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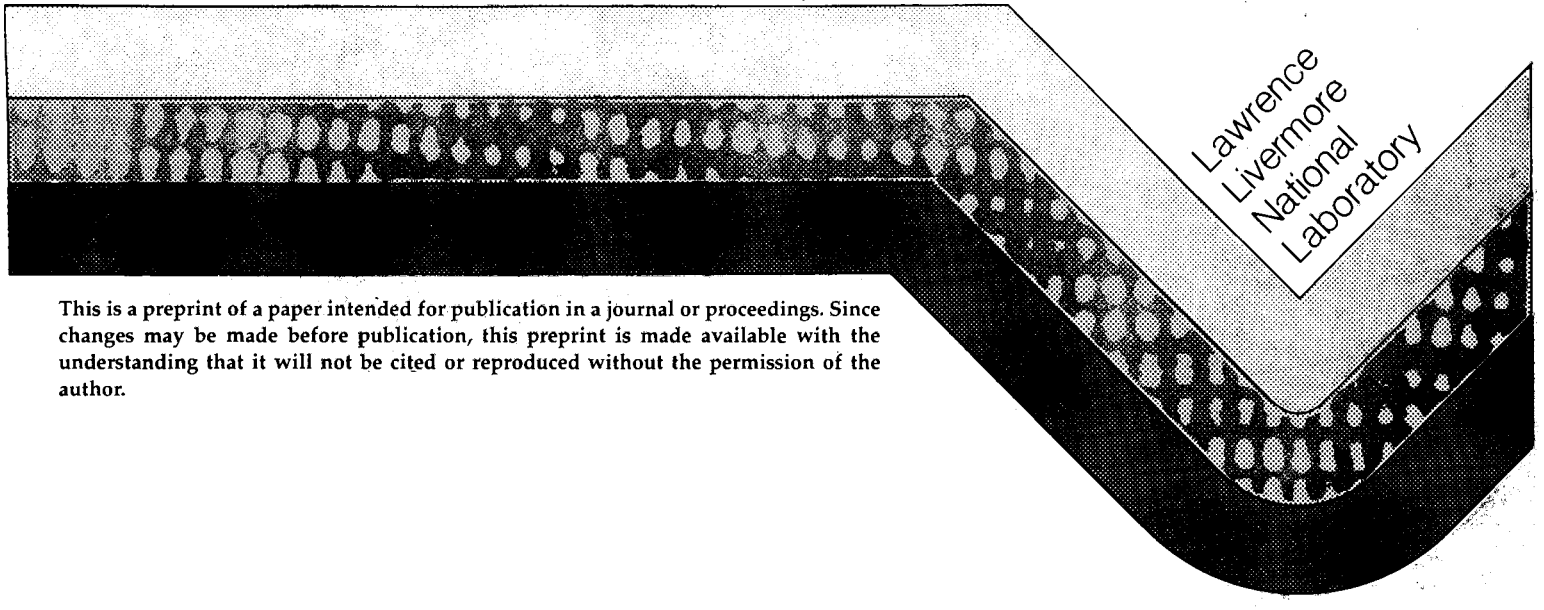

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ABSTRACT

We have simulated the global cycle of reactive nitrogen in a three-dimensional chemistry-transport-deposition model. Our model is a Lagrangian parcel model in which trace species react and are carried in constant-mass air parcels; the parcels are advected by winds calculated by an atmospheric general circulation model (GCM).

Here we present simulations of the nitrogen cycle with January and July meteorological conditions calculated by the NCAR Community Climate Model. The GCM calculated winds, clouds, precipitation and other variables at nine levels in the atmosphere with a horizontal resolution of approximately 4.5° latitude and 7.5° longitude. The geographical distributions of emission sources of reactive nitrogen were prescribed in the model according to the best available estimates. The sources are due to fossil fuel combustion, lightning discharges, soil microbial activity, biomass burning and stratosphere-troposphere exchange. The model includes the basic chemical reactions of NO, NO_2, and HNO_3 calculated with prescribed distributions of OH and O_3. The model predicts atmospheric concentrations of NO_x ($NO+NO_2$) and HNO_3 throughout the globe at nine altitudes. In addition, deposition of nitrogen in precipitation and in dry processes is also calculated.

We present global maps of calculated atmospheric concentration with emphasis on the surface atmospheric concentration of NO_x. Comparisons between calculated and observed atmospheric concentrations and deposition rates are made for several parts of the world. The long-range transport of NO_x is documented from the model by comparing the ratio of surface NO_x concentrations for all sources to those for natural sources only.

I. INTRODUCTION

Nitrogen oxides are important for global photochemistry because they determine whether O_3 is produced or destroyed. Elevated concentrations of $O_3$are of concern because O_3 affects the growth of plants and the respiratory systems of man and other animals (Tilton, 1989; Reich and Amundson, 1985), because it absorbs infrared radiation and contributes to the greenhouse warming (Ramanathan et al., 1985), and because it is a key player in the photochemistry of hydroxyl, the most important chemical scavenger in the atmosphere (Logan et al., 1981; Penner, 1990). In regions of high NO_x concentrations, a photochemical sequence, initiated by the reaction of CO with OH, leads to O_3 production:

$$\begin{aligned} CO + OH &\rightarrow CO_2 + HO_2 \\ HO_2 + NO &\rightarrow NO_2 + OH \\ NO_2 + h\nu &\rightarrow NO + O \\ O + O_2 &\rightarrow O_3 \end{aligned} \qquad (1)$$

Net: $$CO + h\nu \rightarrow CO_2 + O_3 + O_2$$

At low NO_x concentrations, the second reaction listed above, the reaction of HO_2 with NO, is slow. Instead, HO_2 reacts with O_3 and the reaction sequence initiated by the reaction of CO with OH leads to O_3 destruction:

$$\begin{aligned} CO + OH &\rightarrow CO_2 + HO_2 \\ HO_2 + O_3 &\rightarrow OH + O_2 + O_2 \end{aligned} \qquad (2)$$

Net: $$CO + O_3 \rightarrow CO_2 + 2O_2.$$

If the ratio of the concentration of NO to O_3 is greater than the ratio of the reaction rate coefficients k_2/k_1 (where k_2 is the rate coefficient for the reaction of HO_2 with O_3 and k_1 is the rate coefficient for the reaction of HO_2 with NO), the first sequence above is faster and O_3 is produced. For typical O_3 concentrations, this occurs when NO_x (=NO + NO_2) concentrations are around 20 to 50 ppt. Because observed concentrations of NO_x in ocean regions are near this limit, large portions of the atmosphere are close to values where the reaction sequence (1) may begin to dominate over reaction sequence (2) if NO_x concentrations increase. Indeed, fossil fuel emissions of NO_x have increased substantially over the last two decades (Hameed and Dignon, 1988). A further increase in these sources could fundamentally alter the atmosphere by turning vast portions from regions which are typically regions of net O_3 destruction to regions of net O_3 production.

In addition to its importance for O_3 and the photochemistry of the troposphere, reactive nitrogen is also important because NO_3^-, the end product of the reactive nitrogen cycle, is a key component of acid rain and a key nutrient for both ocean phytoplankton and for land biota.

In this paper, we describe our simulations of the global cycle of reactive nitrogen. We use a three-dimensional chemistry-transport-deposition model. Our model is a Lagrangian model in which trace species react and are carried in constant-mass air parcels; the parcels are advected by winds calculated by the NCAR Community Climate Model (CCM), a nine-layer general circulation model (Pitcher et al., 1983; Williamson, 1983). In section II, we describe the model, together with our specification of the reactive nitrogen sources. Our results for surface concentrations of reactive nitrogen are given in section III, together with a comparison of our predicted concentrations and deposition amounts with measurements. Our conclusions appear in Section IV.

II. MODEL DESCRIPTION

The model we use is based on the GRANTOUR model described in Walton et al. (1988). A full description of the modifications needed to describe the nitrogen cycle together with a comprehensive comparison of the model results to measurements is presented in Penner et al. (1990). Here, we outline the basic features of this model. The chemistry of reactive nitrogen in the model has been simplified. Thus, we treat reactive nitrogen as NO_x ($NO+NO_2$) and HNO_3. The ratio of NO to NO_2 is determined by the photostationary state such that the reaction of NO with O_3 is instantaneously balanced by photolysis of NO_2:

$$\begin{aligned} NO + O_3 &\rightarrow NO_2 + O_2 \\ NO_2 + h\nu &\rightarrow NO + O \quad . \end{aligned}$$

Transformations between NO_x and HNO_3 follow the reactions:

$$\begin{aligned} NO_2 + OH &\rightarrow HNO_3 \\ HNO_3 + OH &\rightarrow H_2O + NO_x + O_x \\ HNO_3 + h\nu &\rightarrow OH + NO_2. \end{aligned}$$

Here, we have assumed that NO_3 (which is produced by the reaction of HNO_3 with OH) is immediately photolized to produce either NO or NO_2. To calculate the rates of these reactions in the model, we specify the O_3 fields based on measurements, allowing them to vary with latitude, height, and season (Wilcox and Belmont, 1977; Routhier et al., 1980; Oltmans, 1981; Kirchoff, 1984; and WMO, 1985). The concentration of hydroxyl, OH, is specified to vary with latitude and height, according to the predicted concentrations in the LLNL two-dimensional model (Wuebbles, et al., 1987). We also use photolysis rates from the LLNL model, but our reaction rate coefficients which, vary with temperature and pressure, have a longitudenal variation, as well, according to the monthly-averaged temperatures calculated in the CCM0.

Dry deposition velocities are applied to the concentrations of NO, NO_2, and HNO_3 in the lowest 100 mb of the atmosphere according to:

$$\begin{aligned} v_d(NO) &= 0.05 \text{ cm/s} \\ v_d(NO_2) &= 0.25 \text{ cm/s} \\ v_d(HNO_3) &= 0.5 \text{ cm/s}, \end{aligned} \tag{3}$$

which are chosen as representative mean values (Atherton et al., 1990; Finlayson-Pitts and Pitts, 1986). Precipitation scavenging of HNO_3 is assumed to be proportional to the precipitation rate in the CCM. Thus, the rate of removal of HNO_3 from level k in the atmosphere is given by

$$R_j(k) = S_j \, P_j(k) \tag{4}$$

where S_j is assumed to be 4.8 cm^{-1} for stratoform precipitation. For convective precipitation Equation (4) is modified as discussed in Walton et al. (1988) and S_j is set at 9.4 cm^{-1}. These values for S were chosen based on an analysis of six years of data for nitrate scavenging in precipitation on Long Island (Sperber and Hameed, 1986).

The sources of reactive nitrogen in our model are specified according to Table 1. Figure 1 shows the distribution of these sources with latitude and longitude in the model. Except for the stratospheric source (which varies only with latitude), all of the sources in Table 1 are stronger over land areas. Fossil fuel is by far the largest source of NO_x, and its dominant contribution to the total of all sources is seen in the maximum contours over North America, Europe, and Japan and Eastern Asia. The biomass burning source (specified here with an annual average source function) is a major contributor in the tropics and Southern Hemisphere, while soil microbial sources shift in importance from the Southern Hemisphere in January to the Northern Hemisphere in July, according to source rates that are set to zero in deserts and for sub-freezing temperatures and take on values that are approximately one half the average emission factors given for a Colorado grassland and a tropical forest soil by Williams et al. (1987) and Kaplan et al. (1988), respectively. Though very large relative to other sources, the contribution of anthropogenic sources to NO_x concentrations in remote areas has, until recently, been considered negligible due to the relatively short lifetime (a few days) for conversion of NO_x to HNO_3 followed by rainout and deposition of HNO_3. In the following, we show that these sources play a substantial role in maintaining the concentrations of NO_x and HNO_3 in remote areas.

III. RESULTS

Figures 2a and 2b show the predicted NO_x surface concentrations for January and July with all sources represented in the model. In January, the surface concentrations of NO_x over Eastern North America and Europe reach values as high as 4 ppb. In July, the maximum surface concentration contours are only 1 and 2 ppb, respectively. The smaller concentrations in July are the result of higher concentrations of OH in the summer hemisphere. This acts to convert NO_x to HNO_3 more quickly. Also to be noticed are the relatively large concentrations of NO_x over South America, Africa, and Asia. These result from a combination of biomass burning and soil microbial sources in the tropics and fossil fuel and soil sources in Asia.

We have attempted to validate our model by comparison of the predicted concentrations and wet deposition values with measured quantities. A comparison of the measured and predicted deposition of nitrate in precipitation at a set of remote locations is given in Table 2. As shown there, the model is within a factor of two of the observations at most of these sites with some of the predictions being high and some being low relative to the measurements. As reported in Penner et al. (1990), the model also does well in predicting the removal of nitrate by precipitation in the United States, especially in summer. In Europe,

Table 1. NO_x sources used in the model simulations.

Source	Emission Rate (Mt N/yr)	Description
Fossil-fuel combustion	22.4	The 1980 fossil-fuel source distribution given in Hameed and Dignon (1988).
Lightning discharges	3.0	The three-dimensional distribution is estimated with the procedure described by Hameed et al. (1981). NO_x produced by cloud-to-cloud lightning flashes was distributed, with a profile that is constant in density between 75 and 506 mb, while that from cloud to ground was distributed from the surface to 339 mb. The total source strength was based on the estimate of Borucki and Chamiedes (1984) and is similar to that of Hameed et al. (1981).
Soil microbial activity	10.0	Distribution on land prescribed according to land type as described in text.
Production in stratosphere	1.0	The latitudinal and vertical distribution were determined by the rate of production of odd nitrogen from the reaction of N_2O with $O(^1D)$, as determined in the LLNL 2-D transport kinetics model (Wuebbles et al., 1987).
Biomass burning	5.8	Distribution on land according to land type as described in Hao et al. (1989).

the predicted rainout is too small, especially in January, perhaps because the winds in the CCM are too high and the model placement of precipitation fields is incorrect relative to the observed fields and the emissions (see Penner, et al., 1990). Sensitivity tests, in which the precipitation removal coefficient S_j (Equation 4) was increased by a factor of 2, did not change the agreement, showing that essentially all of the nitrate that comes into contact with a precipitation event is removed. The comparison of the predicted and observed wet deposition at remote areas shown in Table 2, confirms that, overall, the transport of nitrate to remote regions is relatively well represented.

Figure 3 shows a comparison of the predicted vertical profiles of HNO_3 at a variety of longitudes with the profiles measured by Huebert and Lazrus (1980) during the GA-METAG aircraft experiments. Panel (a) compares the model to the data taken in remote Pacific Ocean locations while panel (b) compares the model to data from North American continental locations. Huebert and Lazrus used a chemical reaction to convert HNO_3 vapor

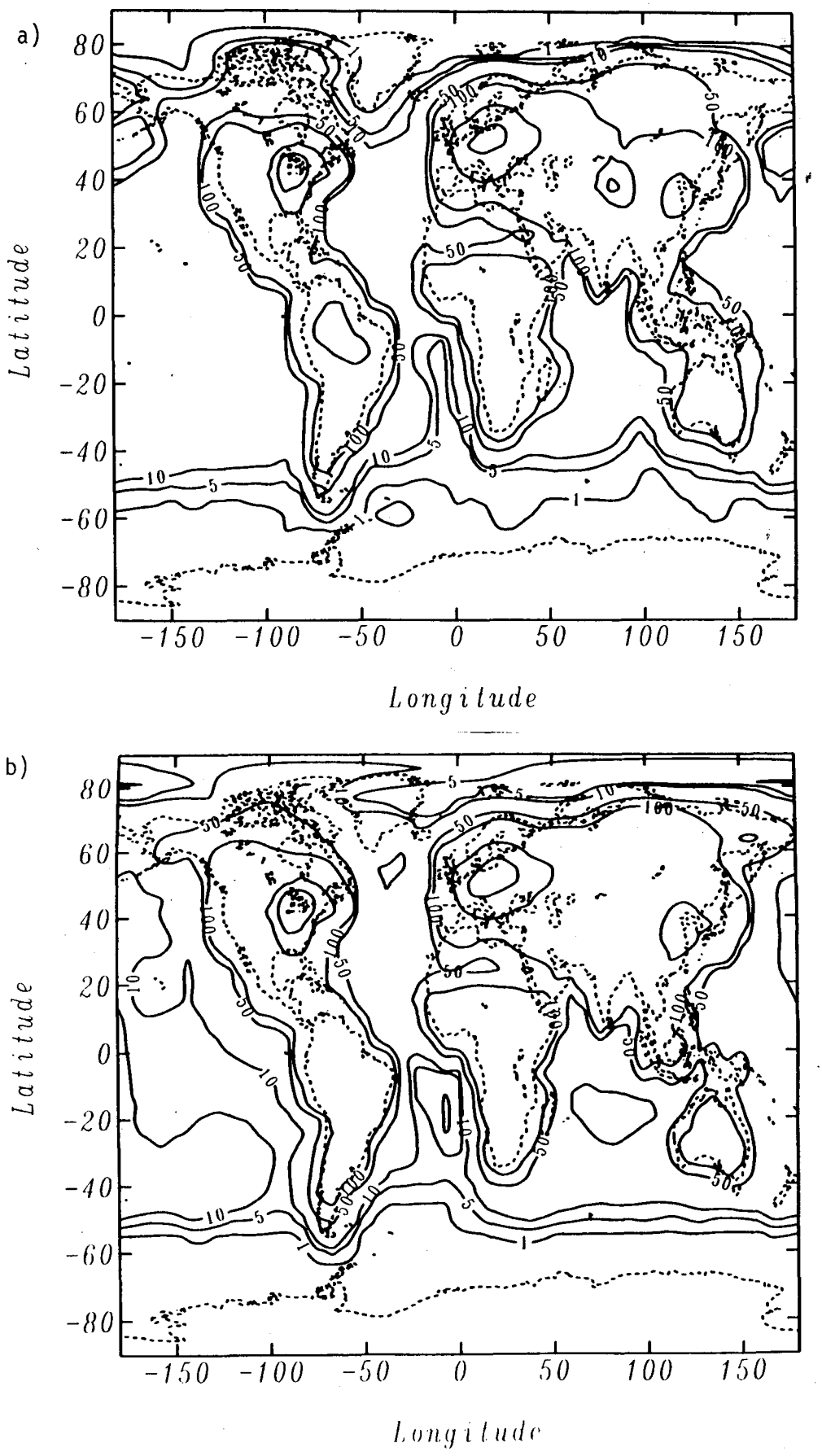

Figure 1. The distribution of the sum of all sources used in the model (see Table 1) for (a) January and (b) July. Contour intervals are 1, 5, 10, 50, 100, 500, 1000, and 1500 kg N/km^2-yr.

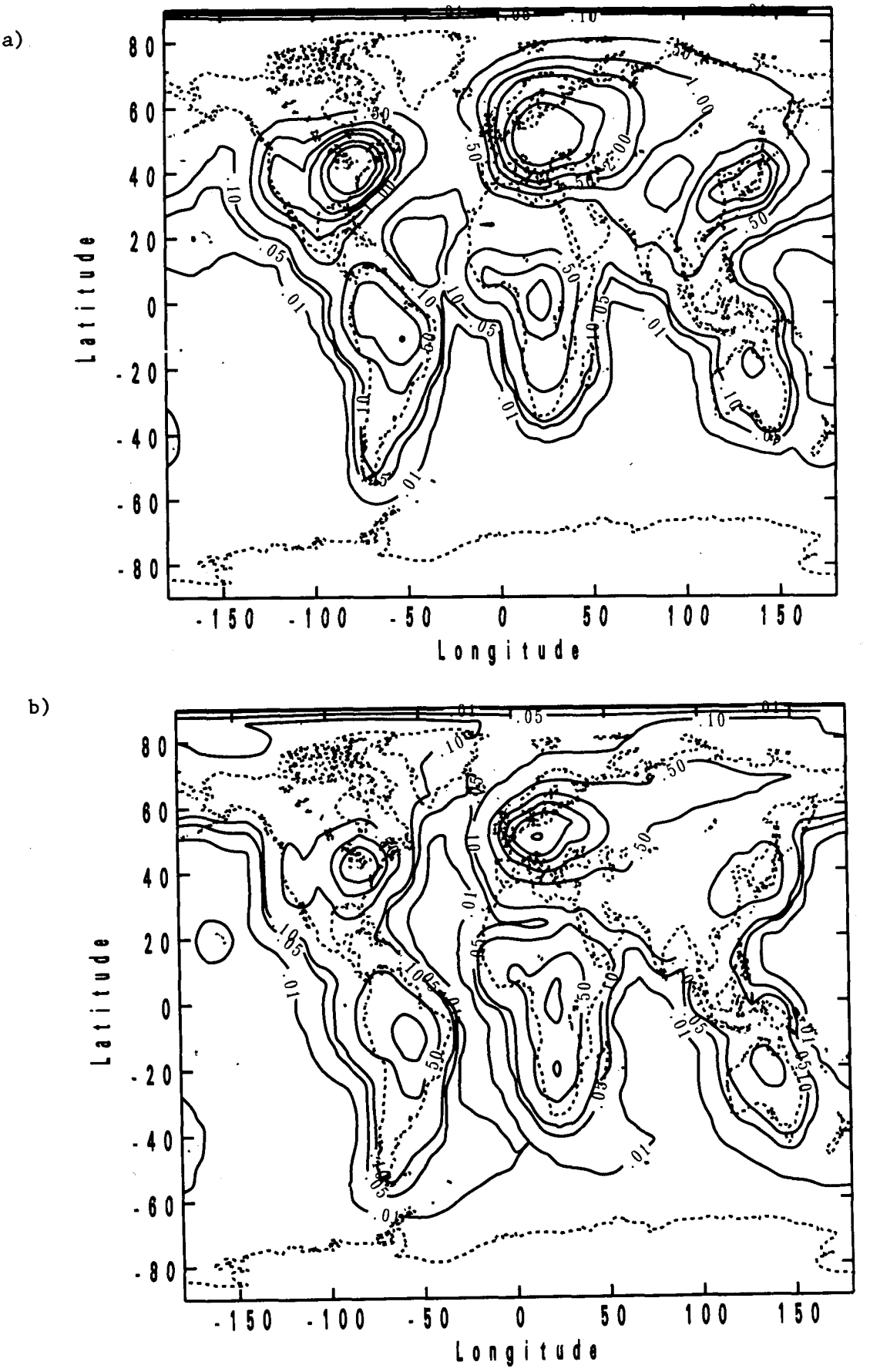

Figure 2. Model calculated distributions of NO_x surface mixing ratios for (a) January and (b) July in ppbv when all sources listed in Table 1 are considered. Contour intervals are 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 ppbv.

Table 2. Comparison of measured and calculated wet deposition in μmoles/liter at remote stations.

			JANUARY		JULY		
Site	Lat.	Lon.	Data	Model	Data	Model	Reference
Point Barrow, Alaska[a]	71N	157W	–	–	0.4	2.2	Dayan et al., 1985
Poker Flat, Alaska[b]	65N	147W	–	–	2. 1	1.7	Dayan et al., 1985
Denali National Park, Alaska[b]	64N	149W	2.1	2.6	2. 7	1.9	Knapp et al., 1988
Adrigole, Ireland[a]	52N	10W	3.0	1.3	6.6	11.4	Keene, 1988
Mauna Loa, Hawaii[b]	20N	156W	1.1	0.5	1.1	0.7	Knapp et al., 1988
American Samoa[b]	14S	171W	0.3	0.6	0.3	0.6	Knapp et al., 1988
Katherine, Australia[c]	14S	132E	4.3	2.5	–	–	Likens et al., 1987; Keene, 1988
Amsterdam Island[c] (Indian Ocean)	38S	78E	1.7	0.5	1.2	0.9	Keene, 1988

[a]The observations represent an average of two years of data.

[b]The observations represent an average of at least three years of data.

[c]The observations represent an average of six years of data.

in air to a nonvolatile nitrate salt; this means that all acidic nitrogenous gases contribute to the measured concentration. It is therefore possible that in addition to the vapor-phase nitric acid and particulate nitrate, an unspecified amount of PAN and pernitric acid was included in their measurement. The predicted values in remote areas are in reasonable agreement with the measured concentrations, but those over continental areas are somewhat high. Figure 4 displays a comparison of the same data with a latitudenal profile of the predicted concentrations in the boundary layer (Figure 4a) and in the free troposphere (Figure 4b). The free tropospheric values appear to be somewhat high.

In contrast to the comparison of our predictions with the data of Huebert and Lazrus, where we tend to be somewhat high, the predicted concentrations from the model appear to be low relative to the surface concentrations of nitrate measured during the SEAREX program (Savoie et al., 1989a). Savoie et al. (1989 a,b) measured nitrate using a high-volume sampling system and their measurements refer to total inorganic nitrate (i.e., particulate nitrate plus gaseous HNO_3), but it is believed that much of the nitrate is present in the particulate form. Figure 5 shows the average of our January and July predicted HNO_3 concentrations together with the measured concentrations at the SEAREX Pacific Island stations. Here we assume that our predicted HNO_3 vapor would be converted to particulate nitrate in this marine environment. The solid lines in this figure indicate the 95% confidence levels of the measured mean concentration. The symbols marked "A" in

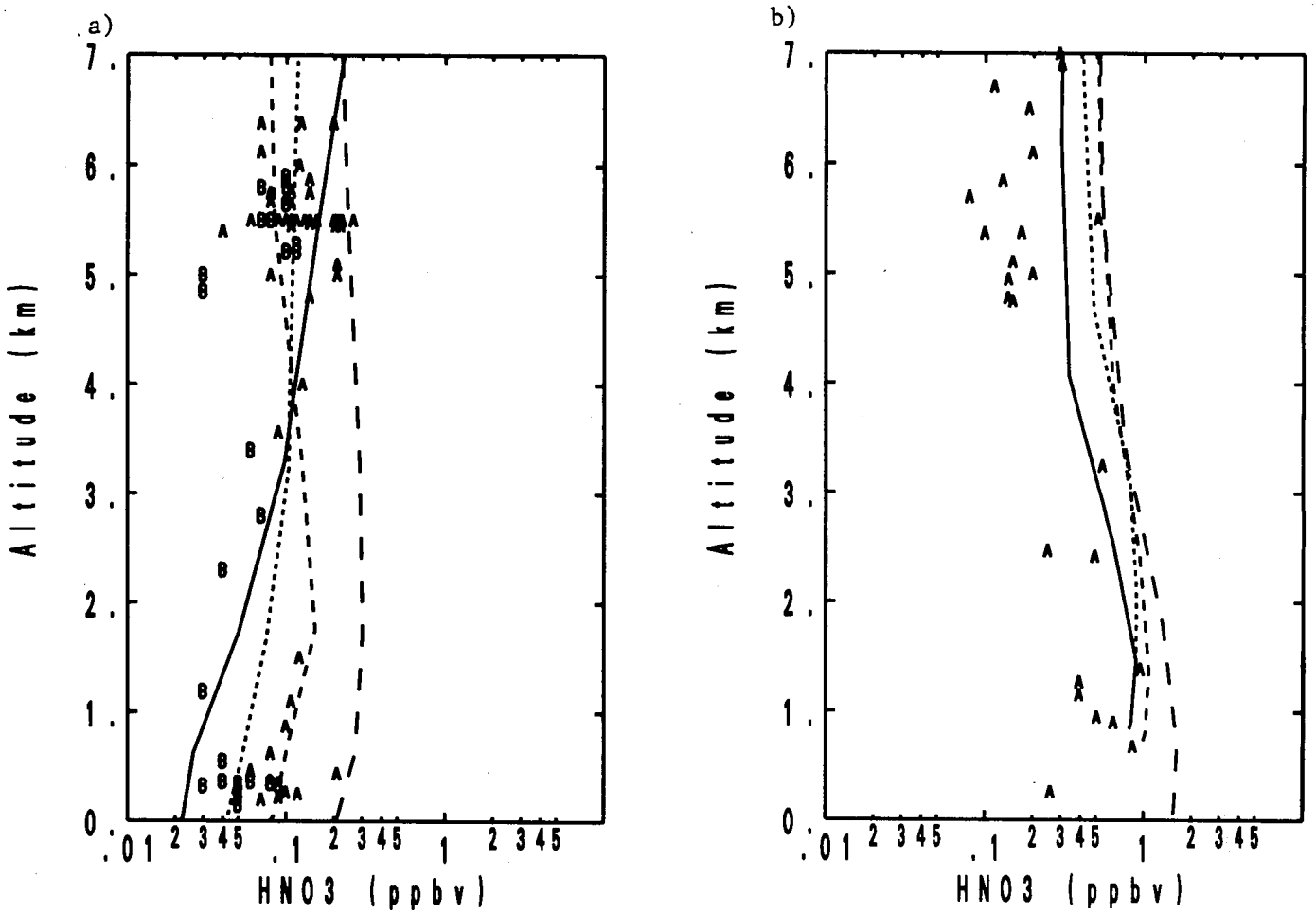

Figure 3. Vertical profiles of HNO_3 are compared with measurements of HNO_3 by Huebert and Lazrus (1980). The symbol A refers to measured mean concentrations while symbol B refers to a measured upper limit where the value of HNO_3 lies between zero and the symbol B. In panel (a) the July model results for the Pacific Ocean (125W) are compared with Huebert and Lazrun's Pacific Ocean measurements. Latitudes shown are 40S (line), 20S (short dash), 0 (longer dash), and 20N (longest dash). Panel (b) shows model predictions for continental locations at 40N and 120W (line), 110W (short dash), 100W (longer dash), and 90W (longest dash) in July along with the continental North American data of Huebert and Lazrus (1980).

this figure show the predicted concentrations for the model with 3 Mt N from lightning. The symbols marked "B" show the predicted concentrations for a simulation in which the source of NO_x from lightning is increased to 10 Mt N/yr. For the latter simulation, the agreement with the data of Savoie et al. is much better. Increasing the lightning source from 3 to 10 Mt has a much larger effect on the predicted concentrations in the mid-Pacific than does a change in the surface-based soil microbial source. This is shown by symbol "C" in the figure, which considered an increase in the soil microbial source from 10 to

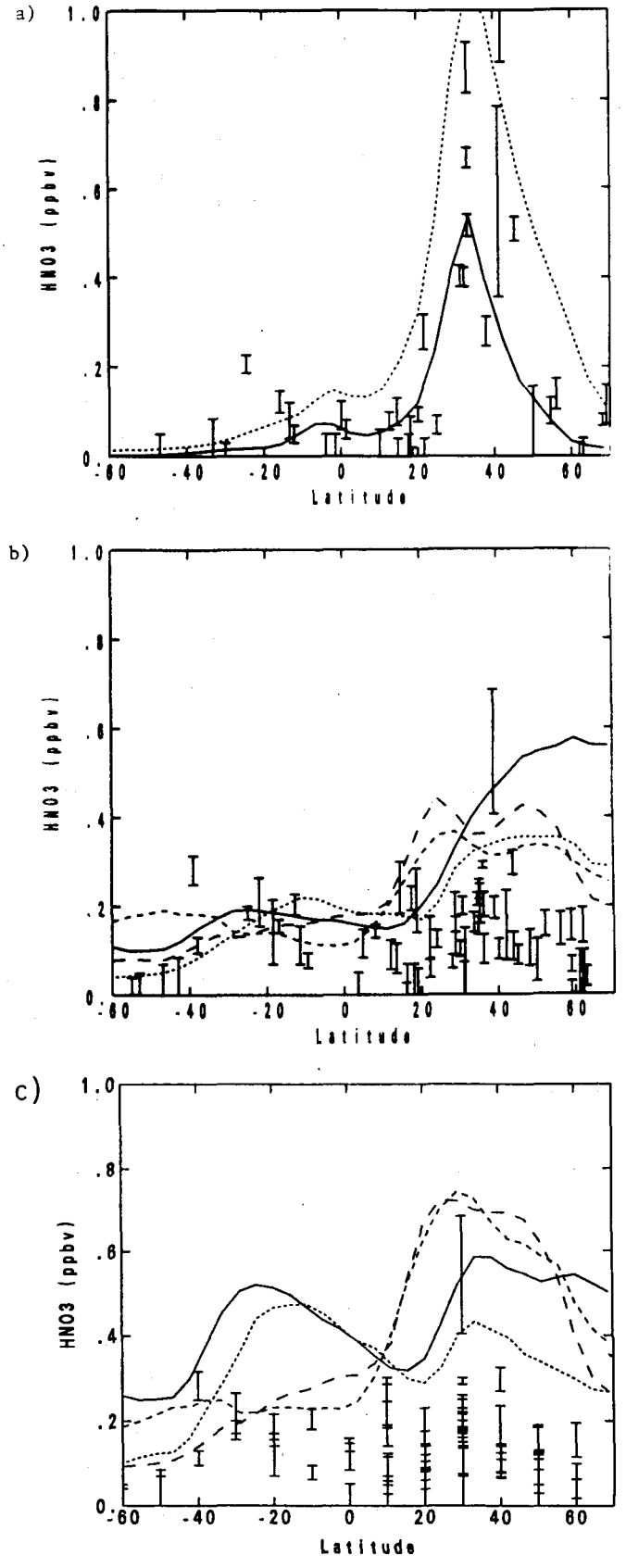

Figure 4. Predicted HNO_3 profiles for the 112.5W meridian for January and July. Also presented are the latitudinal profiles measured by Huebert and Lazrus (1980) during August and September, 1977 and May and June, 1978. Panel (a) shows model results for 991 mb using the sources specified in Table 1 along with boundary layer measurements. January and July calculations are shown by a solid line and short dashed line, respectively. Panel (b) shows model results for 500 mb and 664 mb, using the sources specified in Table 1 along with free troposphere measurements. Panel (c) shows model results for 500 mb and 664 mb with the lightning source increased from 3 Mt N/yr to 10 Mt N/yr. In panels (b) and (c), the calculations are for January, 500 mb (solid line) and 664 mb (short dash), and for July, 500 mb (longer dash), and 664 mb (longest dash), respectively.

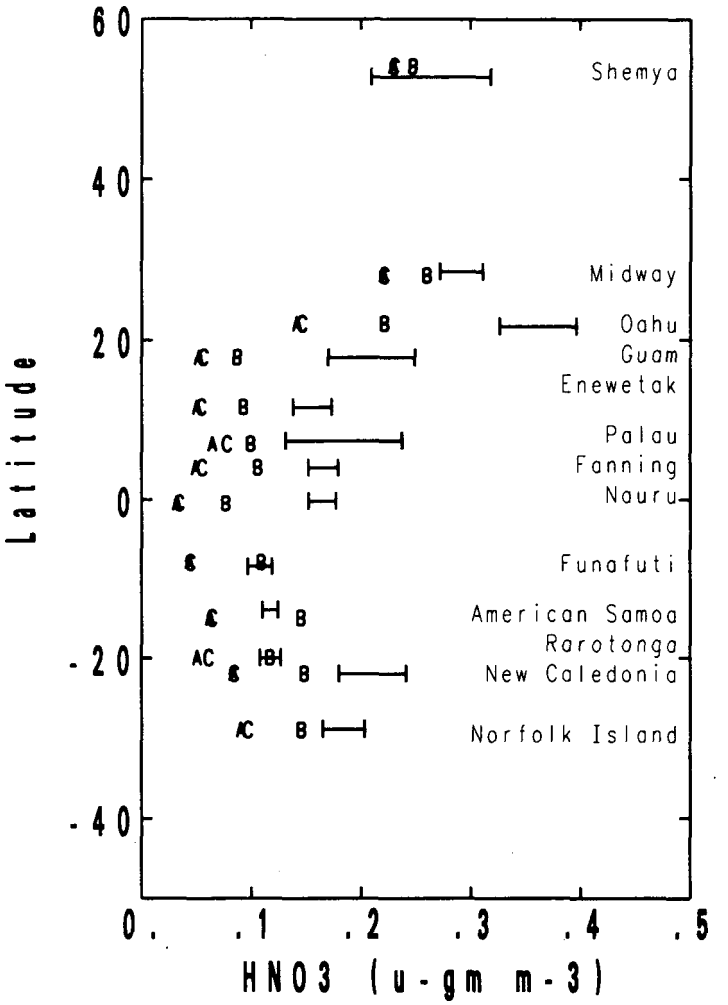

Figure 5. The mean January and July model predictions of surface HNO_3 concentrations in microgram/m^3 for various Pacific Ocean locations. Symbol A represents the standard model with sources as indicated in Table 1. Symbol B represents a model run in which the lightning source was increased from 3 to 10 Mt N/yr while symbol C represents a run in which the soil source was increased from 10 to 15 Mt N/yr. Also shown are the 95% confidence levels of the measured mean concentrations of inorganic nitrate measured by Savoie et al. (1989a).

15 Mt N/yr. These symbols nearly overlay those from the model run with only 10 Mt N from soils.

Although the comparison of the model results with 10 Mt N from lightning to the data of Savoie et al. is much better than the comparison with only 3 Mt N, increasing this source degrades our agreement with the data of Huebert and Lazrus (1980). This is demonstrated in Figure 4c which shows a comparison between the measurements of Huebert and Lazrus (1980) and the model predicted concentrations in the free troposphere with the lightning source increased from 3 Mt N/yr to 10 Mt N/yr. For 10 Mt N, the predicted concentrations appear to be about a factor of 2 too high relative to those measured.

There are several possible explanations for these contrasting results. First, there may be a marine source of nitrate that contributes to the surface-based measurements of Savoie et al. (1989a) but is not represented in the model (note also comments of Savoie et al., 1989a). A marine source of nitrate is consistent with the observation of a nitrate component to the marine signature from the principal component analysis for arctic aerosol reported by Li and Winchester (1989). The marine nitrate source may not contribute to the free-tropospheric concentrations of nitrate measured by Huebert and Lazrus (1980) if it is removed quickly by deposition processes, for example. Second, the aircraft-based measurements of HNO_3 may be low. Aircraft-based observations of nitrate are notoriously difficult. For example, it is possible that some loss of nitrate occurs along the inlet tubes between tropospheric air and the filter samplers. Also, recent experiments have shown that different techniques can give different abundances of nitrate (Singh, private communication, 1990). Thus, further research is needed to determine whether the upper level nitrate measurements need to be revised. The third possible reason for the discrepancy between our predictions at the SEAREX sites relative to the measurements and our predictions of HNO_3 in the upper troposphere relative to the data of Huebert and Lazrus (1980) is deficiencies in the model chemistry. Thus, the model may not properly account for the contribution of PAN (peroxyacetyl nitrate) and other organic nitrates to the dispersion of reactive nitrogen from land-based sources. While it is clear that PAN is an important reactive nitrogen carrier at lower levels and perhaps throughout the troposphere in the winter hemisphere (indeed, Singh et al. (1986) measure concentrations as high as 500 ppt in many remote areas in the winter), its importance as a reactive nitrogen carrier in the summer hemisphere is apparently not yet established. Thus, measurements in the summer hemisphere, particularly those above about 4 km are reported to be only several tens of ppt by some authors (Rudolph et al., 1987), but average values near 125 ppt as reported by others (Singh et al., 1990). Values of only a few tens of ppt would be close to our predicted NO_x concentrations at upper altitudes over coastal and mid-ocean locations, but values of over 100 ppt would be several times larger. The latter concentration, if present over large regions of the upper troposphere, would indicate that PAN should be considered as an important carrier of reactive nitrogen even in the summer hemisphere and might explain why our predictions are high relative to the upper-air measurements of Huebert and Lazrus (1980) but low relative to the boundary layer measurements of Savoie et al. (1989 a,b). Further research and measurements should clarify which of the above three explanations is most plausable.

IV. CONCLUSIONS

Figure 6 shows the ratio of our predicted surface concentrations of NO_x for all sources in July to the predicted surface concentrations for natural sources only. (In this figure, the 3 Mt lightning source has been used). As shown there, vast areas of the globe have experienced increased concentrations of NO_x as a result of man's activities. These increased concentrations may have already contributed to the increased concentrations of O_3 that have been observed at many Northern Hemisphere continental sites (Angell and Korshover, 1983; Bojkov, 1986; Janach, 1989; Volz and Kley, 1988; Logan, 1985). According to our model, it appears that increases in O_3 may also be possible over large regions in the Southern Hemisphere and over the oceans.

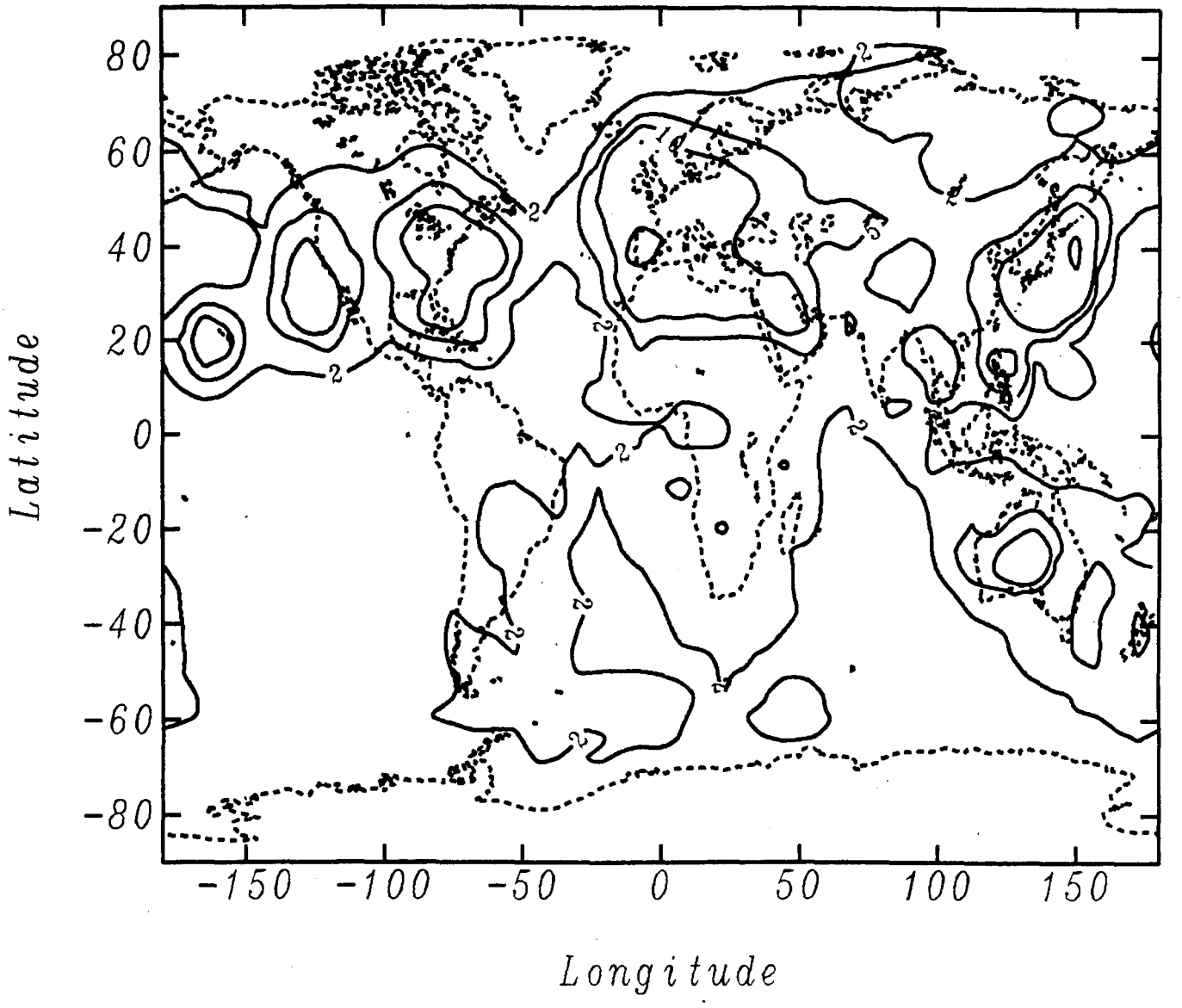

Figure 6. The ratio of the predicted surface concentrations of NO_x for all sources in July to the predicted surface concentrations for natural sources only. The calculation with natural sources only included soil microbial activity, lightning discharges, and production in the stratosphere (see Table 1). The increased concentrations in the Northern Hemisphere are mainly the result of fossil fuel burning, while both fossil fuel burning and biomass burning contribute in the tropics and Southern Hemisphere.

We have shown that we are able to successfully simulate many of the observed features of the reactive nitrogen cycle in the troposphere. Many significant problems remain to be addressed. In particular, there is a need to quantify the role of anthropogenic sources of NO_x in the global budget of O_3. The spatial extent of the contribution of anthropogenic sources of NO_x to surface concentrations is unexpected. In the future, we hope to extend our model in order to quantify the role of anthropogenic sources of NO_x in the global budget of tropospheric O_3.

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