above 4 km, indicating strong lightning activity. Above that height, all 4 runs overestimate NO_x up until 10 km height, when measurements and modeled results (except the PICK20 run) agree again. Pickering et al. (1996) points out that convection was unusually active during the TRACE A campaign in Brazil. The fact that all but the $NoLtNO_x$ run overestimate NO_x in that region suggest that the lightning production in our model may be biased high there. This could be a further indication of PR92's tendency to overestimate lightning over the tropical continents.

Figure 13 show the total NO_x scatterplots for 3 runs in this study, namely the $NoLtNO_x$, PICK5 and PICK20 runs for data above 5 km. The plots are done for the entire set of airborne observation campaigns in the Emmons et al. (2000) dataset where NO_x measurements were available. The 5 km lower limit was chosen because, as seen from the vertical profile plots, it is where the values for the different runs generally start to separate. The $NoLtNO_x$ run shows a distinct trend to underestimate observed values throughout the entire concentration range, but particularly in the upper range. The PICK5 shows the best fit of all runs, both burden- and distribution wise, although the EVEN5 run (not pictured) resulted in a very similar correlation coefficient (r^2=0.4655) and a lower slope (0.65866). It is interesting to notice that, in spite of these two runs having markedly different NO_x vertical distributions, the difference in the scatter plots is small. We believe this to be due to the lack of observation at key locations where the largest differences could be expected. On the other hand, the PICK20 run shows a clear tendency to overestimate the observations data throughout the entire range, particularly at the upper end, confirming the tendency already seen in the vertical profile plots.

The effects of the vertical distribution and source magnitude of $LtNO_x$ have been addressed before in a number of modeling studies. Tie et al. (2001) and Stockwell et al. (1999) point out that including lightning-NO_x emissions in their models produces better agreement with observations. In another study, Tie et al. (2002) conclude, based

on vertical profile plots, that simulations with a production of 7 Tg(N)/yr of NO_x from lightning uniformly distributed in clouds, and 3.5 Tg(N)/yr in the upper regions of clouds produce the best agreement with observations. The differences between our modeled results and the latter study are notable. While there may be many factors to account for this, including the use of different models, we believe that the use of the Hack (1994) convection scheme in Tie et al. (2002) is fundamental in accounting for these differences since it is unable to simulate deep convective mixing well. From our results, it is apparent that it is not possible, based on vertical profiles alone, to arrive at a solid conclusion as to which run yields the best agreement with observations, and while the scatter plots afford an extra measure of objectivity to our analysis, we can only state with a certain degree of confidence that in our simulations the NoLtNO_x and PICK20 runs underestimate and overestimate, respectively, the observations enough not to be considered as realistic assumptions. We believe that the combination of the low availability of observational data, particularly in critical areas, such as the continental tropics (see Fig. 8), the large scatter in the available observations and the many uncertainties in modeling lightning NO_x and other NO_x sources calls for exercising caution when coming to conclusions about its source magnitude based on simple comparisons with observations. More observations campaigns, such as TROCCINOX (http://www.pa.op.dlr.de/troccinox), specifically aimed at reducing the uncertainties in the source of NO_x from lightning and in key regions, such as the tropical continents, are therefore needed.

7. Conclusions

We have investigated the effects of different assumptions concerning the source magnitude and vertical placement of lightning-produced NO_x on total NO_x as well as on O_3, OH, HNO_3 and PAN using the chemical transport model MATCH-MPIC. Our results show these trace gases to be very sensitive to both parameters. Global increases in NO_x in the tropics compared to a run with no NO_x from lightning are simulated assum-

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ing a 5 Tg(N)/yr LtNO_x production rate and a vertical distribution according to Pickering et al. (1998). Since these enhancements occur primarily in the tropical upper troposphere, the produced NO_x, along with all other trace gases resulting from its chemistry, have the potential to be transported over long distances to pristine areas, greatly enhancing concentrations in those places. However, under the present circumstances, we believe that the uncertainties in our knowledge of the production of NO_x from lightning, such as 1) the horizontal distribution of lightning, which we address in a separate study, 2) the energy produced by each type of discharge and number of NO molecules per unit energy, along with 3) the low number of observation campaigns available, make it extremely difficult to determine a "best" vertical distribution and source magnitude. We can say, however, that our results points towards a 0 Tg(N)/yr of NO_x from lightning as being too low and 20 Tg(N)/yr as being too high a production rate. This underscores the need for further measurement campaigns, particularly in the tropical continental regions, where lightning activity is prevalent, as well for improved lightning parameterizations for use in 3-D global chemistry transport models.

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Table 1. Global estimates of lightning-produced NO_x (values prior to 1995 adopted from Lawrence et al. (1995)).

REFERENCE (type of estimate)	Molec.(NO)/unit energy ($\times 10^{16}$ molec./J)	Molec.(NO)/flash ($\times 10^{25}$ molec./flash)	Number of flashes (flashes/s)	$LtNO_x$ production rate (Tg(N)/yr)
Tuck (1976)[a]	–	1.1	500	4
Chameides et al. (1977)[a]	3–7	6–14	400	18–41
Noxon (1976)[c]	–	10	500	37
Chameides (1979)[a]	8–17	16–34	400	47–100
Dawson (1980)[a]	–	0.8	500	3
Hill et al. (1980)[a]	–	1.2	100	0.9
Levine et al. (1981)[b]	5±2	0.5	500	1.8±0.7
Kowalczyk and Bauer (1982)[a]	–	10	500	5.7
Peyrous and Lapyere (1982)[b]	1.6	3.2	400	9.4
Drapcho et al. (1983)[c]	–	40	100	30
Chameides et al. (1987)[d]	–	–	–	7
Franzblau and Popp (1989)[c]	–	300	100	220
Sisterson and Liaw (1990)[a]	–	8.2	200	12
Liaw et al. (1990)[e]	–	–	–	81
Lawrence et al. (1995)[e]	–	2.3(1–7)	100(70–150)	2(1–8)
Kumar et al. (1995)[c]	–	0.5	100	2
Ridley et al. (1996)[c]	–	–	100	2–5
Levy et al. (1996)[a]	–	–	–	2–6
Price et al. (1997a)[c]	10	–	70–100	12.2(5–20)
Price et al. (1997b)[a]	10	–	–	13.2(5–25)
Wang et al. (1998)[b]	–	3.1	30–100	2.5–8.3
Nesbitt et al. (2000)[c]	–	0.87–6.2	57	0.9
Navarro-Gonzales et al. (2001)[b]	15±5	–	–	–
Huntrieser et al. (2002)[c]	–	2.7×10^{21} molec/m flash	–	3
Christian et al. (2003)[c]	–	–	44±5	–
Fehr et al. (2004)[c]	–	21	–	–

[a] Theoretical estimate
[b] Laboratory-based estimate
[c] Field observations-based estimate
[d] Thunderstorm extrapolation-based estimate
[e] Review-based estimate

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Table 2. MATCH-MPIC runs done for this study.

RUN	$LtNO_x$ production (Tg(N)/yr)	Vertical distribution
$NoLtNO_x$	0	Density-weighted[a]
EVEN2	2	Density-weighted[a]
EVEN5	5	Density-weighted[a]
EVEN10	10	Density-weighted[a]
PICK2	2	Pickering et al. (1998)
PICK5	5	Pickering et al. (1998)
PICK10	10	Pickering et al. (1998)
PICK20	20	Pickering et al. (1998)
ANVIL2	2	Five uppermost layers of cloud
ANVIL5	5	Five uppermost layers of cloud

[a] Evenly-distributed mixing ratio

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Table 3. Burdens of the NoLtNO$_x$ runs (in Tg for NO$_x$ and O$_3$ and $\times 10^6$ molec for OH) and relative increases (in percent) of the burdens of the different trace gases for the whole globe and tropics (T) for the different runs with respect to the LtNO$_x$ runs.

Trace gas	Burden in NoLtNO$_x$ run	Relative increase vs. NoLtNO$_x$ run						
		P2	P5	P10	P20	E2	E5	E10
NO$_x$	0.14	9.1	19.5	31.9	51.2	6.4	14.4	24.9
NO$_x$(T)	0.05	16.6	36.4	60.6	98.2	11.9	27.3	47.8
Ozone	377.1	6.8	14.1	21.8	30.7	4.9	10.6	17.6
Ozone (T)	138.5	9.9	20.8	32.3	45.6	7.1	15.7	26.2
OH	0.17	13.2	27.8	43.1	61.3	9.6	21.1	35.1
OH (T)	0.09	16.4	34.8	54.8	78.4	11.9	26.5	44.6
HNO$_3$	0.15	14.2	35.6	69.6	135.2	11.6	29.1	59.8
HNO$_3$ (T)	0.07	21.4	54.7	109.6	217	17.6	44.7	90.7
PAN	0.37	14.2	28.9	43.2	57.4	9.7	21.3	34.9
PAN (T)	0.13	8.1	51.7	24.8	33.2	5.5	12.0	19.8

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Table 4. Regional annual mean airmass-weighted OH concentrations ($\times 10^6$ molec/cm^3) and relative increases vs. NoLtNO$_x$ (in parenthesis) for the different LtNO$_x$ vertical distributions.

REGION	NoLtNO$_x$	EVEN5	PICK5
Below 750 hPa 90° S–30° S	0.54	0.58 (+7.4%)	0.59 (+9.3%)
Below 750 hPa 30° S–0°	1.25	1.45 (+16%)	1.43 (+14.4%)
Below 750 hPa 0°–30° N	1.44	1.59 (+10.4%)	1.56 (+8.3%)
Below 750 hPa 30° N–90° N	0.82	0.85 (+3.7%)	0.85 (+3.7%)
750–500 hPa 90° S–30° S	0.48	0.55 (+14.6%)	0.56 (+17%)
750–500 hPa 30° S–0°	1.21	1.53 (+26.4%)	1.56 (+28.9%)
750–500 hPa 0°–30° N	1.44	1.71 (+18.8%)	1.72 (+19.4%)
750–500 hPa 30° N–90° N	0.72	0.77 (+6.9%)	0.77 (+6.9%)
500–250 hPa 90° S–30° S	0.34	0.40 (+17.6%)	0.42 (+23.5%)
500–250 hPa 30° S–0°	0.67	0.93 (+38.8%)	1.07 (+59.7%)
500–250 hPa 0°–30° N	0.87	1.13 (+29.9%)	1.27 (+46%)
500–250 hPa 30° N–90° N	0.52	0.57 (+9.6%)	0.58 (+11.5%)

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Table 5. Set of campaign regions, campaigns names and coordinates used in this study to compare against model output.

Region	Region name	campaign	Date	Coordinates, deg.
1	Africa-South	TRACE-A	21 Sept.–26 Oct. 1992	25 S–5 S, 15–35
2	Atlantic-S	TRACE-A	21 Sept.–26 Oct. 1992	20 S–0, 340–350
3	Natal	CITE-3	22 Aug.–29 Sept. 1989	15 S–5 N, 325–335
4	E-Brazil	TRACE-A	21 Sept.–26 Oct. 1992	15 S–5 S, 310–320
5	E-Brazil Coast	TRACE-A	21 Sept.–26 Oct. 1992	35 S–25 S, 310–320
6	Ontario	ABLE3-B	6 July–15 Aug. 1990	45 N–60 N, 270–280
7	California	CITE-2	11 Aug.–5 Sept. 1986	35 N–45 N, 235–250
8	Pacific-Tropics-W	PEM-West-A	16 Sept.–21 Oct. 1991	5 S–15 N, 155–165
9	Philippine-sea	PEM-West-A	16 Sept.–21 Oct. 1991	5 N–20 N, 135–150
10	Japan-Coast-E	PEM-West-A	16 Sept.–21 Oct. 1991	15 N–40 N, 135–150

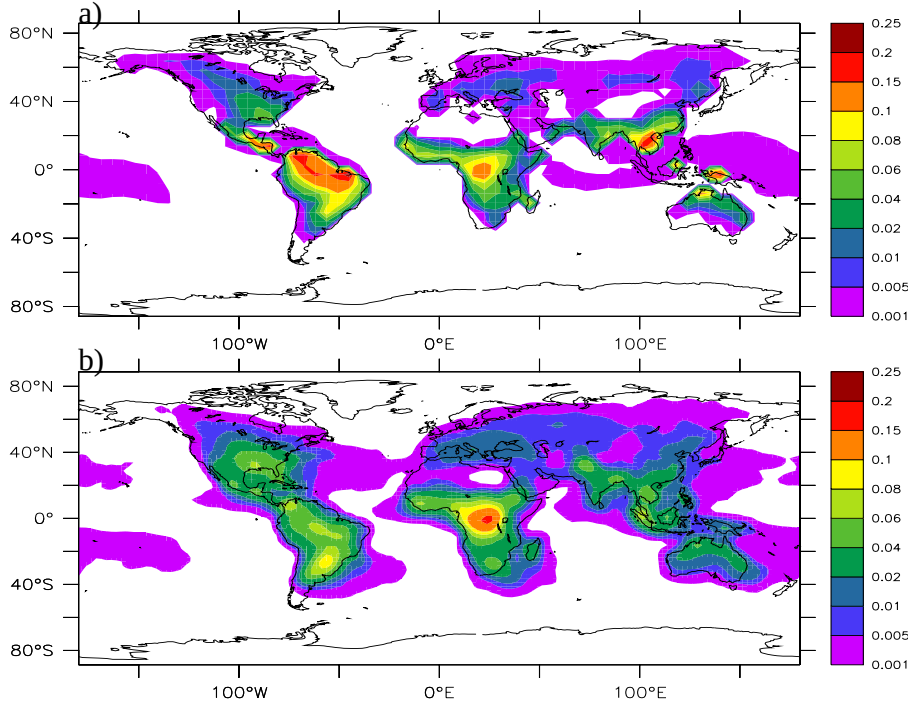

Fig. 1. Averaged flash activity from **(a)** MATCH-MPIC for 1997 and from **(b)** OTD/LIS for 1995–2003 in flashes/km^2/day.

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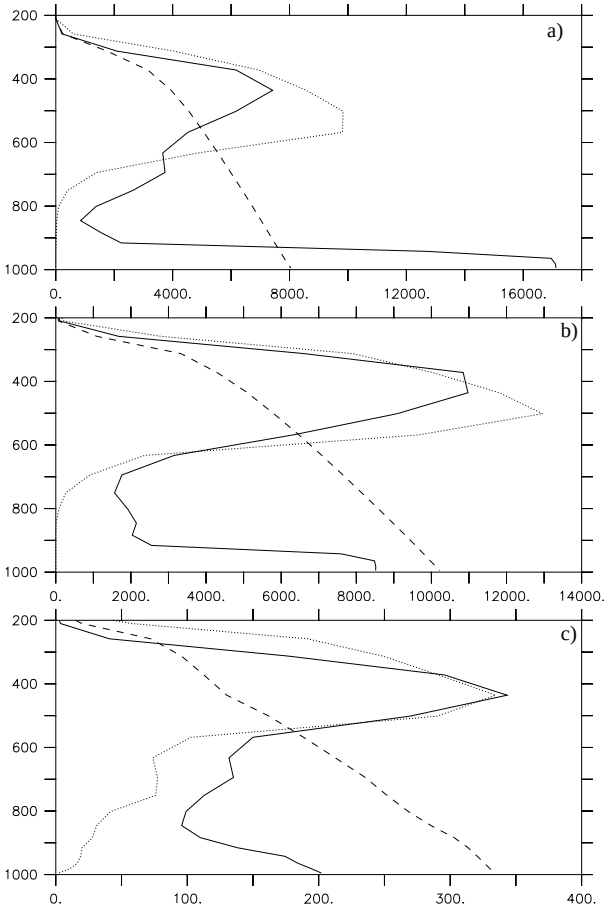

Fig. 2. Global mean vertical distribution profiles of the lightning NO_x source, in kg/m^3/s, for the three vertical distributions in this study, PICK (solid line), ANVIL (dotted line) and EVEN (dashed line), for the PICK distribution's three cases: **(a)** midlatitude continental, **(b)** tropical continental and **(c)** tropical marine (bottom). Vertical axis scale in hPa.

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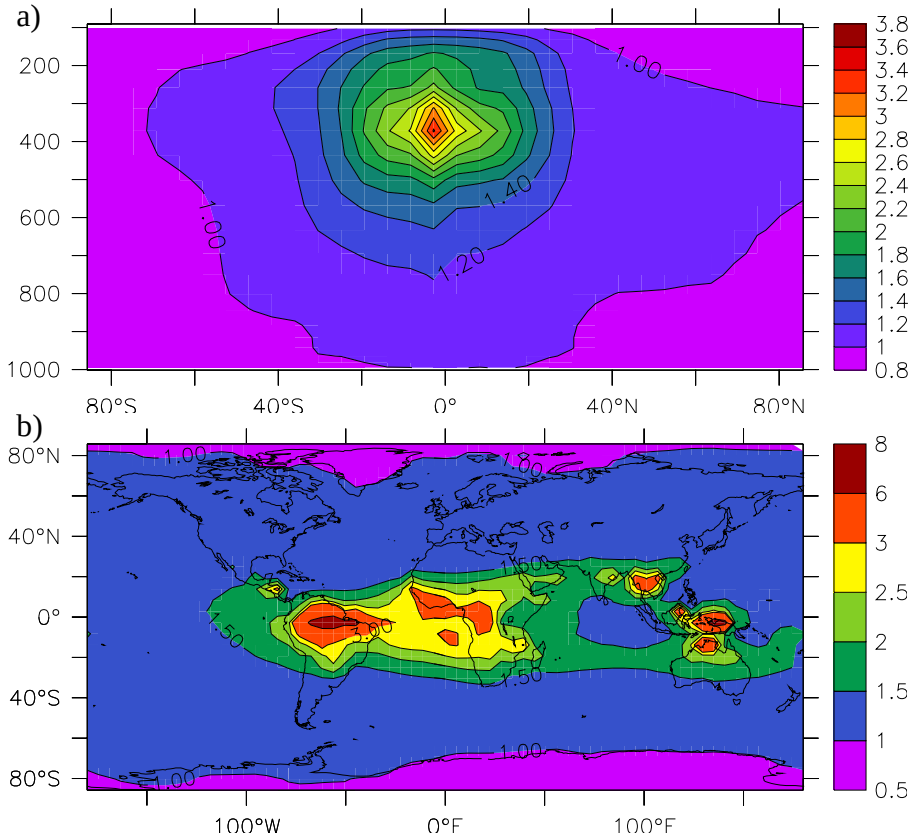

Fig. 3. Ratio of **(a)** annual zonal means and of the **(b)** horizontal distributions at 300 hPa of NO_x for the PICK5 and NoLtNO_x runs.

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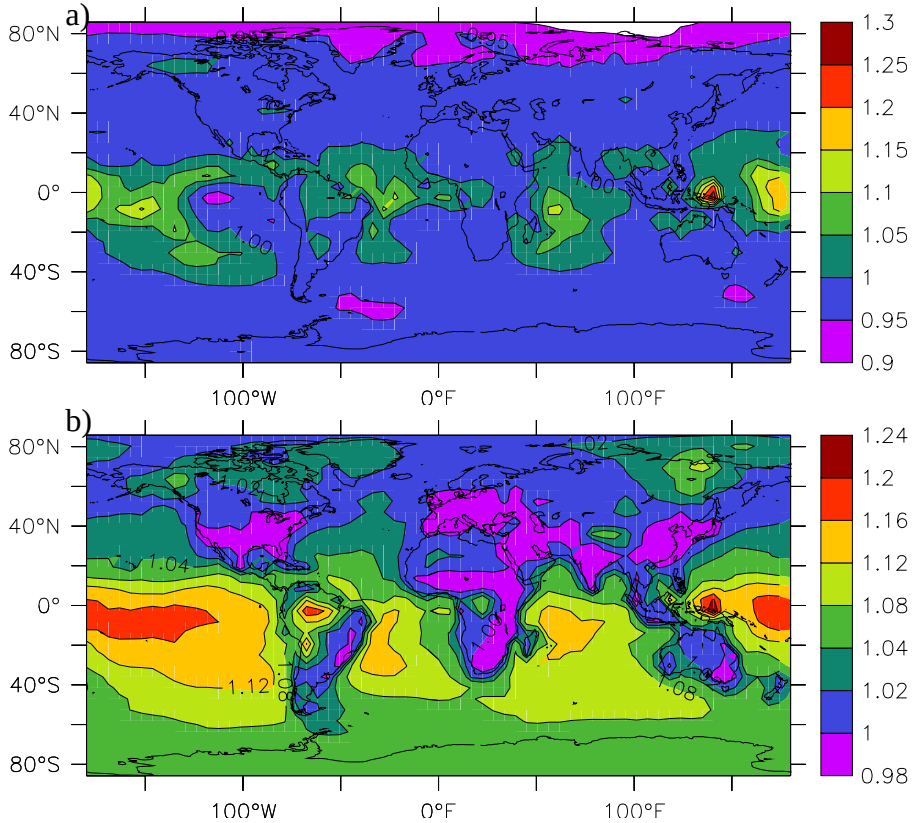

Fig. 4. Ratio of the horizontal distributions at 1000 hPa of **(a)** NO_x and **(b)** OH for the PICK5 and NoLtNO_x runs.

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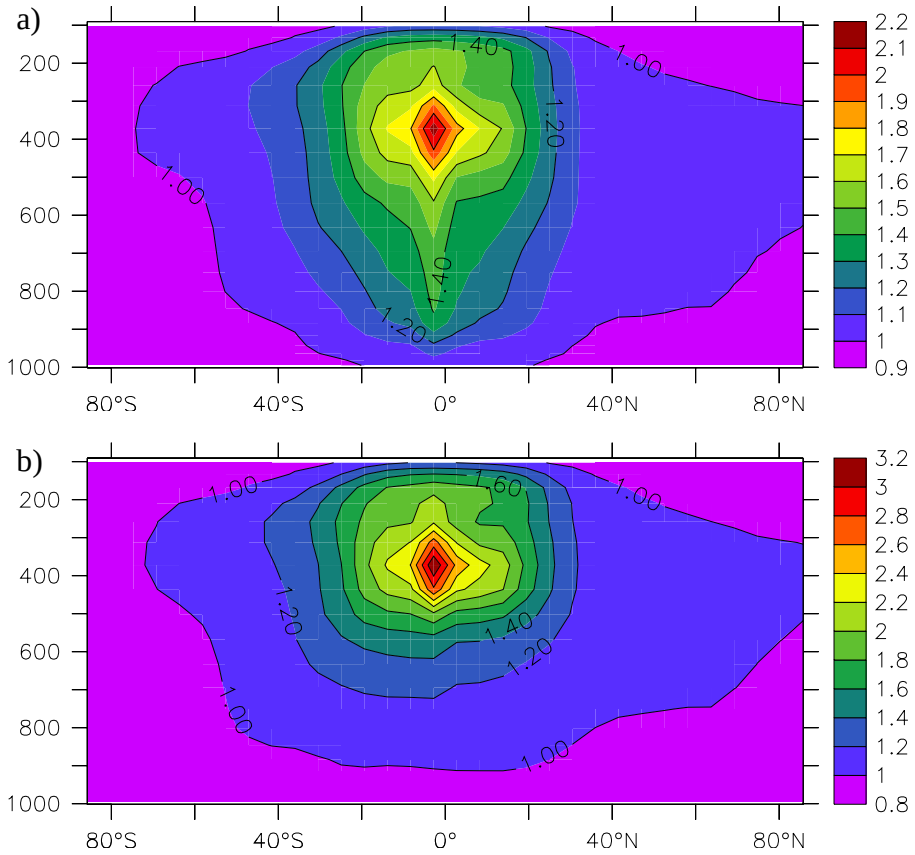

Fig. 5. Ratios of the annual zonal means of the **(a)** ANVIL5 and **(b)** EVEN5 runs to the NoLtNO$_x$ run for total NO$_x$.

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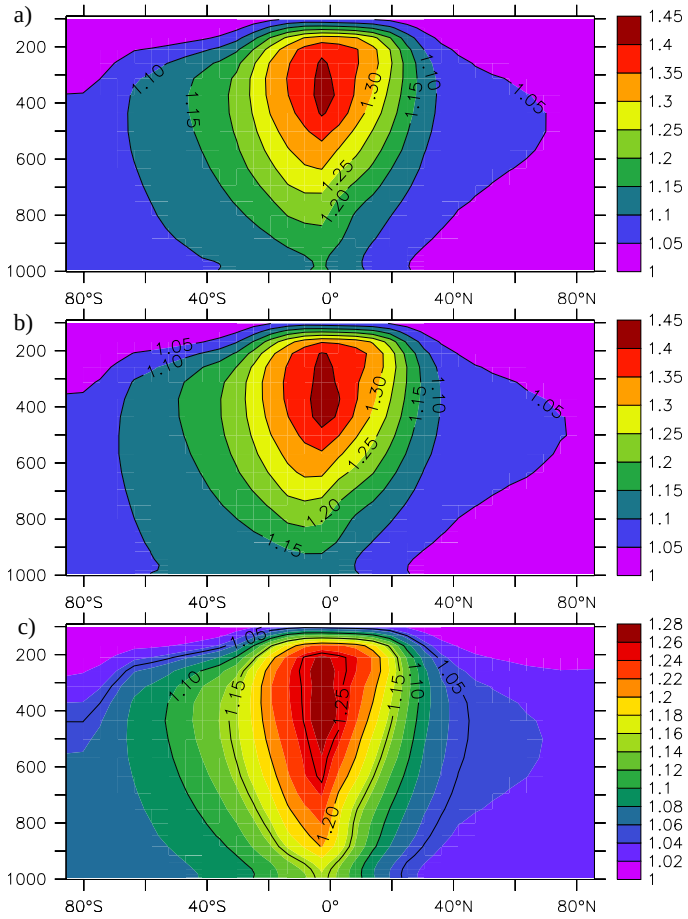

Fig. 6. Ratios of the annual zonal means of the **(a)** PICK5, **(b)** ANVIL5 and **(c)** EVEN5 runs to the NoLtNO$_x$ run for O_3.

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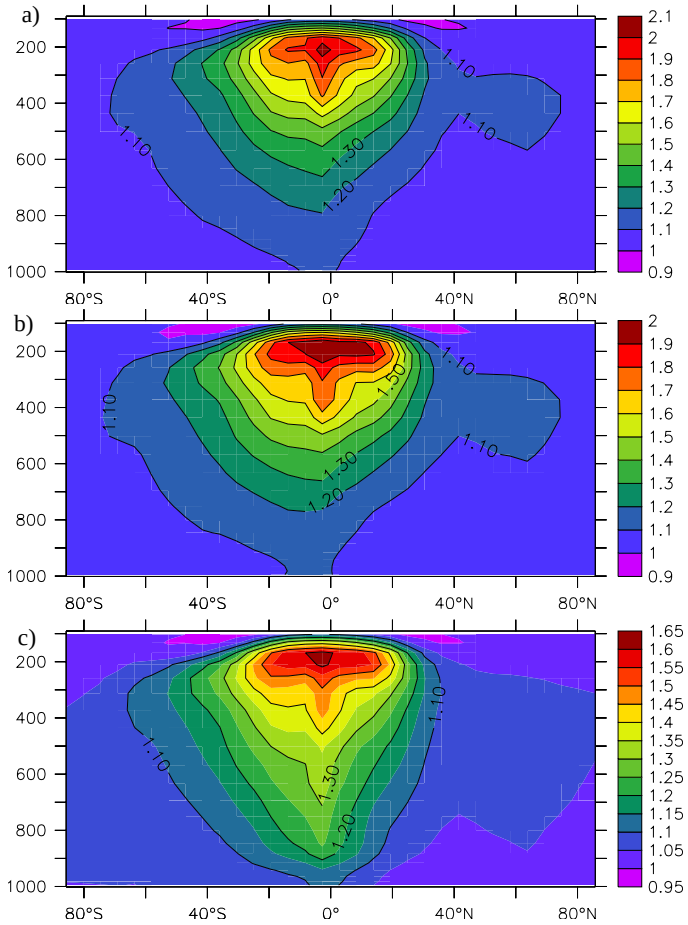

Fig. 7. Ratios of the annual zonal means of the **(a)** PICK5, **(b)** ANVIL5 and **(c)** EVEN5 runs to the NoLtNO$_x$ run for OH.

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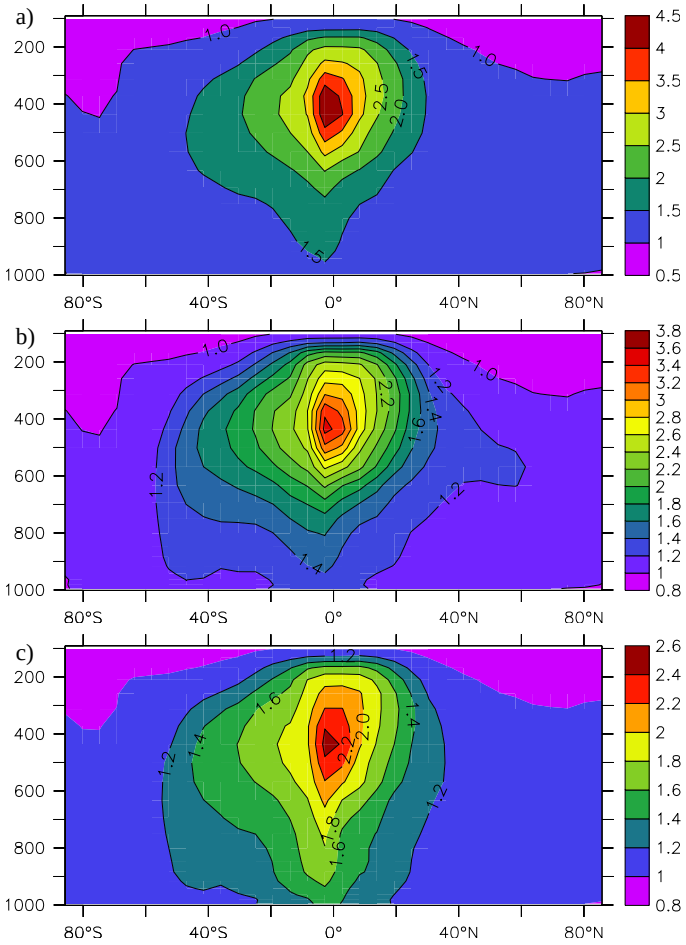

Fig. 8. Ratios of the annual zonal means of the **(a)** PICK5, **(b)** ANVIL5 and **(c)** EVEN5 runs to the NoLtNO$_x$ run for HNO$_3$.

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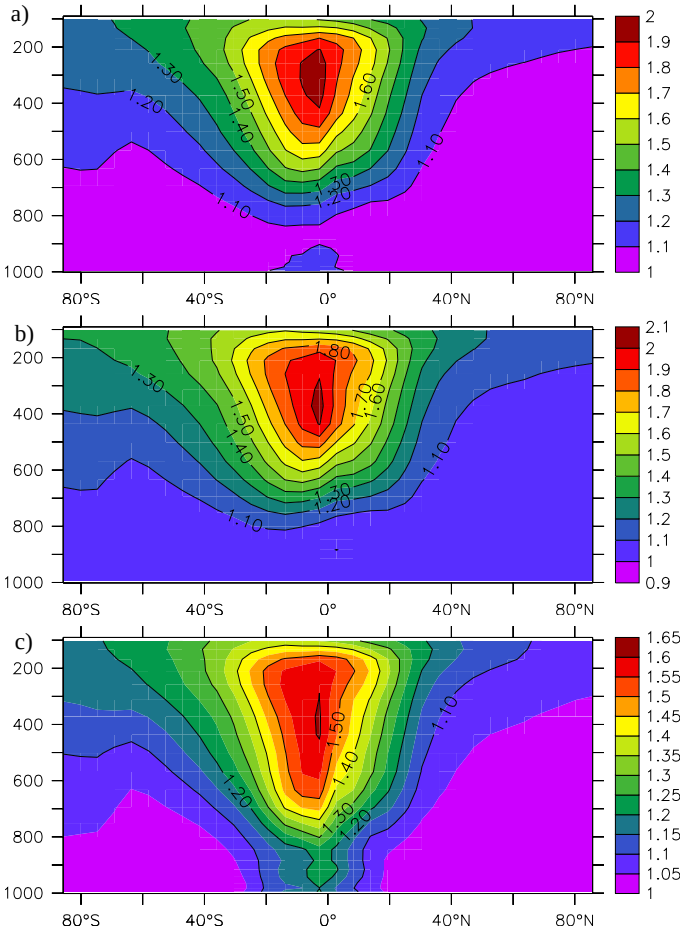

Fig. 9. Ratios of the annual zonal means of the **(a)** PICK5, **(b)** ANVIL5 and **(c)** EVEN5 runs to the NoLtNO$_x$ run for PAN.

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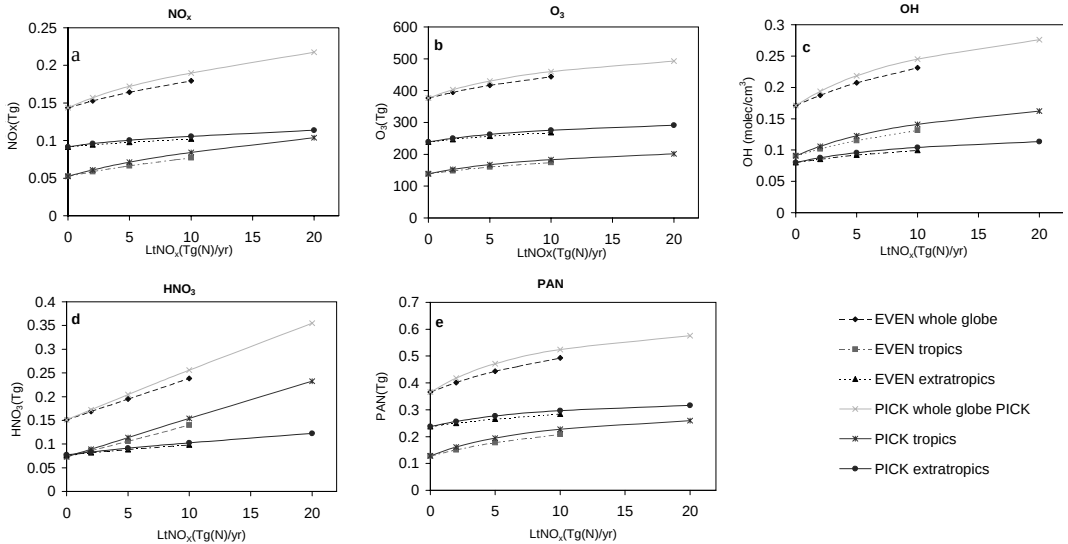

Fig. 10. Burdens of **(a)** NOx, **(b)** O_3, **(c)** OH, **(d)** HNO_3 and **(e)** PAN, for the PICK and EVEN series of runs for the tropics and extratropics.

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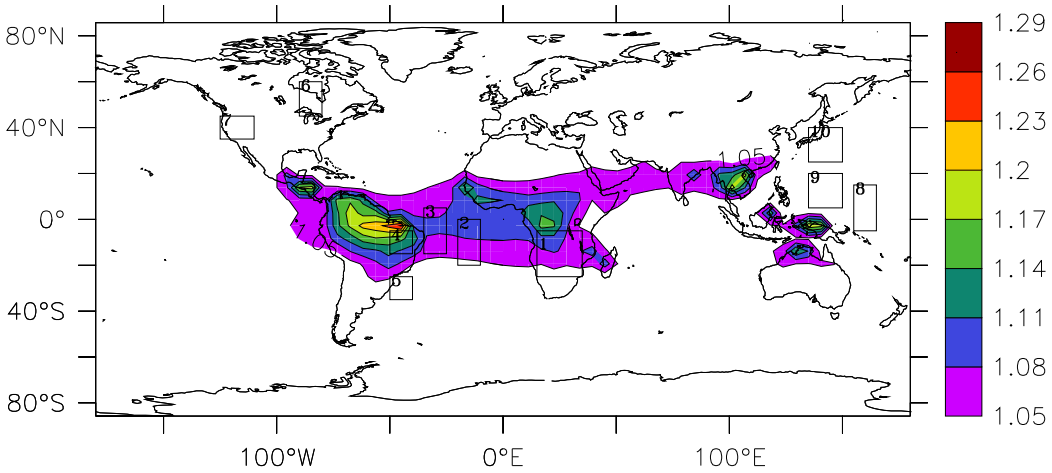

Fig. 11. Campaign regions (within boxes), superimposed on the ratio of the annual horizontal distribution of NO_x from the PICK55 and NoLtNO_x runs.

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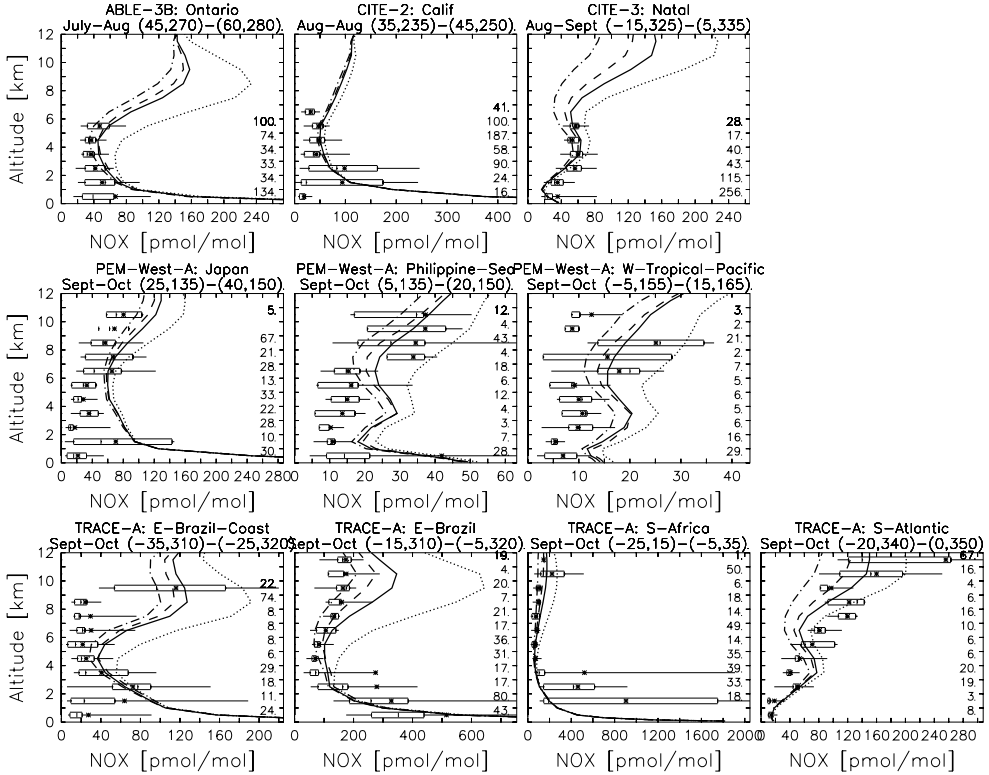

Fig. 12. NO_x profiles for different campaign regions and for $NoLtNO_x$ (dash-dotted line), EVEN5(dashed line), PICK5(solid line) and PICK20 (dotted line) runs. The boxes and whiskers contain the central and side 40% of the observations. On the right-hand side are the number of observations at each altitude. Inside the whisker boxes, the median and mean values are represented by an asterisk and vertical line, respectively.

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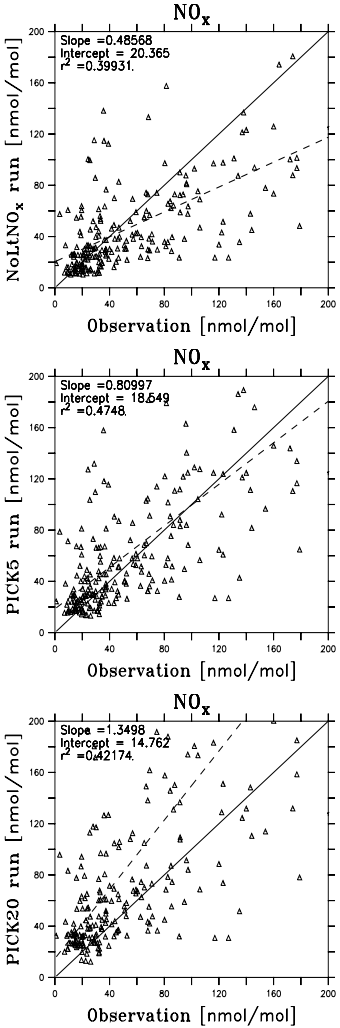

Fig. 13. Scatter plots of the NoLtNO$_x$, PICK5 and PICK20 runs against airborne observation campaign data above 5 km.

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