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Three-dimensional study of the relative contributions of the different nitrogen sources in the troposphere

J.-F. Lamarque, G.P. Brasseur, and P.G. Hess

Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado

J.-F. Müller

Belgian Institute for Space Aeronomy, Brussels

Abstract. A three-dimensional study of the relative importance of the different odd nitrogen sources in the troposphere is discussed. In order to consistently simulate the chemistry, all the sources are considered simultaneously but each nitrogen emitted is characterized by a given flavor. This allows us to follow the evolution of nitrogen from each source without affecting the overall chemical system of the atmosphere. The model results suggest that the NO_x concentration in the southern hemisphere is mostly dominated by the lightning source, while the northern hemisphere odd nitrogen burden results mainly from the influence of fossil fuel combustion, aircraft, and lightning emissions. In particular, in the upper tropospheric northern hemisphere midlatitudes, approximately 25-30% of the NO_x is due to aircraft, 15-20% to fossil fuel combustion sources at the surface, and 15-20% to lightning, assuming that the global fleet of aircraft releases 0.44 TgN/yr and that lightning produces 5 TgN/yr. The sensitivity of these figures to several parameters (aircraft and soil source strengths, as well as the lightning source strength and its vertical distribution) is also studied.

1. Introduction

Nitrogen oxides (NO_x=NO+NO_2) are critical components of the troposphere which directly affect the abundance of tropospheric ozone [*Crutzen*, 1974] and OH [*Levy*, 1971]. As a consequence, they directly influence the oxidizing capacity of the atmosphere [*WMO*, 1991]. It is, therefore, essential to understand the processes that control the concentration of NO_x in the troposphere. In particular, it is important to assess the relative importance of the anthropogenic emissions of NO_x, which have significantly increased over the last decades. Because of their increase, the anthropogenic emissions of NO_x have enhanced the level of ozone both in the boundary layer and probably in the free troposphere. Because ozone is a greenhouse gas, these emissions have the potential to impact climate. Moreover, it has been identified that the radiative forcing due to an ozone change is highest near the tropopause level [*Lacis et al.*, 1990]. This point is of particular interest as the upper troposphere/lower stratosphere is the region in which most aircraft emissions are released. Also, nitrogen emitted in the upper troposphere is much more efficient in enhancing ozone than ground-based emissions [*Liu et al.*, 1987; *WMO*, 1991; *Hauglustaine et al.*, 1994]. This has the consequence that relatively small emissions of NO_x from aircraft could play an unexpectedly large role. As aircraft emissions are expected to grow [*NASA*, 1993] due to increasing air traffic, it is necessary to assess the importance of the aircraft source relative to the other sources and, specifically, to natural sources. The goal of this study is to identify the relative importance of each source of odd nitrogen and, in particular, evaluate the potential effect of aircraft emissions.

Two-dimensional studies such as those of *Ehhalt et al.* [1992] or *Hauglustaine et al.* [1994] provide simple approaches to study the impact of aircraft emissions but suffer from being unable to adequately represent three-dimensional chemical and dynamical atmospheric processes. On the other hand, three-dimensional studies of the contribution from various sources are either characterized by consideration of a single source [*Levy and Moxim*, 1989; *Kasibhatla*, 1993; *Kasibhatla et al.*, 1991; *Kasibhatla et al.*, 1993] or using simple (reduced) chemistry [*Penner et al.*, 1991]. In neither case is the atmospheric chemistry treated in a fully consistent manner. In particular, the response of ozone to a variation in NO_x depends nonlinearly on the amount of NO_x present [*Liu et al.*, 1987]. As a consequence, if one source of odd nitrogen is left out of the calculation, then the changes in NO_x and ozone associated with this missing source may be different than its actual effect. Therefore, by not considering simultaneously all the sources of nitrogen,

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all the previous studies have, to an unknown extent, miscalculated the effect of a single source NO_x to its budget. This study will examine the influence of the individual sources taken all together.

The approach adopted in the present study is to use a relatively detailed tropospheric chemistry mechanism and look at the evolution of the nitrogen species according to their sources; in other words each source of odd nitrogen is characterized by a "flavor" and each flavor can therefore be followed, as it is affected by transport and subject to chemical reactions. This approach is exact and allows the accurate identification of the portion of nitrogen associated with each source, as long as the chemistry of the nitrogen family is linear (see the appendix). The case of N_2O_5 requires special attention.

The paper is organized as follows: in section 2, the three-dimensional chemistry transport model used in this study is briefly described, along with the method used to tag the nitrogen species to a specific source. The results are discussed in section 3, first as zonal means and then as time series at specific locations. In addition, a sensitivity study to the strength of the lightning, aircraft, and soil sources is performed and comparisons with available observations are presented. Finally, conclusions are drawn in section 4.

2. Model Description and Design of the Experiments

The model used in this study is the Intermediate Model of the Annual and Global Evolution of Species (IMAGES) model developed by *Müller and Brasseur* [1995]. This model has a horizontal resolution of 5 degrees in latitude and longitude. It is formulated in the vertical in terms of σ-coordinate with 25 levels. Among these levels, five are in the boundary layer and three in the stratosphere while the rest spans the troposphere. In order to limit the computer time needed to perform the integration, monthly averaged winds and temperature provided by the European Center for Medium-Range Weather Forecasts (ECMWF) analyzed data are used. The effect of wind variability at timescales shorter than 1 month is parameterized by an eddy diffusivity proportional to the wind variance. Transport of long-lived chemical species is simulated using the semi-Lagrangian advection scheme of *Smolarkiewicz and Rasch* [1991]. Convective transport is parameterized by an array of probability transfer coefficients [*Costen et al.*, 1988], dependent on time and location of deep convection as deduced from the International Satellite Cloud Climatology Project (ISCCP) data.

In its standard form, the chemical mechanism includes 41 chemical compounds, 125 chemical reactions, and 26 photodissociations. The model accounts for chemical transformation, surface emissions, dry and wet deposition, and aerosol conversion of nitrogen oxides (NO_3, N_2O_5). The validation of the model, for both dynamics and chemistry, is reported by *Müller and Brasseur* [1995]. The reader is referred to that paper for more information on the model and the description of the validation procedures and of the results.

Table 1. Nitrogen Sources Adopted in the Model

Source	Size
Aircraft	0.44
Biomass burning	4.50
Fossil fuel	21.70
Lightning	5.00
Soil	6.60
Stratosphere	0.20
Total	38.44

Nitrogen sources measured in teragrams of nitrogen (TgN) per year.

2.1. Description of Nitrogen Sources

As formulated in IMAGES, odd nitrogen is released into the modeled troposphere by six sources: combustion in aircraft engines, biomass burning, lightning, fossil fuel combustion, soil emission, and transport from the stratosphere. The globally and annually averaged sources adopted in the model are listed in Table 1. It must be emphasized that there is a large uncertainty in the size of these sources, especially the lightning and the soil sources. For example, estimates of the soil source ranges from 5 to 12 TgN/yr [*WMO*, 1995]. The uncertainty in the lightning source can be as large as a factor 100 (1 to 220 TgN/yr, *Müller and Brasseur* [1995]) but ranges most probably between 3 and 20 TgN/yr [*WMO*, 1995]. The values used here fall into the lower end of these ranges. Nevertheless, sensitivity to the strength of the lightning, aircraft, and soil sources is discussed in sections 3.4, 3.5 and 3.6 respectively.

In the model, the monthly mean production of NO from lightning is distributed according to the number of lightning flashes detected at dusk by satellite [*Turman and Edgar*, 1982]. The source is explicitly set to zero in the two upper levels of the model (i.e., above 100mbar) and the number of NO molecules produced per unit time and volume is distributed uniformly with altitude throughout the remaining levels. This latter assumption is discussed in section 3.4.

The production of NO from soils depends primarily on soil temperature, vegetation coverage, soil type, nitrate and water concentrations. The monthly averaged global soil emissions from *Müller* [1992, 1993] (at a $5° \times 5°$ resolution) are adopted. Global emissions represent 6.6 TgN/yr in agreement with previously published estimates. About 2.4 TgN/yr are produced by the tropical forests. The global emissions are maximum in July (0.7 TgN/month) and minimum in November

(0.4 TgN/month). A large portion of the uncertainty in the soil source is the result of redeposition of NO_x onto the vegetative canopy [*Bakwin et al.*, 1990]. Indeed, in the real world, only a small fraction of the NO_x emitted from the soil reaches the atmosphere above the canopy. This effect has been taken into account in the evaluation of the soil source strength.

Biomass burning includes deforestation, savanna fires, slash and burn agriculture, fuelwood burning, natural forest fires, and burning of agricultural wastes. Among these, the first two are dominant. NO_x emissions are calculated from estimates of carbon release [*Müller*, 1992] by adopting the NO_x/CO_2 ratio estimated by *Hao et al.* [1991] (forests, 1.4%; savanna, 0.7%; fuelwood, 0.4%; agricultural wastes, 1.7%). The geographical and seasonal variations of the emissions are discussed by *Müller and Brasseur* [1995].

Fossil fuel combustion includes the emissions from oil, gas and coal burning, and industrial activities including waste disposal. Again, the surface emissions are taken from *Müller* [1992]; they account for geographical and seasonal variations. The geographical distribution is determined from population density and the location of industries. The seasonal variation is determined from the seasonal variation of fossil fuel use. It is clear from Table 1 that, globally, the fossil fuel source is the dominant source. In addition, because of its geographical distribution (almost exclusively in the northern hemisphere), this source should be the major contributor of NO_x in the lower to middle troposphere of the northern hemisphere.

Another anthropogenic source is provided by aircraft emissions. The aircraft emissions contribute significantly to the abundance of NO_x in the upper tropospheric midlatitudes of the northern hemisphere. The three-dimensional distribution of aircraft emissions is taken from the NASA scenario A [*NASA*, 1993] and is interpolated to the model grid. The global source of NO_x by aircraft adopted in this study accounts for 0.44 TgN/yr and represents approximately 2% of the source of NO_x due to fossil fuel combustion at the surface. Other emission inventories suggest that the aircraft source could be larger by a factor of 2 [*WMO*, 1995].

The influx of NO_x produced from N_2O destruction in the stratosphere represents an additional source of nitrogen for the troposphere. This influx is associated with stratosphere-troposphere exchange. As the model does not resolve (both in time and space) all the processes involved in the exchange, the stratospheric source is represented by a seasonally varying upper boundary condition that fixes HNO_3 at the model top (50mbar). This upper boundary condition accounts for an influx of 0.2 TgN/yr into the troposphere. This integrated value is smaller than in some previous studies [*Kasibhatla et al.*, 1991; *Ehhalt et al.*, 1992]. However, it is within the estimated values of *Murphy and Fahey* [1994], although at the low end of their best estimates.

2.2. Design of the Numerical Experiments

In this set of experiments, nitrogen atoms are tagged according to their source. This enables us to accurately isolate the amount of nitrogen associated with a single source without affecting the overall chemical scheme of the model. Nitrogen originally emitted as one species (e.g., NO) is tagged so that it can be followed during all subsequent chemical transformations (e.g., to NO_2 and subsequent products). This tagging procedure always allows the origin of a nitrogen atom contained in a chemical species to be monitored.

If, for example, we consider only two sources of nitrogen, the total NO mixing ratio can be written as the sum

$$\mathrm{NO} = \mathrm{XNO} + \mathrm{YNO}$$

where XNO and YNO refers to the mixing ratio of NO associated with sources X and Y respectively. It is therefore possible to express all the chemical reactions for the X and Y flavors of NO so that the chemical scheme in the model is equivalent to a scheme where all the emissions (X+Y) are grouped into a single species. This is shown in more detail in the appendix. Every chemical species containing nitrogen is tagged using the same procedure described above for NO. As described in the introduction, this approach is necessary to keep the overall chemical scheme equivalent in each simulation. The only species for which the effects of two flavors can interfere is N_2O_5, since this compound is produced by the combination of two other nitrogen species (NO_2 and NO_3). The implication of this characteristic is discussed in more detail in the appendix.

For practical reasons, each simulation has been carried out with only two flavors at a time. In this case, X can be associated with a particular source, while Y is associated with the five remaining sources. To represent the effect of each source requires a total of six runs (each of 2 years). The comparison of the total nitrogen species (X + Y) from each run showed no noticeable differences with a control run in which all the sources were considered simultaneously. Furthermore, for each simulation k (with $k = 1, 6$), the relationship

$$\sum_{\substack{i=1 \\ i \neq k}}^{6} \mathrm{X}_i = \mathrm{Y}_k$$

was verified to an accuracy of a few percent. Local differences can indeed arise from inaccuracies in the transport (which is, as constructed in the model, a nonlinear process, especially due to the flux correction procedure) as the mixing ratio of X species exhibits large gradient (as they originate from a single source), with a different shape for every different source. As numerical models have difficulties handling strong gradient, differences can be expected. It must nevertheless be clear that these are local differences, not globally integrated differences. As a consequence the mixing ratio X_i, from

the i^{th} simulation (or equivalently for the i^{th} source), can be used to compute the relative importance of that particular source to the total burden of atmospheric nitrogen $\sum_{k=1}^{6} X_k$.

3. Results

As will be shown later, a key result of this study is the large importance of the lightning source throughout the free troposphere. The contribution to the NO_x concentration from this source is surprisingly robust, despite its relatively small size (see Table 1). In the lower troposphere, fossil fuel combustion (in the northern hemisphere) and soil emissions and biomass burning (in the southern hemisphere) are the main contributors. Using the sources size listed in Table 1, the zonally and seasonally averaged contribution from the aircraft source never exceeds 25% and is confined to the northern hemisphere.

3.1. Zonal Means

In this section, the contribution from each source (expressed in percent) is defined as the ratio of the NO_x concentration associated with each single source to the total amount of NO_x present at the same location, that is,

$$\text{contribution from source } i \;=\; \frac{X_i}{\sum_{k=1}^{6} X_k} \qquad (1)$$

where X_i (i=1,...,6) represents the NO_x concentration associated with the source i. For the rest of the paper, NO_x is defined as

$$NO_x \;=\; NO + NO_2 + NO_3 + HO_2NO_2.$$

The different contributions are displayed as zonal averages for the month of January (Plate 1).

Aircraft emissions have almost no influence in the southern hemisphere as the contribution from this source (as defined by (1)) never reaches more than 1-2% (Plate 1a). Most aircraft fly north of 30°N and the transport from these regions to the southern hemisphere is slow. Also, the influence is confined to altitudes between 7 and 12 km as other sources are proportionnally more important than the aircraft source in the rest of the troposphere. Indeed, in the upper troposphere and lower stratosphere, the stratospheric source is dominant. At lower altitudes, in the northern hemisphere, the major contributions are from the lightning and fossil fuel sources (Plate 1c and d).

The influence of the biomass burning source is only significant in the tropical lower troposphere (Plate 1b). There is also evidence of convective transport as the relative contribution associated with this source extends well into the free troposphere. However, although convective transport effectively transports NO_x produced by biomass burning from the boundary layer into the upper troposphere, its contribution to upper tropospheric NO_x is less than 10% primarily due to the presence of lightning (see Plate 1c). The contribution from the biomass burning source is, therefore, significant only in the lower troposphere.

The influence of the lightning source (with a global and annual average assumed to be 5 TgN/yr) is displayed in Plate 1c. It is clearly the largest source over a large portion of the southern hemisphere troposphere where anthropogenic influences are small. In the tropical troposphere, the contribution from the lightning source even reaches more than 70%. Odd nitrogen produced by the lightning source is relatively important (20-30%) in the northern hemisphere primarily due to transport (local sources are small in January north of 20°N). As the lifetime of NO_x is relatively short, transport of odd nitrogen from the tropics to the midlatitudes requires recycling of NO_x through longer-lived reservoir species such as peroxyacetyl nitrate (PAN) and nitric acid (HNO_3).

Fossil fuel emissions of NO_x are clearly the dominant contributor in the lower troposphere of the northern hemisphere (Plate 1d). As for the aircraft emissions contribution (Plate 1a), there is a a strong interhemispheric gradient. There is also evidence of vertical convective transport from the boundary layer to the middle and upper troposphere as the contribution from the fossil fuel combustion extends well into the free troposphere (up to 10 km of altitude).

Soil emissions (Plate 1e) are qualitatively similar to those from biomass burning but their contribution in January are nevertheless twice as large, although the mean annual strength of the two sources is similar (see Table 1). Neither source is maximum in January. The seasonal cycle of the sources is described in more detail in the next section.

Finally, the contribution of the stratospheric source is only important to the troposphere above 10 km (Plate 1f). This is true everywhere except near the south Pole where the vertical wind computed from the ECMWF analysis indicates a strong descent, which could be unrealistic.

3.2. Latitude-Season Description

In order to show the relative contribution of each source (as defined by (1)) for a given region of the atmosphere, the results from the simulations are displayed as seasonally averaged zonal means over latitudinal bands of 30° width for the 200mbar and 900mbar pressure levels (Plate 2). Within each box, the sum of all contributions is 100%.

At 200mbar (≈10 km) and with the assumptions made for the size of the different NO_x sources (Table 1), the lightning source of NO_x is clearly dominant throughout the entire southern hemisphere, contributing up to 80% of the local NO_x concentration (Plate 2a). In the northern latitudes the contribution of the stratospheric source varies with season and peaks in December through February (DJF), as expected from the

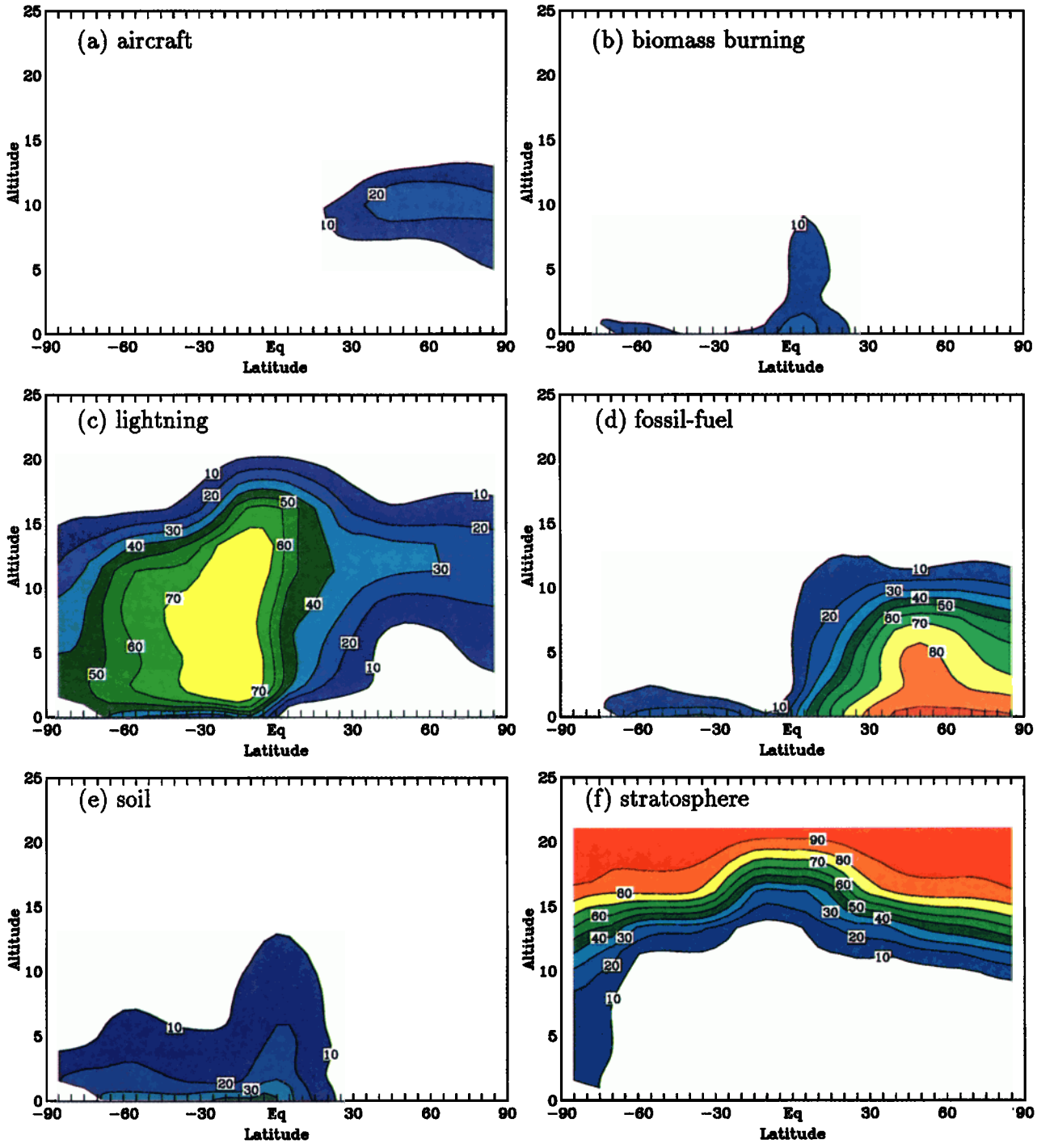

Plate 1. Latitude-altitude representation of the January zonal mean contribution (in percent, see equation (1)) to NO_x from nitrogen emissions by (a) aircraft, (b) biomass burning, (c) lightning, (d) fossil fuel combustion, (e) soil, and (f) stratosphere.

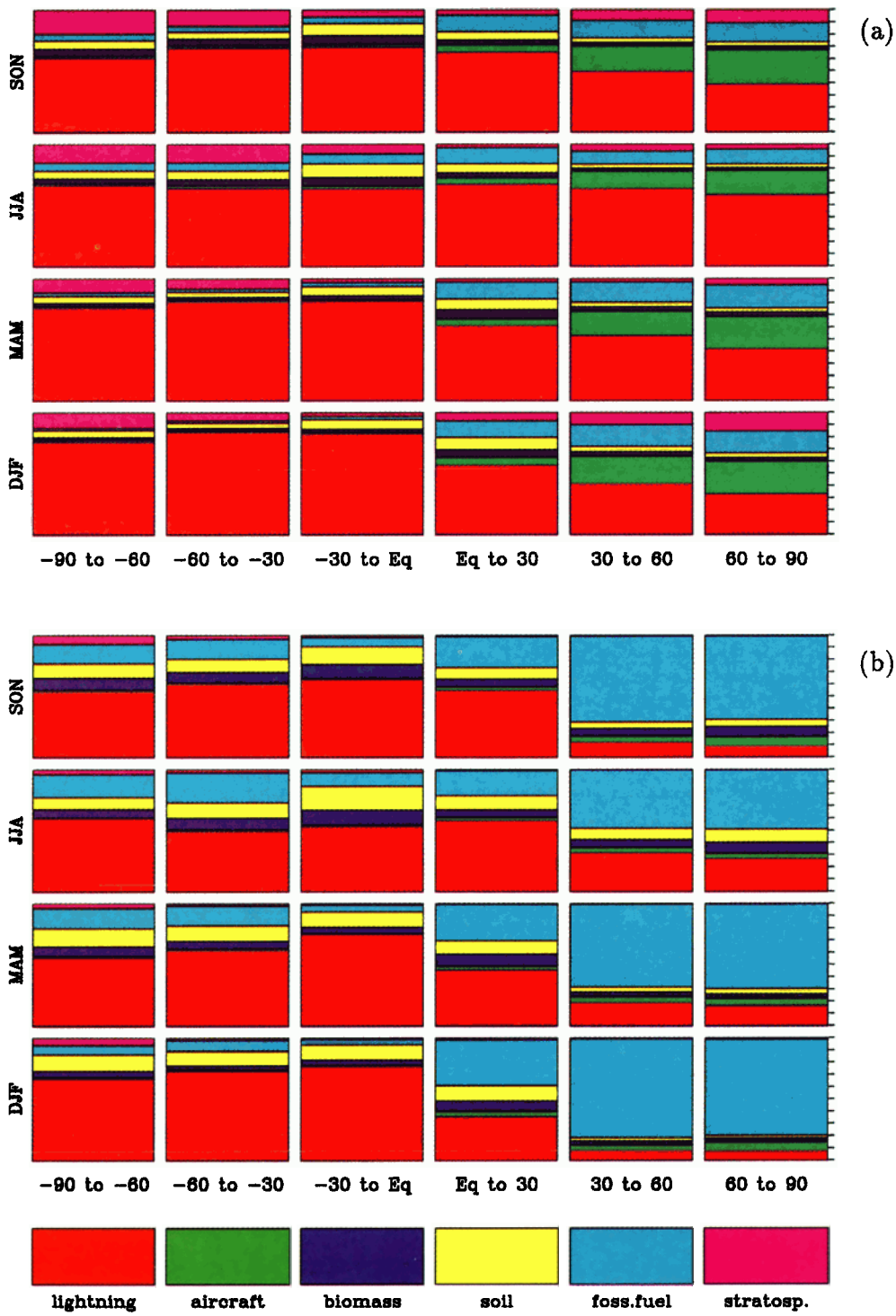

Plate 2. Latitude-season representation of the relative contribution from all sources to NO_x. Data is zonally, seasonally, and latitudinally (over a band of 30°) averaged. The total in each box is 100%; (a) for the 200mbar surface, (b) for the 900mbar surface.

climatology of the lower stratospheric residual circulation [*Rosenlof*, 1995]. The contribution from lightning peaks in summer in the northern latitudes, as emissions from fossil fuel combustion are at a minimum and emissions from lightning are at a maximum. However, the contribution from lightning is an important component throughout the year in the northern hemisphere upper troposphere. At 200mbar, there is no region in which the biomass burning source or the soil emissions is of significant strength, even though some of the NO_x emitted by these sources is rapidly transported from the boundary layer to the upper troposphere by deep convection. It is also interesting to note that although a large fraction of the emissions from aircraft is concentrated over the northern Atlantic ocean, the emitted NO_x clearly spreads over most of the northern hemisphere poleward of 30°N. Finally, at that altitude, the contribution from the aircraft source (20-30% all year long) is very close to the contribution from the fossil fuel combustion, although the latter is globally 50 times larger.

In the southern hemisphere winter and spring, a fraction (5-10%) of the upper tropospheric NO_x is due to fossil fuel combustion, a source primarily located in the northern hemisphere. Transport of polluted air from the northern hemisphere to the southern hemisphere is sufficiently vigorous to affect the NO_x concentration there, in addition to small local sources from fossil fuel combustion. Although the NO_x concentration associated with fossil fuel combustion is 2 orders of magnitude smaller in the southern hemisphere than in the region of emission, these small levels ($\approx$1pptv) are of significance in the remote areas of the southern hemisphere. It must be noted that the transport characteristics of IMAGES have been compared to observations; in particular, using Kr^{85}, the interhemispheric transport, as represented by IMAGES, has been shown to be realistic (*Müller and Brasseur* [1995], see their Figure 4).

At 900mbar, poleward of 30°N, there is a strong seasonal cycle in the relative importance of the fossil fuel source, as can be expected from the seasonal cycle in fuel combustion (Plate 2b) and from the fact that natural emissions peak in summer. The fossil fuel source accounts for about 90% of the NO_x concentration in winter and 50% in summer. In the tropical regions and in the southern hemisphere, it is clear that four sources are of primary importance: fossil fuel combustion, soil emissions, biomass burning, and lightning. In these regions, the fossil fuel source represents a much smaller portion and the lightning source a much larger portion than in the northern hemisphere. Biomass burning never exceeds 20%. Soil emissions dominate the non-lightning NO_x sources between 30°S and the equator. Finally, in the extratropical southern hemisphere, the fossil fuel source is significant, despite the very small continental area of this hemisphere covered by this source. However, as the contributions from the other sources are very small south of 30°S, the local anthropogenic sources are sufficiently significant to account for about 20% of the NO_x at 900mbar. Aircraft and stratospheric sources are not important at this level of the atmosphere.

3.3. Time Series

By looking at the temporal evolution of the different contributions to the total NO_x abundance at a particular location, it is possible to identify the major sources responsible for the presence of NO_x at the surface, for that location. Furthermore, using sites with available observations, the total NO_x concentration as simulated by the model can be compared with observations. A thorough validation of the model is published by *Müller and Brasseur* [1995]; the purpose of this section is therefore to identify some key features of the model simulations. The stations are chosen to be in remote locations, with one oceanic and one continental site chosen. The locations for which we display time series are Mauna Loa Observatory, Hawaii (20°N, 155°W, 3.4km) and Niwot Ridge, Colorado (40°2′N, 105°32′W, 3.05km). The major contribution to NO_x in the lower northern hemisphere troposphere is due to fossil fuel emissions (Plate 2b). It is expected that this source is dominant at the surface as well.

At Mauna Loa Observatory (MLO), the calculated amount of HNO_3 (Figure 1a) is much lower than observed as it is the case for other three-dimensional chemistry-transport models [*Penner et al.*, 1991]. Furthermore, NO_x concentrations calculated by IMAGES (Figure 1b) are also lower than observed. On the other hand, the amount of PAN (Figure 1c) is relatively well reproduced. Fossil fuel emissions (probably transported from the Asian continent) are the primary source of nitrogen species over Hawaii. The contribution from lightning is of the same order of magnitude than the contribution from fossil fuel only between July and September. From the distribution of the different contributions to the odd nitrogen budget at MLO, it appears that the most straightforward way to improve the simulation of HNO_3 over MLO would be to increase the transport from Asia. This requirement is consistent with the analysis of radon abundance derived at MLO by transport models (D. Jacob et al., Intercomparison and evaluation of global atmospheric models using ^{222}Rn and other short-lived tracers, submitted to the *J. Geophys. Res.*, 1996; N. Mahowald, personal communication, 1996). Nevertheless, this should also imply higher PAN, which seems to be in good agreement with the observations. Furthermore, increased transport would not help improving the simulation of the HNO_3/NO_x ratio (not shown). Therefore, other possible improvements could be to increase other sources of NO_x (lightning in particular) and to parameterize more accurately the heterogeneous processes in IMAGES.

At Niwot Ridge (Figure 1d), the summer peak of HNO_3 is fairly well reproduced but the winter minimum is slightly larger than in the observations. This suggests

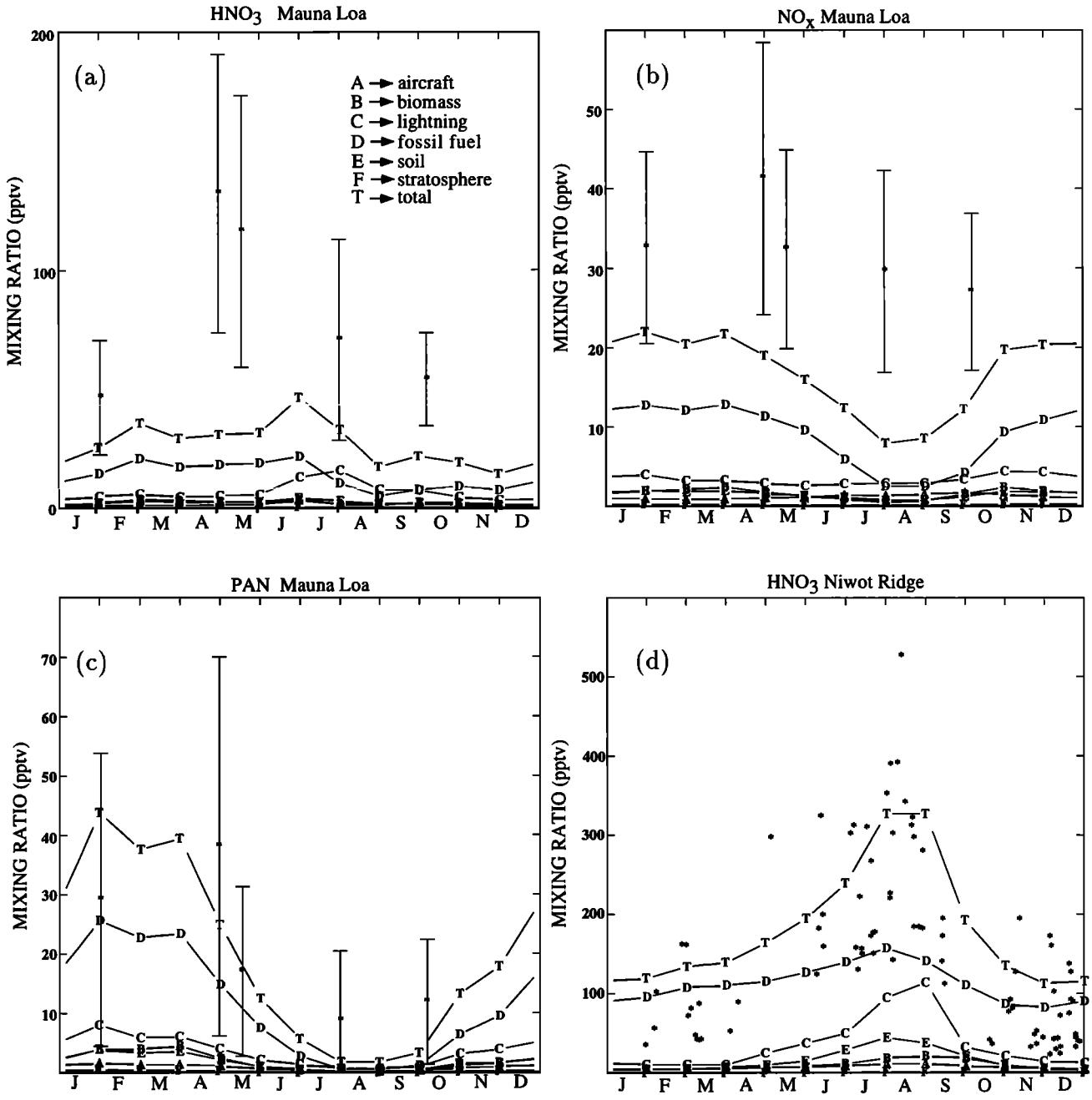

Figure 1. Time evolution of the relative contribution of the different sources to (a) HNO_3 at Mauna Loa, (b) NO_x at Mauna Loa, (c) PAN at Mauna Loa, (d) HNO_3 at Niwot Ridge. The curve labels A-F stand, respectively, for aircraft, biomass, lightning, fossil fuel, soil and stratosphere. The total mixing ratio curve is labeled T. In Figure 1a to 1c, the observed data is from MLOPEX 2 (data archive) while in Figure 1d it is taken from *Parrish et al.* [1986].

that its wet and/or dry removal of HNO_3 could be too weak over the United States. A comparison of the total deposition of the nitrogen species over north America as simulated in IMAGES (E.A. Holland et al., The spatial distribution of atmospheric nitrogen deposition and its impact on terrestrial ecosystems, submitted to the *J. Geophys. Res.*, 1996) with the model results published by *Galloway et al.* [1994] shows that the odd nitrogen removal in IMAGES is indeed lower by 10-20% over most of the United States. As at MLO, the main contribution to the odd nitrogen budget at Niwot Ridge is due to the fossil fuel burning emissions. Of the other sources, soil emissions and lightning are the most important.

In conclusion, in this model study, the main source of odd nitrogen compounds at the surface in the north-

ern hemisphere is due to fossil fuel combustion even in remote areas. This is also true for longer-lived species such as HNO_3.

3.4. Sensitivity to Lightning Source

In section 3.2, the importance of the lightning source has been identified, for both the northern and southern hemispheres. Nevertheless, as described in section 2.1, there is a large uncertainty in the amount of NO_x that is produced globally and annually by lightning. It is therefore interesting to assess the sensitivity of our model results (presented in section 3.2) to the intensity of the lightning source. For that purpose, we consider lightning source strengths of 2 and 10 TgN/yr, respectively, instead of the 5 TgN/yr used above. Because one emphasis of this paper is on aircraft emissions, the discussion in this section focuses on the 200mbar surface. Furthermore, as the contribution of fossil fuel emissions is large in the northern hemisphere below 500mbar, a change in the lightning source is not expected to affect substantially the odd nitrogen budget in the lower troposphere of the northern hemisphere.

The results corresponding to the simulation with a lightning emission of 2 TgN/yr are shown in Plate 3a. In the southern hemisphere, lightning remains the dominant source and contributes to a minimum of 45-50% of the total source of NO_x at all times. At high southern latitudes (poleward of 60°S), where the ligthning contribution is small, soil emissions become fairly significant, accounting for more than 20% in winter. The importance of soils is a clear indication of the effectiveness of convective transport from the boundary layer to the upper troposphere. The nitrogen source associated with biomass burning never exceeds 15% of the total. In the northern hemisphere, the contribution from lightning to the NO_x budget is always less than 50%. In this case aircraft emissions account for 30-40% of the NO_x poleward of 60°N. This is in good agreement with other published results [*Ehhalt et al.*, 1992; *Hauglustaine et al.*, 1994].

Shown in Plate 3b are the results for the simulation assuming a lightning source of 10 TgN/yr. As expected by extrapolating the results from the simulations performed with smaller lightning sources, the lightning source becomes by far the largest contributor to NO_x on the 200mbar surface at all locations throughout the year. The lowest contribution by lightning is found in winter poleward of 60°N, where it accounts for 50% of the NO_x concentration. With a lightning source of 10 TgN/yr, the aircraft contribution is always smaller than 20%.

In an attempt to constrain the lightning source, NO_x concentrations calculated on the 200mbar level are compared with available measurements. Figure 2 shows the latitudinal variation of the calculated NO_x mixing ratio for lightning sources of 2, 5, and 10 TgN/yr for each season. It is clear that as the amount of NO_x produced by lightning increases, the amount of NO_x increases everywhere. This increase, however, is not linear. Note in particular that, in the winter season (DJF), the cross-equatorial gradient of NO_x reverses between the 2 TgN/yr and 10 TgN/yr cases.

For these three cases, the range of modeled NO_x is generally within the range of the measured values [*Kley et al.*, 1981; *Drummond et al.*, 1988; *Carroll et al.*, 1990; *Ehhalt et al.*, 1992; *Ridley et al.*, 1994; *Weinheimer et al.*, 1994; *WMO*, 1995]. However, in summer, the mixing ratio of 320ppt calculated between 30°N and 60°N for the 10 TgN/yr case is larger than the measurements except those of Ehhalt et al. These latter measurements may have been influenced by rapid transport from the boundary layer and may not be representative of the mean state of the atmosphere (D.H. Ehhalt, personal communication, 1995). Furthermore, for other seasons and/or other locations, the 10 TgN/yr simulation tends to overpredict the NO_x mixing ratio compared to the observations. As the upper tropospheric NO_x simulated in the case of a lightning source of 10 TgN/yr is somewhat larger than the upper limit of the observations, this suggests that each year a relatively low lightning source (lower than 10 TgN) is released in the atmosphere by thunderstorms. This conclusion agrees with the likely estimated source from lightning listed by *WMO* [1995].

Important factors in our calculations are both the strength of the lightning source and its vertical distribution. As the efficiency of NO_x in catalyzing the production of ozone can be larger in the upper than in the lower troposphere [*Liu et al.*, 1987], it is important to refine estimates of the distribution of this source as a function of altitude [*Ridley et al.*, 1995].

In this study, so far, the NO_x produced by lightning (i.e. the number of molecules produced per unit time and unit volume) was assumed to be constant with altitude. This has the consequence that, as the density decreases with altitude, the lightning source of NO_x becomes increasingly more important with increasing altitude. In order to assess the importance of this assumption, the vertical distribution of lightning was changed so that it is weighted by density. As a consequence, the lightning source of NO_x (on a mixing ratio basis) from lightning is constant with altitude. In two simulations using this altered lightning source of 5 TgN/yr, the respective contributions of lightning and aircraft to the odd nitrogen budget are isolated. At 200mbar (where the major change occurs), in comparison with the control experiment, the annually averaged contribution of the lightning source to the NO_x budget clearly decreases by 10 to 20% poleward of 30° (Figure 3a). As a consequence, the contribution of the aircraft source increases in the same region by a few percent, accounting for 30% of the NO_x burden at 200mbar, instead of the 20% contribution found in the control experiment.

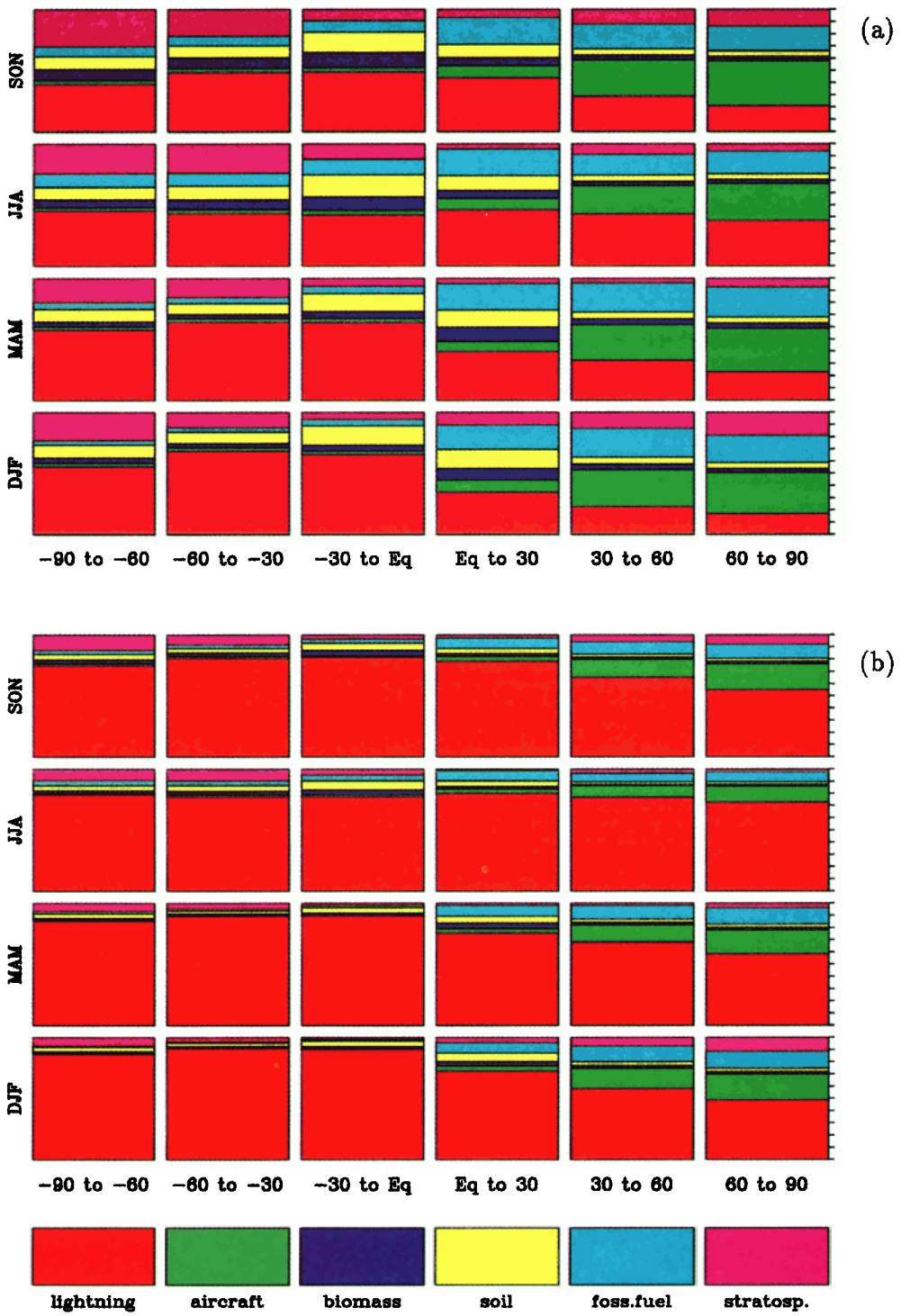

Plate 3. (a) Same as Plate 2a but for a lightning source of 2 TgN/yr; Plate 3b same as Plate 3a but for a lightning source of 10 TgN/yr.

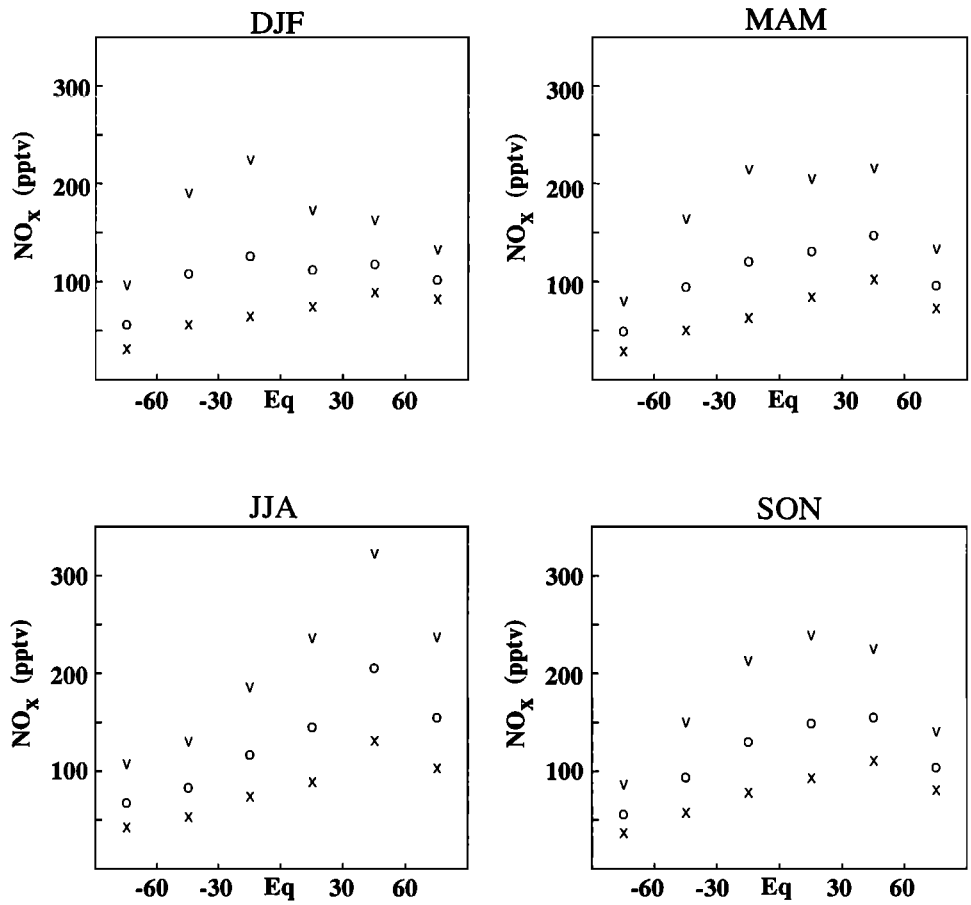

Figure 2. NO_x mixing ratio (in parts per trillion) on the 200mbar surface averaged as in Plate 2a. The X, O, and V correspond to the mixing ratio in the case of a lightning source of 2 TgN/yr, 5 TgN/yr, and 10 TgN/yr, respectively.

3.5. Sensitivity to the Aircraft Source

In this study, the aircraft source has a global average of 0.44 TgN/year. Considering the uncertainty [*WMO*, 1995] in the evaluation of the size of the aircraft source and the possible increase in the subsonic fleet, a run with an aircraft source twice as large (i.e., 0.88TgN/year instead of 0.44) is used to quantify the sensitivity of the model to the size of this source. In the case of increased aircraft emissions, the proportion of NO_x originating from aircraft can reach levels up to 40-50% in the upper tropospheric northern latitudes, for seasonal averages (not shown). On the 200mbar surface, for an annual average, the consequence is an increase of the contribution from the aircraft source by approximately 50% (Figure 3b), similar to the increase seen in the experiment in which the lightning source was reduced to 2 TgN/yr (see section 3.4). The important point to notice is that doubling the source does not double the contribution of NO_x by aircraft. This is easily understood by the fact that, as NO_x is locally increased by the emissions, both the numerator and denominator of the ratio of the NO_x contribution from a single source to the total NO_x increase. As a consequence, future increases in aircraft emissions will become less important on a percentage basis.

3.6. Sensitivity to the Soil Source

As described in section 2.1, emission of nitrogen from soils is also only partially known, with a size estimated to be in the range of 5-12 TgN/year [*WMO*, 1995]. As the control run uses 6.6TgN/year (see Table 1), we ran a simulation in which the soil emissions were doubled. As could be expected from Plate 2b, no noticeable effect occurs on the 200mbar surface. On the other hand, in the annual average, the contribution from soils reaches more than 50% (compared with 30% in the control run) at 900mbar for the area located between 30°S and the Equator (not shown).

4. Conclusions

In order to determine the relative contribution of each odd nitrogen source on the atmospheric concentration of NO_x, a three-dimensional global chemistry transport model has been modified so that each source is identified by a particular "flavor". This tagging procedure has been shown to accurately describe the chemical transformations of the emitted species while allowing the isolation of the contribution of each source to the total nitrogen budget. As the NO_x chemistry is highly nonlinear, it can be expected that there will be differences between the method used in this study and the

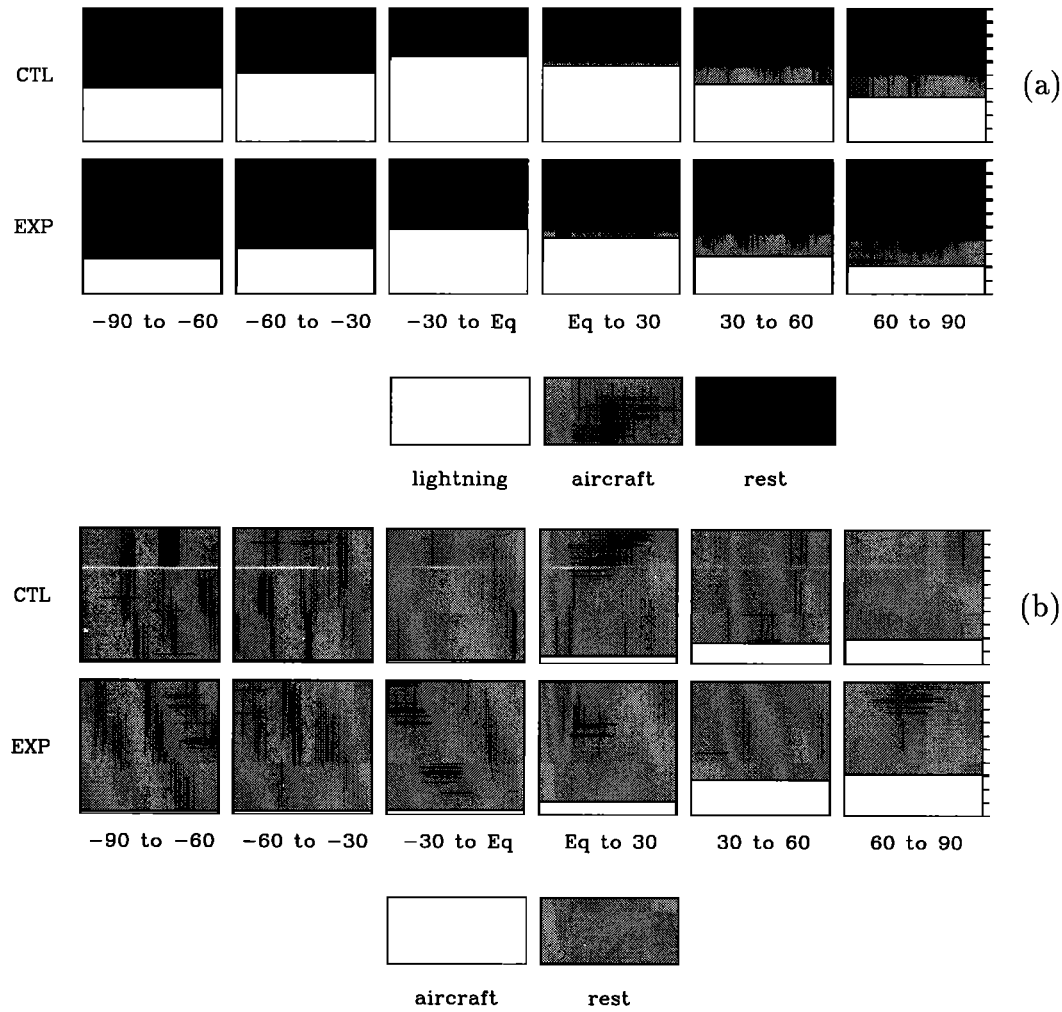

Figure 3. Latitudinal representation of the annual average of the contribution on the 200mb surface from (a) the lightning and aircraft sources for the control experiment (labeled CTL) and for the experiment (labeled EXP) with a modified vertical distribution (see text for details) and (b) the aircraft source for the control experiment (labeled CTL) and for the experiment (labeled EXP) with a doubled aircraft source (see text for details).

more usual approach of removing one source or considering only a single source. As an example, the contribution from the aircraft source (for January), computed as the difference between a run with all sources and a run with no aircraft source is shown as Figure 4. It is clear that, although the present plot is not fundamentally different than Plate 1a, there is a difference in the extent of the 20% contour. Larger differences can in fact be expected for regions where the contribution of the considered NO_x source is large, such as the fossil fuel emissions or the lightning source.

The results confirm the strong importance of the lightning source, even in the upper troposphere at northern midlatitudes despite its relatively small size. In this region, the contribution from aircraft emissions is also substantial. The stratospheric source does not account for more than 10-15% of the zonally averaged NO_x in the upper troposphere. This result is consistent with the finding of *Kasibhatla et al.* [1991], but is different from the conclusions of *Ehhalt et al.* [1992].

A striking feature of the model is the importance of the lightning source throughout the atmosphere south of 30°N, regardless of the season, even for a global production of NO_x from lightning as low as 2 TgN/yr. Near the surface (900mbar), the fossil fuel emissions are a very significant portion of the atmospheric NO_x concentration, dominating the other sources poleward of 30°N.

The aircraft NO_x source (assumed to be 0.44TgN/yr) accounts for 20-30% at 200mbar of the atmospheric NO_x at most, if the lightning source represents 5TgN/yr. This figure is slightly less than most of the previous studies [*Ehhalt et al.*, 1992; *Hauglustaine et al.*, 1994]. The main reason for the comparative reduction in the aircraft source contribution of the aircraft source to the NO_x budget is the strong contribution of the lightning source over most of the globe at 200mbar. Similarly, the contribution of the stratospheric source to the troposphere is always small at midlatitudes in the northern hemisphere. When the lightning source is increased

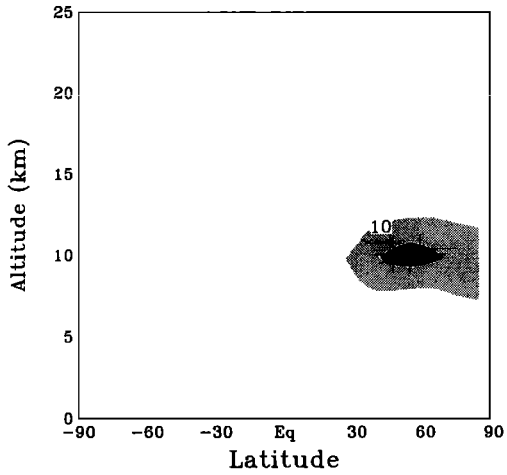

Figure 4. Latitude-altitude representation of the January zonal mean contribution (in percent, contour every 10%) to NO_x from nitrogen emissions by aircraft, computed as the difference between a run with all sources and a run with no aircraft source (see text for details).

from 2 to 10 TgN/yr, the contribution of aircraft emissions decreases from 40 to 20%, respectively.

Time series of NO_x, HNO_3, and PAN at the surface clearly demonstrates that the largest contribution to these species in the northern hemisphere is due to emission of NO_x from fossil fuel combustion. Over ther remote Pacific ocean, the contribution of the lightning source is occasionally (summer months) larger than of the fossil fuel source. This is due to the combined effect of enhanced production from lightning and reduction from fossil fuel combustion in eastern Asia during the summer months. However, at Mauna Loa Observatory, the simulated time evolution of NO_x has a much stronger seasonal cycle than that suggested by the observations. In particular, the summer minimum found in the model calculation is not present in the data. The preponderance of the fossil fuel source in the lower troposphere has an important implication for the terrestrial biosphere receiving the deposited nitrogen. Indeed, the increased supply of nitrogen associated with human activities and the related fertilization of soils may increase the uptake of atmospheric CO_2 by the terrestrial biosphere, possibly accounting for a fair portion of the missing CO_2 sink (E.A. Holland et al., The spatial distribution of atmospheric nitrogen deposition and its impact on terrestrial ecosystems, submitted to the *J. Geophys. Res.*, 1996; *Townsend et al.*, [1996]).

The very large portion of the nitrogen budget associated with lightning throughout the troposphere clearly illustrates the need for a better understanding of the strength, vertical, and geographical distribution of odd nitrogen emissions associated with lightning discharges in thunderstorms. Along the same line, the uncertainty associated with soil emissions and biomass burning is fairly large and a better understanding of these sources could alter the conclusions of this analysis, especially for the lower to mid troposphere.

Appendix: Applicability of the Tagging Procedure

To illustrate the applicability of the tagging procedure described in section 2.2, we discuss the following particular case. Consider, for example, the reaction

$$\mathrm{NO} + \mathrm{HO_2} \xrightarrow{k_1} \mathrm{NO_2} + \mathrm{OH} \qquad \text{(A1)}$$

with reaction coefficient k_1. The mixing ratio of NO and NO_2 can be written as

$$[\mathrm{NO}] = [\mathrm{XNO}] + [\mathrm{YNO}] \qquad \text{(A2)}$$

$$[\mathrm{NO_2}] = [\mathrm{XNO_2}] + [\mathrm{YNO_2}] \qquad \text{(A3)}$$

where XNO and YNO represent flavors X and Y of NO. As a consequence, (A1) can be rewritten as the set of two equations (with the same reaction rate k_1 as in (A1))

$$\mathrm{XNO} + \mathrm{HO_2} \xrightarrow{k_1} \mathrm{XNO_2} + \mathrm{OH} \qquad \text{(A4)}$$

$$\mathrm{YNO} + \mathrm{HO_2} \xrightarrow{k_1} \mathrm{YNO_2} + \mathrm{OH} \qquad \text{(A5)}$$

The conservation equations for the mixing ratios of the different chemical products are therefore expressed by

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{dt}}[\mathrm{XNO_2}] &= k_1\,[\mathrm{XNO}]\,[\mathrm{HO_2}] \\
\frac{\mathrm{d}}{\mathrm{dt}}[\mathrm{YNO_2}] &= k_1\,[\mathrm{YNO}]\,[\mathrm{HO_2}] \\
\frac{\mathrm{d}}{\mathrm{dt}}[\mathrm{OH}] &= k_1\,[\mathrm{XNO}]\,[\mathrm{HO_2}] + k_1\,[\mathrm{YNO}]\,[\mathrm{HO_2}].
\end{aligned}$$

One can easily show that these equations are equivalent to the conservation equations written without nitrogen splitting.

For the nonlinear terms in nitrogen, this method can also be applied. If we consider the case of the reaction

$$\mathrm{NO_2} + \mathrm{NO_3} \xrightarrow{k_2} \mathrm{N_2O_5} \qquad \text{(A6)}$$

one can, as in (A2) and (A3), apportion the mixing ratio of NO_2 and NO_3 into its X and Y components. Consequently, four different flavors of N_2O_5 must be defined, so that (A6) can be rewritten as

$$\begin{aligned}
\mathrm{XNO_2} + \mathrm{XNO_3} &\xrightarrow{k_2} \mathrm{XXN_2O_5} \\
\mathrm{XNO_2} + \mathrm{YNO_3} &\xrightarrow{k_2} \mathrm{XYN_2O_5} \\
\mathrm{YNO_2} + \mathrm{XNO_3} &\xrightarrow{k_2} \mathrm{YXN_2O_5} \\
\mathrm{YNO_2} + \mathrm{YNO_3} &\xrightarrow{k_2} \mathrm{YYN_2O_5}.
\end{aligned}$$

The cross terms XY and YX are products of a reaction between an X flavored nitrogen with an Y flavored nitrogen. The reverse reaction (or any dissociation of N_2O_5) produces at the same time an X and an Y product. It is straightforward to verify that the resulting conservation equations for NO_2, NO_3, and N_2O_5 are equivalent to the original conservation equations.

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G.P. Brasseur, P.G. Hess, and J.-F. Lamarque, NCAR/ACD, P.O. Box 3000, Boulder, Co, 80307-3000. email: brasseur@ncar.ucar.edu; hess@ncar.ucar.edu; lamar@ncar.ucar.edu.

J.-F. Müller, Belgian Institute for Space Aeronomy, Avenue Circulaire 3, B-1180 Brussels, Belgium.

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