

Distribution of Stratospheric Nitric Acid Vapor

A. L. LAZRUS AND B. W. GANDRUD

National Center for Atmospheric Research,¹ Boulder, Colo. 80303

(Manuscript received 19 November 1973, in revised form 8 January 1974)

ABSTRACT

Stratospheric nitric acid vapor was collected by sorption on cellulose filters impregnated with dibutoxyethylphthalate. The sampling was conducted by both stratospheric aircraft and balloons from 53S to 65N up to altitudes of 37 km. Results indicate concentrations increase with higher latitudes. The most concentrated layer extends from about 20 to 27 km in polar regions, and higher at lower latitudes. The present data indicate a seasonal variation in concentration. Stratospheric nitrate does not appear to be appreciably associated with stratospheric aerosol. The observed concentrations are in reasonable agreement with theoretically computed profiles. The transport rate of stratospheric nitric acid into the troposphere balances the computed production rate of stratospheric nitric oxide from nitrous oxide.

1. Introduction

This study is a continuation of a preliminary report substantiating the existence of nitric acid vapor in the stratosphere by means of a direct sampling technique (Lazrus *et al.*, 1972). We have since obtained information to indicate the spatial variability of the nitric acid layer, and to a lesser extent, its seasonal fluctuations. Evidence is further presented to indicate the effect of transport control on nitric acid distribution in the lower stratosphere, the extent to which it is associated with stratospheric aerosol, and the rate at which it is transported into the troposphere. Values of nitric acid vapor in tropical tropospheric air are also given.

The existence of nitric acid in the stratosphere has important ramifications for estimating the climatic impact of supersonic transports. The nitrogen oxides generated by these aircraft would be capable of catalytically diminishing concentrations of ozone in the stratosphere, and would thereby change the intensity of ultraviolet light reaching the earth's surface (Crutzen, 1972). Nitrogen dioxide is readily oxidized by hydroxyl radical to nitric acid vapor. Since hydroxyl radicals are formed by reaction of water vapor in the ozone layer, it is possible that the nitrogen oxides would be converted to nitric acid rapidly enough to significantly reduce their influence on the ozone layer. Though nitric acid vapor is itself photodissociated back to nitrogen dioxide and is also destroyed by hydroxyl radicals (Johnston and Whitten, 1973), these reactions are sufficiently slow for the concentration of nitric acid vapor to build up to significant values in the lower stratosphere. Thus, it is believed that nitric oxides are ultimately removed from the lower stratosphere in the

form of nitric acid. This hypothesis is tested in the present paper in the case of naturally occurring nitrogen oxides and nitric acid vapor in the stratosphere. The source of this material is primarily nitrous oxide, formed biogenically at the earth's surface and attacked by excited atomic oxygen in the stratosphere to form nitric oxide (Crutzen, 1971).

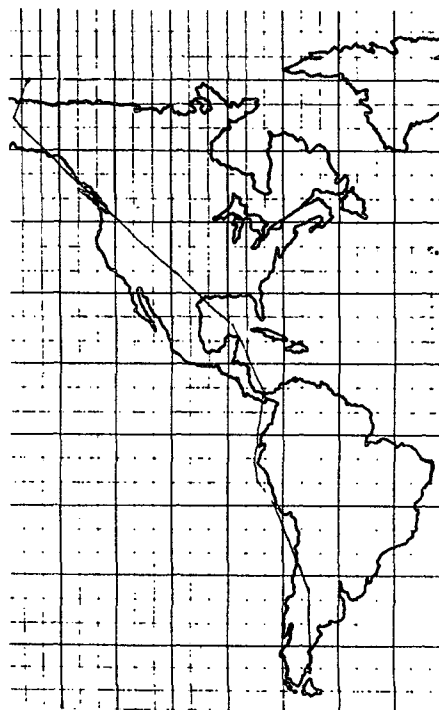


FIG. 1. Track for aircraft sampling of the stratosphere in the AEC's project "Airstream."

¹The National Center for Atmospheric Research is sponsored by the National Science Foundation.

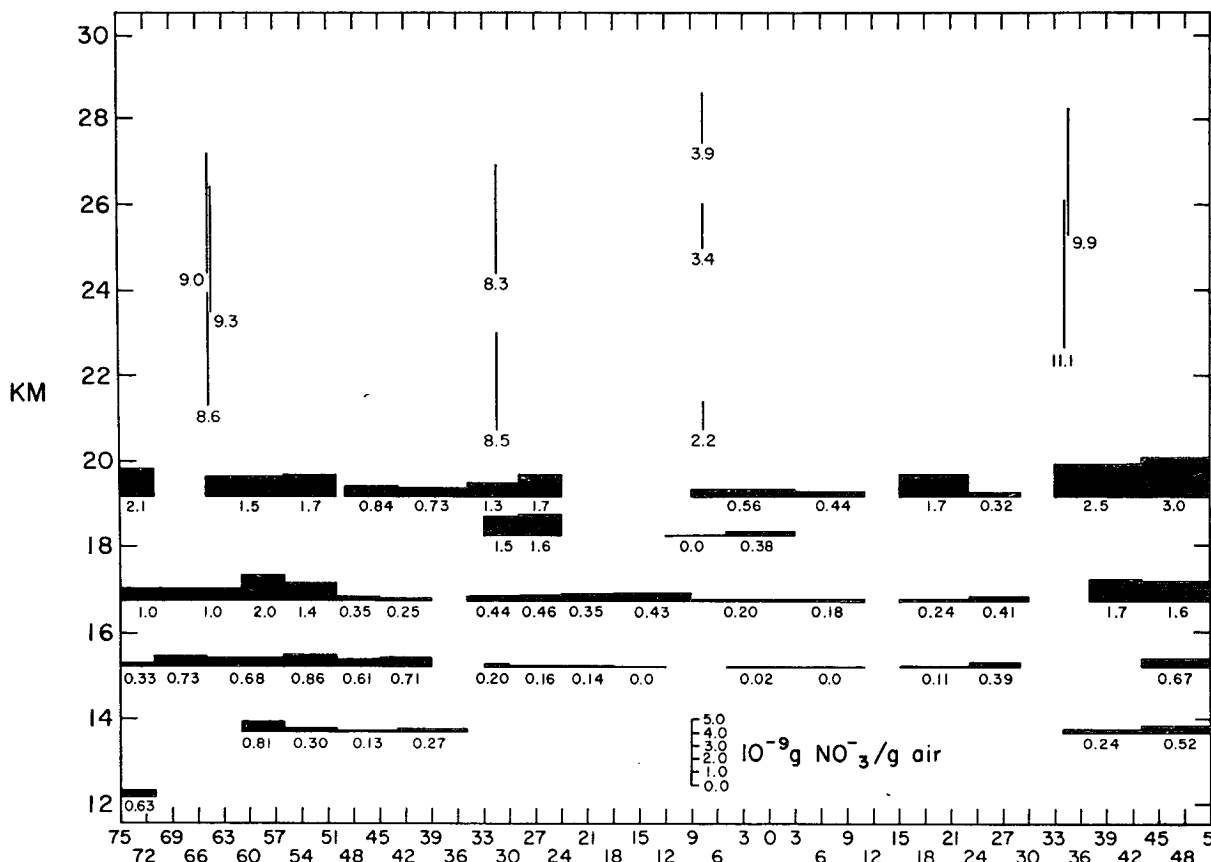


FIG. 2. Spring 1971 nitric acid concentrations as functions of height and latitude (abscissa) from aircraft and balloon sampling. Concentrations are given in ppm and are also indicated by the height of the bars. The lower edge of the bar represents the altitude at which the sample was taken. Width of the bar at 19.3 km and below represents the latitude range over which the sample was collected by the WB57-F aircraft.

A second possibility is that the nitrogen oxides will react with compounds in the exhaust of the SST (e.g., SO₂) and thereby be removed as aerosols. The reaction of SO₂ and NO₂ under the influence of ultraviolet light to form a solid aerosol has been studied (Urone *et al.*, 1971). Furthermore, since SO₂ is most likely the precursor of naturally occurring sulfate aerosol in the stratosphere, it might also be expected

to form a stable aerosol with NO_x. Data are given here regarding the extent to which nitrate is associated with naturally occurring stratospheric aerosols.

2. Experimental

The samples are collected in both the aircraft and balloon experiments by adsorption on IPC 1478 filters. This filter, composed of cellulose fibers impregnated with dibutoxyethylphthalate, is first subjected to a pretreatment to remove water soluble impurities (Gandrud and Lazrus, 1972). Comparative field tests on WB57F aircraft indicated that the pretreatment introduces no loss in collection efficiency for either aerosols or nitric acid vapor. This was further confirmed in the case of aerosols by means of the environmental test chamber of the AEC Health and Safety Laboratory.

The distinction between particulate nitrate and nitric acid vapor was made by sampling both on IPC 1478 filters and on polystyrene filters. Sulfate particle collections were comparable on each filter, but the nitrate was practically absent on the polystyrene filter (Table 1). Laboratory simulation showed that the polystyrene filter papers did not adsorb nitric acid

TABLE 1. Summary of nitrate and sulfate particle measurements.

Date	Altitude (km)	Latitude (N)	Longitude (W)	Weight ratio NO ₃ ⁻ /SO ₄ ²⁻	Mixing ratio NO ₃ ⁻ (ppbm)
4 December 1969	17	34°30'	102°55'	0.00	0.00
4 December 1969	17	37°20'	102°30'	0.00	0.00
4 December 1969	18	46°30'	101°30'	0.00	0.00
4 December 1969	18	47°48'	101°45'	0.00	0.00
4 December 1969	18	33°30'	102°40'	0.00	0.00
4 December 1969	18	34°20'	103°35'	0.00	0.00
17 October 1970	18	33°30'	101°05'	0.34	0.30
17 October 1970	19	34°20'	91°10'	0.00	0.00
30 August 1973	18	33°30'	101°05'	0.15	0.093

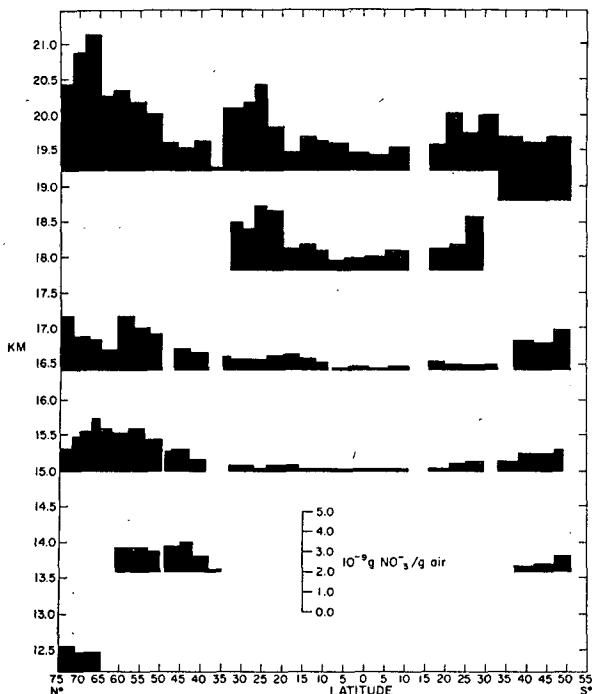


FIG. 3. As in Fig. 2 except for fall 1971 aircraft sampling.

vapor, whereas the impregnated IPC 1478 filter was effective (Lazrus *et al.*, 1972).

The measurements of nitric acid vapor by this technique are in agreement both with theoretical prediction and with infrared radiometry as will be shown later.

The sampling network consisted of the AEC aircraft and balloon stratospheric monitoring programs. The aircraft sampling was accomplished by means of WB57F aircraft sampling between tropopause height and 63,000 ft along the track indicated in Fig. 1. The aircraft are equipped with tubular air foils situated outside the fuselage. A remotely operated sample changer sequentially lowers the 41-cm diameter filters into the air foil for the chosen sampling period, and then returns it to a sample folder which is isolated from the foil by duct seals. Thus, each filter is exposed to ambient air only during sampling. On each flight, two filters were exposed for only 5 sec each to provide contamination control blanks. Sampling periods were about 30 min.

Air flow through the filters during balloon sampling was maintained by either turbine pumps or air ejector systems at the higher altitudes. On each balloon flight an additional sample was included only for the purpose of providing a contamination control blank.

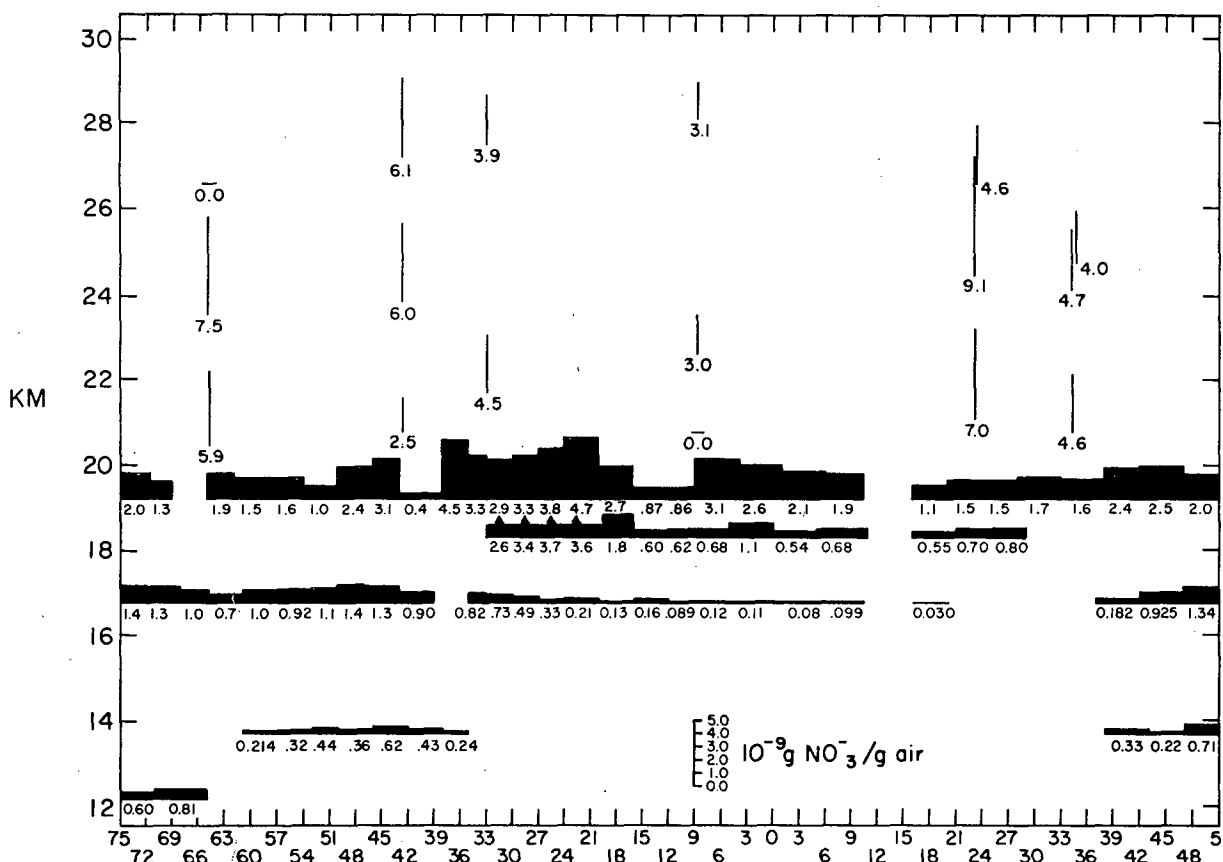


FIG. 4. As in Fig. 2 except for spring 1972 aircraft and balloon sampling.

In the case of aircraft sampling the control filters generally did not contain nitrate above our detection limit. In the balloon sampling, the contamination correction averaged 8% of the sample size. The range of detection limits was $3-7 \times 10^{-9}$ gm m⁻³ ambient, depending upon altitude and sampling time.

Further details of the sampling and chemical analysis have already been described (Lazrus *et al.*, 1972).

3. Concentration and distribution

The latitude distributions of nitric acid obtained by aircraft are shown in Figs. 2-4, along with the balloon data. Though aircraft sampling is completed within a few days, the balloon sampling requires several months. The balloon flights at a given location are generally completed in several days. One should therefore bear in mind that though all the data are indicative of a given season, they are not obtained simultaneously.

The samples collected at 15.3 km during spring 1971 indicate values below the detection limit in subtropical tropospheric air. This is not surprising since HNO₃ would be easily removed by rainout or washout in tropospheric air. The concentration gradients become quite steep between 19 and 21 km, with most of the nitric acid existing above this altitude. Steep concentration gradients are similarly observed by infrared spectrometry (Murcray *et al.*, 1972). The latitude distribution at the higher altitudes is more clearly seen in

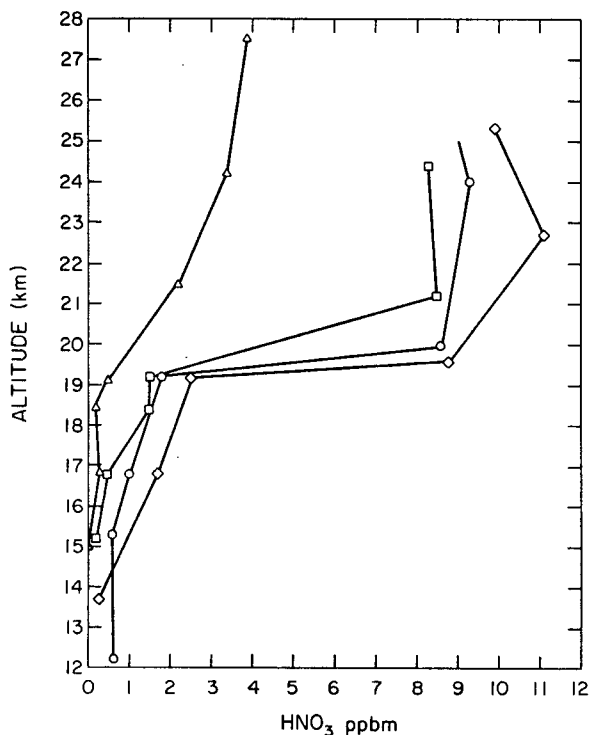


FIG. 5. Vertical profiles of HNO₃, Spring 1971: Δ 8°27'N, \square 31°26'N, \circ 64°39'N, \diamond 34°12'S.

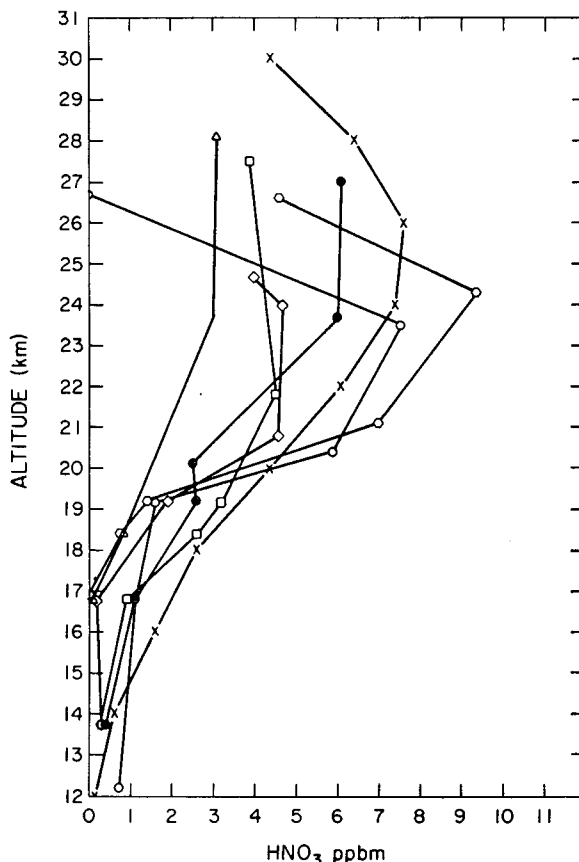


FIG. 6. Vertical profiles of HNO₃, Spring 1972: Δ 8°27'N, \square 32°51'N, \circ 64°39'N, \bullet 42°30'N, \diamond 23°26'S. The theoretical curve is shown by the x's.

the vertical profiles drawn from balloon and aircraft data (Figs. 5-7). The data during the Northern Hemisphere spring of both years indicate low concentrations over the equator with values increasing toward higher latitudes.

The Southern Hemisphere values corresponding to late fall tend to be higher. Balloon flights were made during each season only at 34S. Fortunately these samples permit an initial insight into possible seasonal effects. Indeed the data (Fig. 8) suggest a tendency for concentrations during winter and spring to be higher than in summer and mid-fall. The two Southern Hemisphere profiles with high concentrations were both determined in late fall.

Though the amount of data is too skimpy to be conclusive, it does suggest seasonal and geographical trends in concentration analogous to those of ozone (Dütsch, 1971).

A concentration profile for nitric acid vapor, not taking into account seasonal or meridional variability, has been computed by Crutzen (1973) and is shown for comparison in Fig. 6. It is seen that the observed profiles are quite comparable with the theoretical.

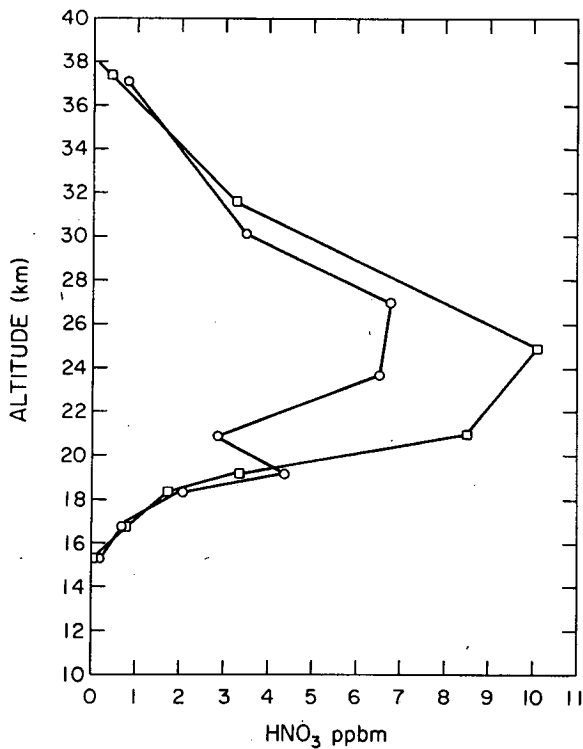


FIG. 7. Nitric acid profiles, Spring 1973: □ 32°51'N, ○ 34°12'S.

Given the extent of the variability observed, these results are in reasonable agreement with those obtained by infrared irradiance measurements (Murcray *et al.*, 1972).

The nitric acid profile at 65N diminished to below our detection limit at altitudes of 26–27 km in spring 1972. Recent data collected during April 1973 at 33N and 34S have extended our observations to 37 km, as shown in Fig. 7. The nitric acid vapor is still present at small but measurable concentrations at this altitude. The curve suggests that nitric acid concentrations are very low above 40 km at these latitudes. The data also suggest (Fig. 6) that the top of the layer decreases in height as latitude increases.

It is interesting to note that in Fig. 7, as in the earlier data, the amount of nitric acid vapor observed is larger in spring than in mid-fall.

Nitric oxides in the stratosphere are oxidized to nitric acid which is relatively inert in the lower stratosphere (Johnston, 1971; Crutzen, 1971). It is therefore believed that most of the oxidized nitrogen molecules are removed from the stratosphere predominantly as a nitrate. It has been suggested that this nitrate may be removed either as nitric acid vapor, or as an aerosol. From the data summarized in Table 1, it is apparent that only a small fraction of the nitrate will be removed in aerosol form. Using a quasi-empirical atmospheric transport model successfully tested with radioactive aerosols (Krey and Krajewski, 1970), one computes a

flux of 2×10^5 tons of stratospheric sulfate aerosol across the tropopause, annually. Using the average ratio of nitrate to sulfate found on the polystyrene filters (0.054), one obtains only 10^4 tons of nitrate transported from the stratosphere as aerosol.

The remainder of nitrate is most likely removed with air exchange into the troposphere as nitric acid vapor. In spite of the fact that the nitric acid and sulfate occur primarily in separate phases, vapor and aerosol respectively, the correlation coefficient between concentrations of nitrate and sulfate measured in our samples collected below 19.3 km was 0.90 and 0.77 in spring and fall 1971, and 0.84 in spring 1972. The similarity in their distribution pattern is illustrated by hand-drawn concentration isopleths in Fig. 9. It seems reasonable to assume that this similarity results from concentration control by dynamic processes in the lower stratosphere, and that the nitric acid vapor is transported into the troposphere in a manner similar to that of both stable and radioactive aerosols. If this is so, one might apply Krey and Krajewski's model derived quasi-empirically from radioactive aerosol data to the observed nitric acid vapor concentrations. This yields a calculated transport of $1.4 \pm 0.7 \times 10^6$ tons of stratospheric nitric acid vapor into the troposphere annually.

Thus, only about 1% of the nitrate removed from the stratosphere annually is transported as aerosol.

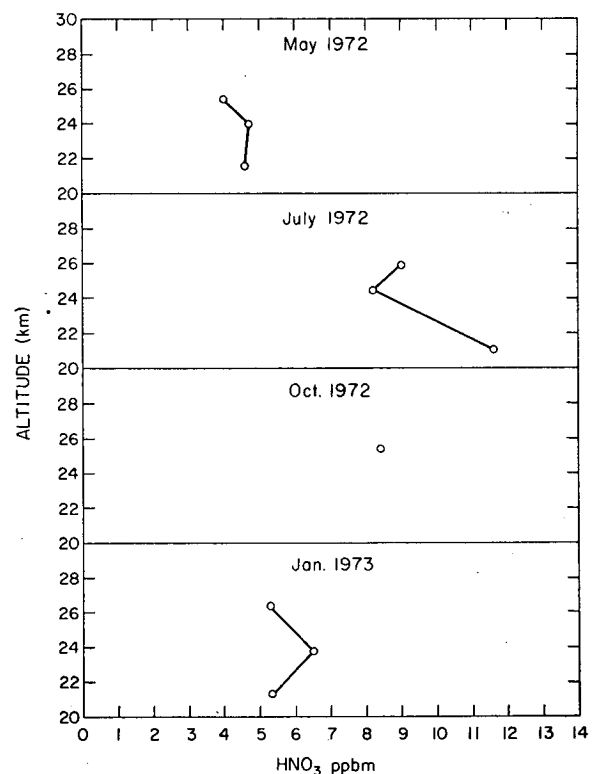


FIG. 8. Seasonal variations of nitric acid concentrations in Southern Hemisphere, 34°12'S.

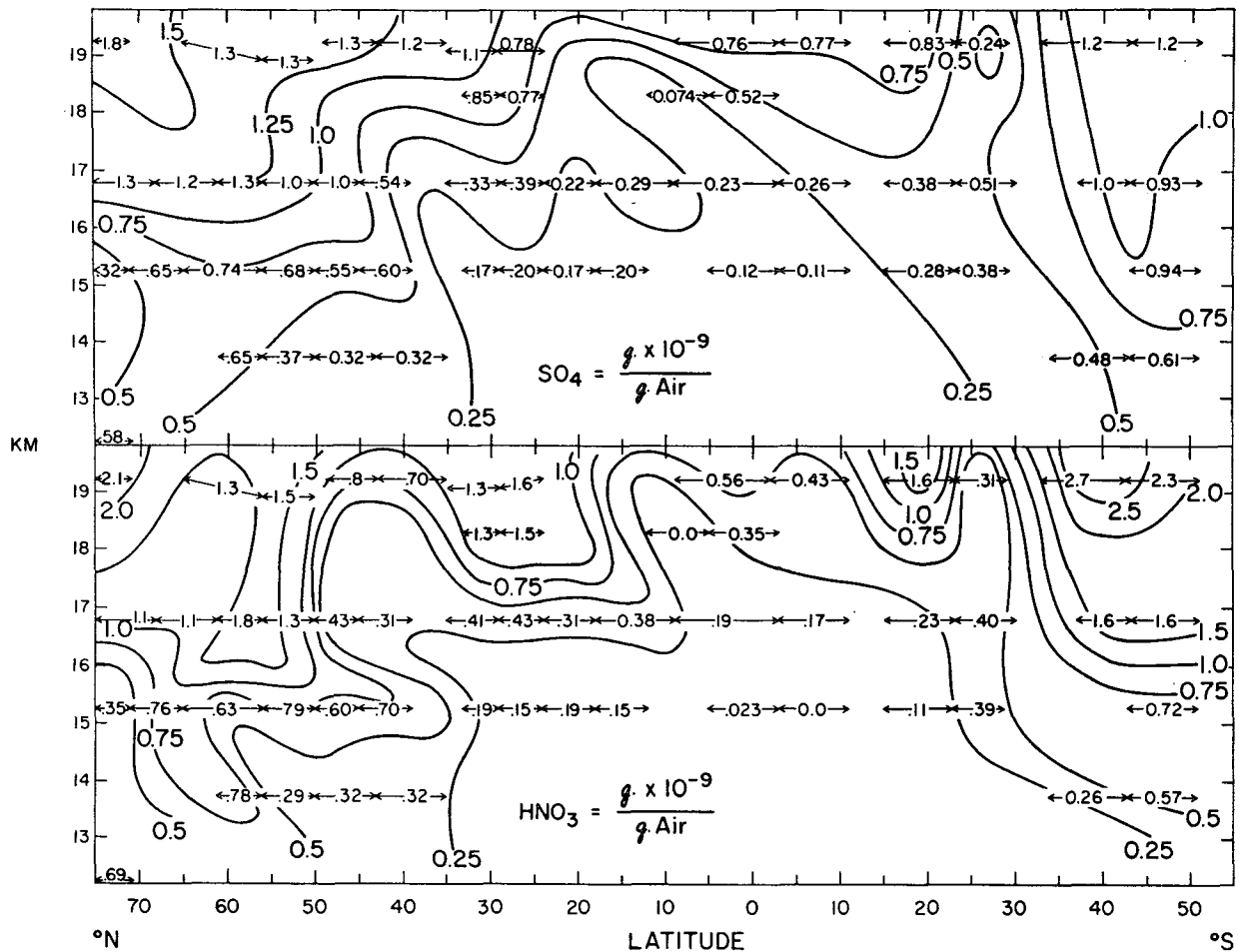


FIG. 9. Hand-drawn concentration isopleths for nitric acid vapor and sulfuric acid aerosol based on aircraft data of spring 1971.

Current chemical models have yielded several estimates of nitrogen oxide production in the natural stratosphere. Estimated nitric oxide production from nitrous oxide by both photodissociation and by reaction with electronically excited oxygen atoms [$O(^1D)$] is shown as $0.3\text{--}0.9 \times 10^8$ molecules $\text{cm}^{-2} \text{sec}^{-1}$ (McElroy and McConnell, 1971), with photodissociation making the smaller contribution. This corresponds to $1 \pm 0.5 \times 10^6$ tons of nitric acid removed annually from the stratosphere to maintain a quasi-steady state concentration of odd nitrogen molecules. A second model (Nicolet and Peeterman, 1972) estimates the nitric oxide production from the reaction of nitrous oxide with atomic oxygen as $1 \pm 0.5 \times 10^8$ molecules $\text{cm}^{-2} \text{sec}^{-1}$. This corresponds to $1.6 \pm 0.8 \times 10^6$ tons of nitric acid transported from the stratosphere annually. The good agreement between the estimates for production of odd nitrogen in the natural stratosphere from N_2O with our value of $1.4 \pm 0.7 \times 10^6$ tons of nitrate removed annually lends considerable credence to the models involved. It further tends to confirm the belief that the

odd nitrogen in the stratosphere is removed primarily as nitric acid vapor.

Nitric acid vapor must enter the troposphere in regions of stratospheric subsidence such as the cyclonic side of jet streams and the South Pole. Indeed, it has been known for some time that snow and soils in the region of the South Pole contain anomalously high concentrations of nitrate and sulfate (Wilson and House, 1965; Claridge and Campbell, 1968).

4. Conclusions

- 1) Nitric acid is concentrated in a layer beginning at about 20 km and extending to 27 km and above, depending on latitude.
- 2) The concentrations increase from equatorial to polar latitudes.
- 3) The present data suggest higher concentrations in winter and spring than in summer and mid-fall.
- 4) The nitric acid does not appear to be significantly associated with natural stratospheric sulfate aerosol.

5) The rate of removal of nitric acid from the stratosphere corresponds well with the estimated rates of production of odd nitrogen molecules.

Acknowledgments. This work is part of a cooperative project with the Division of Biomedical and Environmental Research of the Atomic Energy Commission and with the Climatic Impact Assessment Program of the Department of Transportation.

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