

Photochemistry and Transport of Carbon Monoxide in the Middle Atmosphere

S. SOLOMON,[@] R. R. GARCIA,[#] J. J. OLIVERO,[‡] R. M. BEVILACQUA,^{**} P. R. SCHWARTZ,[∞]
R. T. CLANCY,^{§,†} AND D. O. MUHLEMAN[§]

[@]Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303*

[#]National Center for Atmospheric Research, Boulder, CO*

[‡]on leave at: Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO; permanent affiliation:
Department of Meteorology, Pennsylvania State University, University Park, PA

^{**}Naval Research Laboratory, Washington, DC

[§]California Institute of Technology, Pasadena, CA

[†]present affiliation: Laboratory for Atmospheric and Space Physics, University of Colorado, Boulder, CO

(Manuscript received 26 September 1984, in final form 16 January 1985)

ABSTRACT

Two-dimensional model calculations of the photochemistry and transport of carbon monoxide in the stratosphere, mesosphere, and lower thermosphere are presented. Results are compared to available observations at midlatitudes, where both observation and theory suggest that mesospheric CO abundances are larger on average in winter than in summer. The calculations also indicate that extremely large densities of CO should be found in the polar night mesosphere and upper stratosphere, but at present no high-latitude data are available for direct comparison. However, it is suggested that such a latitudinal distribution implies that the midlatitude region can exhibit unusually large abundances of CO under conditions of large-scale planetary wave activity. Two midlatitude observations during late January 1982 are shown to be consistent with this possibility.

1. Introduction

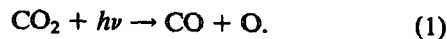
The photochemistry and transport of carbon monoxide in the troposphere (surface to about 12 km) is the subject of a great deal of study, primarily because this species plays a central role in the photochemical smog reactions that produce tropospheric ozone. In the middle atmosphere (from about 10 to 100 km), on the other hand, carbon monoxide is not an active participant in the photochemistry of ozone, and is largely inert with respect to other constituents. In the mesosphere, the photochemical lifetime of carbon monoxide is comparable to those of the transport time scales, and its density there is dependent on both chemical and dynamical processes (see Fig. 1). As a result, this species provides a good tracer with which our understanding of middle atmosphere transport processes may be tested (Hays and Olivero, 1970; Wofsy *et al.*, 1972; Allen *et al.*, 1981), and the study of CO in the middle atmosphere is therefore of interest and importance, in spite of (or because of) its rather unreactive nature.

Observations of mesospheric carbon monoxide can be performed from the ground using microwave methods (e.g., Waters *et al.*, 1976; Kunzi and Carlson, 1982; Clancy *et al.*, 1982), and infrared observations

of this constituent in the stratosphere and perhaps the lower mesosphere are planned as part of the complement of experiments onboard the Upper Atmosphere Research Satellite (to be launched in the late 1980s). Thus, the distribution and variability of carbon monoxide in the middle atmosphere is becoming better characterized than ever before. Microwave studies suggest that greater CO abundances are present in winter than in summer at midlatitudes, which has been interpreted to be a result of downward transport by the mean meridional circulation during the winter season (Clancy *et al.*, 1982, 1984). In this paper, we present a modeling study of the behavior of carbon monoxide in the middle atmosphere. Comparisons of calculations with observations and their inferences for transport processes will be discussed. The calculated variations of this species with respect to altitude and season will be described, and their relevance to transport processes will be explored, for both zonally averaged and for zonally asymmetric conditions (e.g., in the presence of large-scale waves).

2. Photochemistry of carbon monoxide

The primary source of carbon monoxide in the upper part of the middle atmosphere (mesosphere and lower thermosphere) is provided by photolysis of carbon dioxide:



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

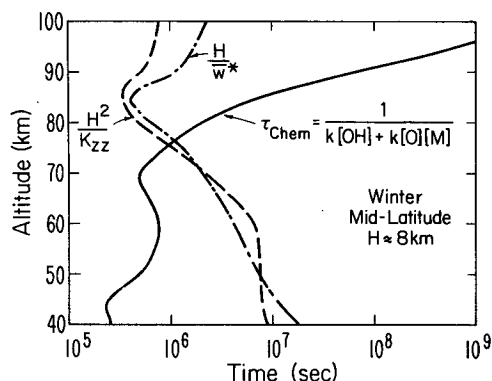


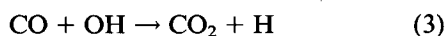
FIG. 1. Photochemical lifetime of CO in the winter mesosphere at 39° latitude, along with the diffusive time constant given by H^2/K_{zz} , where H is the CO scale height and K_{zz} is the vertical eddy diffusion coefficient, and the advective time constant given by H/w^* , where w^* is the residual Eulerian vertical velocity calculated by the model (see Garcia and Solomon, 1983).

Carbon dioxide absorbs strongly in the Schumann-Runge continuum and at Lyman- α wavelengths, and to a lesser degree in the Schumann-Runge bands of molecular oxygen. Thus its photolysis rate becomes rapid only at high altitudes, where substantial fluxes at these wavelengths are available. The effectiveness of this loss process for CO_2 is manifested by the observation of decreases in the CO_2 mixing ratios above about 100 km, where its relative abundance begins to drop from perhaps 330 ppmv to less than 300 ppmv in only about 10 km (e.g., Trinks and Fricke, 1978). Above about 120 km, oxidation of CO_2 by reaction with O^+ also becomes important, but is not considered in this study because our model upper boundary is located at about 116 km. The major chemical loss of CO above about 100 km is due to three-body recombination with atomic oxygen:



but the time constant characterizing the photochemistry is much slower than transport at these altitudes (Fig. 1). Since CO is the long lived product of CO_2 destruction in the lower thermosphere, the observed CO_2 gradient suggests that CO mixing ratios in the lower thermosphere should be of the order of a few tens of ppmv.

Carbon monoxide is also produced in the stratosphere through the oxidation of atmospheric methane, but it is rapidly destroyed there via the reaction:



which is the dominant loss reaction for this species throughout the stratosphere and mesosphere. We note that this process only occurs in the sunlit atmosphere, since OH is produced by reactions involving photolysis (e.g., of H_2O) and its concentration therefore diminishes rapidly in the dark. Our knowl-

edge of the abundance of OH is subject to considerable uncertainty, particularly in the mesosphere, so that the loss rate (3) is probably the largest single uncertainty in photochemical properties that influence CO in the middle atmosphere. Observed CO abundances near the sunlit stratopause are of the order of a few tens of ppbv, about a factor of 1000 times less than those of the lower thermosphere.

It is interesting to note that the chemistry of CO is roughly analogous to that of NO in the middle atmosphere [or, alternatively, $(\text{NO}_x) = (\text{N}) + (\text{NO}) + (\text{NO}_2) + (\text{NO}_3) + 2 \times (\text{N}_2\text{O}_5) + (\text{HNO}_4)$]; most of the NO_x above about 40 km is in the form of NO]. Both CO and NO are produced in large amounts in the sunlit lower thermosphere, and both are destroyed relatively rapidly ($\tau \approx$ days) in the sunlit mesosphere. The abundances of these constituents in the mesosphere thus depend upon the balance between photochemical destruction and downward transport from the thermospheric source region, both by advection through the meridional circulation cell and by vertical eddy mixing (and these two transport processes have similar time scales, as shown in Fig. 1). In the winter mesosphere, advection is directed downward from the thermospheric source region, while in summer, the mean cell is directed upward. Further, the time averaged photolysis reactions which lead to the destruction of these species are slower in winter than in summer, both because of fewer sunlit hours in the day and because of increased attenuation of solar radiation. Thus, these constituents should be present in larger quantities in the winter mesosphere than in summer even if the intensities of vertical eddy transport are equal in both hemispheres. Very large abundances should accumulate in the polar night mesosphere because of the virtual absence of photochemical destruction processes there, so that the much larger abundances characteristic of the lower thermosphere can be transported downward without exposure to sunlight. Similar trends have been predicted for NO (e.g., Garcia and Solomon, 1983) and verified by satellite observations (Russell *et al.*, 1984). We shall make further comparisons between the behavior of NO and CO below.

3. Model description

The model used in these calculations is basically the same as the one described by Garcia and Solomon (1983; 1985) and Solomon and Garcia (1983a). The model computes the two-dimensional dynamical and chemical structure of the middle atmosphere from pole to pole, from about 16 to 116 km. The chemistry includes odd oxygen ($\text{O} + \text{O}_3$), odd nitrogen ($\text{N} + \text{NO} + \text{NO}_2 + \text{NO}_3 + 2 \times \text{N}_2\text{O}_5 + \text{HNO}_4$), odd hydrogen ($\text{H} + \text{OH} + \text{HO}_2$), water vapor, methane, N_2O , HNO_3 , H_2O_2 , molecular hydrogen, and now carbon monoxide and dioxide. Daytime averaged

photolysis rates are calculated every two days of integration and imposed during the sunlit period of the day. In the following, we will point out only briefly the differences between the model used in our previous studies and the present work.

An important change in the description of mesospheric dynamics has been included in this study. Recent work has emphasized the importance of breaking gravity waves in producing both momentum deposition and diffusion in the mesosphere (Lindzen, 1981; Weinstock, 1982; Holton, 1982, 1983). These studies have shown that the propagation and dissipation of small scale gravity waves yields many features of mesospheric dynamics (such as the reversal of the zonal winds above about 90 km and the very cold summer mesopause temperatures) which are in better agreement with observations than those obtained using a simple "Rayleigh friction" parameterization of the momentum drag at these altitudes. In the present study we have incorporated a parameterization of the effects of breaking gravity waves to obtain turbulent diffusion coefficients and momentum deposition for the mesosphere. Our parameterization is basically that of Lindzen (1981), and it is described in detail in Garcia and Solomon (1985). The advantage of such a description is that it provides a physical basis for characterizing some of the important aspects of dynamics in this region. As a result of this parameterization, the meridional circulation of the mesosphere and thermosphere in this study is somewhat more vigorous than that in Garcia and Solomon (1983), and there are seasonal and latitudinal variations in the magnitude of the derived turbulent mixing coefficient because of the selective filtering of upward propagating gravity waves by the zonal winds (see, e.g., Lindzen, 1981; Holton, 1983).

Both CO_2 and CO are calculated in the present model. The chemistry used is that indicated above, and we note that the methane oxidation source of CO and CO_2 is also included in the model. The reaction rate constants used are essentially those of NASA/JPL (1983), and the rate constant used for (2) is $6.6 \times 10^{-33} \exp(-1103/T) \text{ cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. As discussed above, CO is produced in large quantities in the middle thermosphere, above the upper boundary of our model. Therefore, we next discuss how we have treated the downward flux of CO at the model upper boundary. A similar problem exists for odd oxygen, since molecular oxygen photolysis in the thermosphere is also important for its distribution in the middle atmosphere. Transport processes are believed to play an important role in the variation of the flux of atomic oxygen into the lower thermosphere, particularly by summer to winter hemisphere transport in the thermospheric circulation cell, so that the largest downward fluxes are found in winter although the largest production occurs in the summer middle thermosphere. In the case of odd oxygen, we obtain

our upper boundary conditions by using the diffusive fluxes inferred from the MSIS model of observed atomic oxygen density (Hedin *et al.*, 1977) as a function of latitude and season, which are in good agreement with those derived from the thermospheric model study of Kasting and Roble (1981). These fluxes are about twice as large in high latitude winter as in summer as a result of long range transport in the thermosphere. One way to derive a boundary condition for CO is to assume that the relative variations of the flux of CO with respect to latitude and season should be analogous to those of atomic oxygen, because their production and transport mechanisms are similar. Since carbon does not escape from the terrestrial atmosphere we must also impose the additional constraint of global balance between upward and downward flowing carbon constituents, as follows:

$$\int_{\text{pole}}^{\text{pole}} J_{\text{CO}_2}(\text{CO}_2)H_{\text{CO}_2} \cos\phi d\phi = \int_{\text{pole}}^{\text{pole}} F_{\downarrow\text{CO}} \cos\phi d\phi$$

where J_{CO_2} , (CO_2) and H_{CO_2} are the photolysis rate, density and scale height of CO_2 at the model upper boundary (116 km), $F_{\downarrow\text{CO}}$ is the downward flux of CO at the upper boundary, and ϕ is the latitude. We emphasize that this is the boundary condition used for all of the calculations presented in this paper.

The sensitivity of the model results to the adopted upper boundary condition has, however, been checked as follows: We performed a series of calculations in which we assume that all of the CO produced by CO_2 photolysis in the thermosphere at a given latitude is transported locally downward, e.g.,

$$F_{\downarrow\text{CO}} = J_{\text{CO}_2}(\text{CO}_2)H_{\text{CO}_2}.$$

Note that the largest downward fluxes are therefore imposed in the summer hemisphere in this case. Computed CO densities above about 95 km are very sensitive to the choice of upper boundary condition, so that our model results shown above ~ 95 km should be considered as uncertain. Below ~ 95 km, however, we find that the calculated CO abundances are nearly insensitive to the choice of upper boundary condition, because the *in situ* production by carbon dioxide photolysis at these altitudes dominates the downward flux (see also, Allen *et al.*, 1981). Thus the choice of upper boundary condition is not critical for the altitudes of primary interest in this study (30–90 km).

4. Zonal mean conditions

Model calculations including carbon monoxide and dioxide chemistry, and using the gravity wave parameterization, were performed for three complete annual cycles. The transport time scales for the mesosphere and stratosphere are substantially shorter

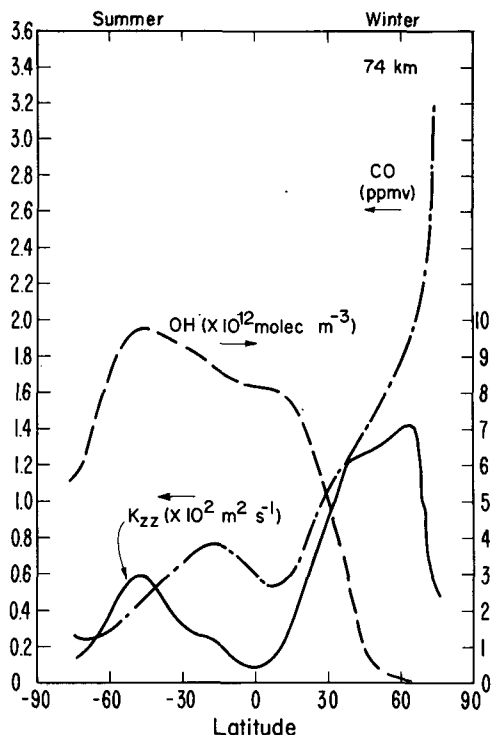


FIG. 2. Calculated latitude gradients of CO, OH (daytime average) and K_{zz} at about 74 km near Northern Hemisphere winter solstice.

than this, and therefore the model is in a quasi-steady state with respect to the annual variations.

One-dimensional model studies have shown that the predicted seasonal variation in CO due to photochemistry alone would yield a maximum in summer, not in winter as observed, suggesting that meridional transport must be important in determining the seasonal changes in CO (Clancy *et al.*, 1982, 1984). In the present model, the computed seasonal variation in CO is related not only to photochemical forcing, but also to meridional transport and its effects on both CO and perhaps water vapor (which provides the primary source of OH in the lower mesosphere). Figure 2 shows the calculated mixing ratio of CO at about 74 km as a function of latitude along with the calculated daytime averaged OH densities and eddy mixing coefficients for winter solstice. The computed gradient in OH is principally due to changes in the penetration of solar radiation with respect to season, with only a minor contribution from seasonal changes in water vapor densities (note that the calculated OH density changes by nearly a factor of 10 from summer to winter at 45 degrees latitude at this altitude, while the calculated change in water vapor abundance here is only about 20%, as shown in Garcia and Solomon, 1985). Note that the reduction in solar illumination in winter which is responsible for these low OH abundances is accompanied by a corresponding reduction in CO produc-

tion through CO_2 photolysis, so that the net effect due to photochemistry alone would be lower CO densities in winter than in summer, as already mentioned. However, meridional transport of CO from the summer to the winter hemisphere (particularly in the region from ~ 80 to 90 km, where the photochemical lifetime of CO is long) leads to enhanced CO mixing ratios in the winter upper mesosphere, as shown in Fig. 3. This reservoir of enhanced CO in winter can then be transported effectively into the OH-poor winter mesosphere and upper stratosphere, both by the descending wintertime circulation and by turbulent eddy diffusion (whose time scales are comparable in an order of magnitude sense—see Fig. 1), leading to very large CO mixing ratios throughout the winter middle and high latitude mesosphere. The gradient in high latitude winter is most pronounced in the lower mesosphere, where the chemical loss rate in the sunlit atmosphere is rapid compared to transport. Thus the protection provided by polar night has a more important influence on the abundance at these altitudes. As previously noted, similar behavior has been predicted for odd nitrogen, and satellite observations of nighttime NO_2 suggest that such long range transport can occur (Russell *et al.*, 1984). Observations of mesospheric and stratospheric CO in high latitude winter would provide important confirmation of this effect, particularly since the photochemistry of CO is believed to be much simpler than that of odd nitrogen. Indeed, systematic observations of the seasonal and latitudinal variations in carbon monoxide, especially near and inside the polar night region could be useful in characterizing the nature and intensity of lower mesospheric vertical transport processes.

Larger diffusion coefficients are obtained in this model in the lower mesosphere in middle and high latitude winter than in summer as a result of gravity wave propagation and breaking, as demonstrated

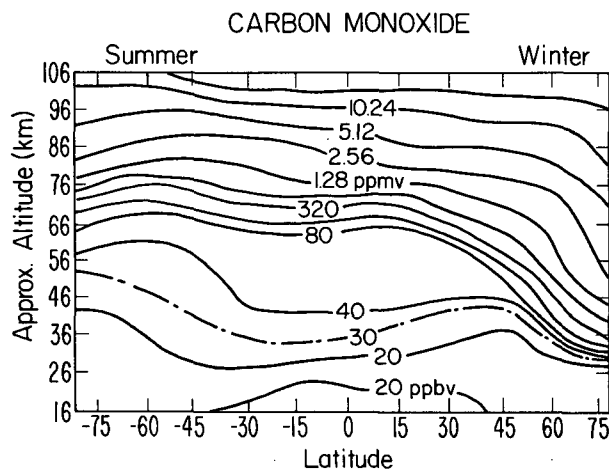


FIG. 3. Calculated CO mixing ratio distribution for solstice.

previously by Lindzen (1981). Downward advection by the mean circulation should, however, result in more CO in winter than in summer even if the intensities of eddy transport were equal in both seasons. It therefore seems appropriate to examine quantitatively whether the calculated seasonal variations in mesospheric CO are due to vertical eddy transport, or to advection by the mean meridional circulation. The competition between diffusive and advective transport of CO at middle latitude is shown schematically in Fig. 4 for the summer and winter. The advective flux convergence dominates the diffusive flux convergence at this latitude above about 75 km, in both seasons, at middle and high latitudes (numerical results for 39° are indicated in the figure as an example). There is a large net convergence of the advective flux of CO in the winter upper mesosphere and a divergence in summer, due to the direction and strength of the mean meridional circulation. The advective and diffusive fluxes therefore tend to cancel in summer, but to add in winter. The stronger eddy diffusion obtained here for the winter mesosphere only adds to this seasonal asymmetry. Thus, the seasonal variation in vertical eddy transport resulting from our model of gravity wave processes affects the details, but not the sense of, the overall trends calculated for mesospheric CO. The importance of meridional advection near 80–90 km in controlling the distribution of mesospheric CO is also revealed by the calculated behavior of CO in the spring. As discussed in detail in Garcia and Solomon (1985), a

pronounced minimum in mesospheric vertical eddy diffusion due to gravity waves is predicted by our model at equinox. This yields a corresponding maximum in atomic oxygen near 100 km in that season. Note that the time scale for vertical transport of CO near 100 km is dominated by eddy diffusion, but that diffusion and vertical advection become comparable at lower altitudes (Fig. 1). Like atomic oxygen, the CO abundance at the 100 km level in our model maximizes in spring. At the lower altitudes of primary interest in this paper (below 90 km), however, the spring minimum in diffusion does not substantially influence the CO abundance because vertical advection is comparable to or faster than diffusive transport.

In summary then, the seasonal and latitudinal structure shown in Fig. 3 may be interpreted as follows: photochemistry produces more CO in the summer hemisphere and in the tropics than in winter. Horizontal advection into the winter hemisphere, however, enhances the winter CO abundances in the region above about 80 km, where the CO lifetime is long. Downward transport, predominantly by vertical advection, can then greatly enhance the CO mixing ratios throughout the winter mesosphere relative to the summer, because of the reduced OH densities there (the importance of the competition between downward transport and photochemical destruction by reaction with OH is particularly evident in the dramatic change in CO mixing ratios near the polar night terminator). Therefore, the calculated behavior of mesospheric carbon monoxide in this model is

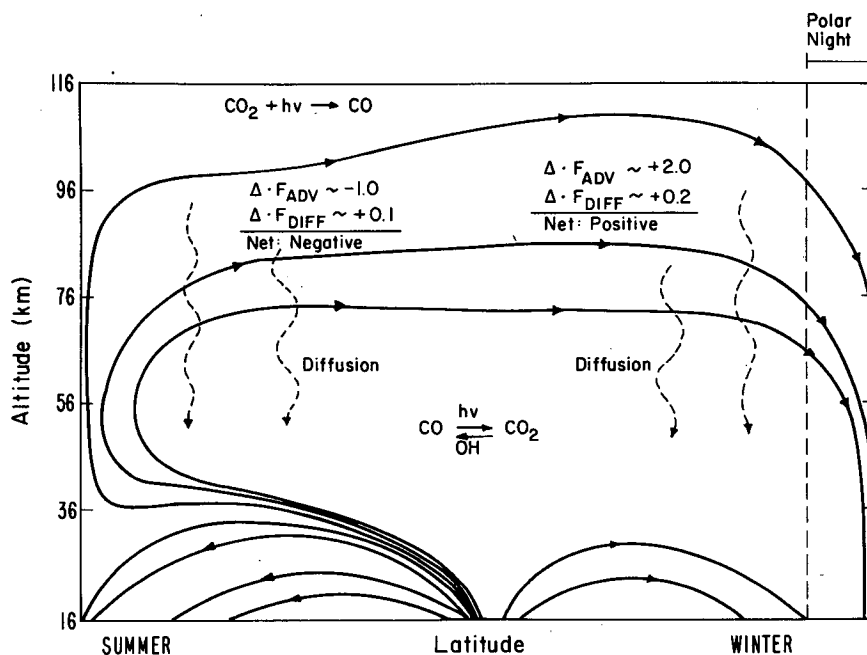


FIG. 4. Schematic diagram of the sources and sinks of CO and the competition between advective and diffusive flux convergence (pptv s^{-1} , at 80 km) for summer and winter at 39° .

dependent on both photochemical and transport processes, as expected from their comparable time scales indicated in Fig. 1.

Figure 5 presents the calculated CO column abundance above 64 km compared to several microwave studies, illustrating the importance of the polar night effect more clearly. The total column is nearly uniformly distributed in all seasons and latitudes between about 60 and 90 km outside of polar night, and between about 45 and 90 km in the polar night region. Observations have indicated that the mesospheric column of CO is about twice as large in midlatitude winter as in summer (Clancy *et al.*, 1982, 1984). A similar seasonal trend is obtained in this model, although the abundances are uniformly smaller than those observed. Note that the observed CO column abundances shown in Fig. 5 were obtained by vertical integration of derived mixing ratio profiles rather than integration of the area under the spectral line (see Clancy *et al.*, 1982, 1984 for discussion of these methods of analysis). Figure 5 also shows how the calculated column abundance of CO would be influenced by reducing the rate constant for the reaction of CO with OH by a factor of 2. This will be discussed in more detail below. The calculated seasonal trend is due principally to downward transport from the thermospheric source region in the winter season, as discussed above. Note, further, the substantial enhancements in the column at high

latitude, and particularly in the polar night region, where the calculated abundances above 64 km exceed $1.0 \times 10^{20} \text{ m}^{-2}$.

Observed and calculated midlatitude profiles are compared in Fig. 6. The observed mesospheric profiles are subject to a good deal of uncertainty, (particularly below 65 km) as shown in the error analysis by Clancy *et al.* (1982) and as indicated in the figure. A fundamental problem in the interpretation of ground-based CO measurements is that the spectral line is sharply peaked, and information about the vertical profile in the lower mesosphere (below about 65 km) can only be obtained by careful analysis of the line wings (e.g., see Clancy *et al.*, 1984, for more details). The line center typically contains the best information about the column above (roughly) 64 km, and the mixing ratios from about 65–75 km.

The stratospheric observations have been obtained by balloon borne infrared and cryogenic sampling methods, and are in good agreement with those calculated. In the mesosphere the calculations are lower than most of the microwave observations, as reflected in the mesospheric column amounts shown in Fig. 5. This might be attributed to inaccuracies in the calculated CO chemical loss or production rates in the mesosphere, or perhaps the vertical transport rates near 80–90 km are underestimated. Changes in the transport description seem unlikely to resolve the observed discrepancies, since the net transport is dominated by advection, at least above 75 km, and an increase (decrease) in the strength of the meridional circulation would yield greater (lesser) CO abundances in winter, but less (more) in summer. Similarly, changes in the intensity of vertical eddy mixing are likely to be dependent on season and latitude, if that mixing is related to breaking gravity waves. Such adjustments would be inconsistent with the observed nearly uniform nature of the differences between calculations and observations as shown in Fig. 5. Thus, it would seem more likely that the photochemistry of the CO loss process may be the cause of the discrepancy, and the calculation with a reduced rate constant for the CO + OH reaction rate illustrates the sensitivity to this parameter. Although this reaction rate has been extensively studied in the laboratory at room temperatures, it has not been examined for mesospheric temperatures in the range of 180–220 K, where the rate constant may well be slower at low pressures. It is also possible that the calculated mesospheric OH densities may be overestimated. This latter possibility is consistent with the fact that calculated ozone abundances near the secondary maximum at 80–90 km are generally underestimated by current models (Allen *et al.*, 1984; Solomon *et al.*, 1983), and ozone is inversely related to OH at those altitudes. Since the present model was formulated with the aim of providing our best estimate for the chemistry and dynamics of this region, we have not

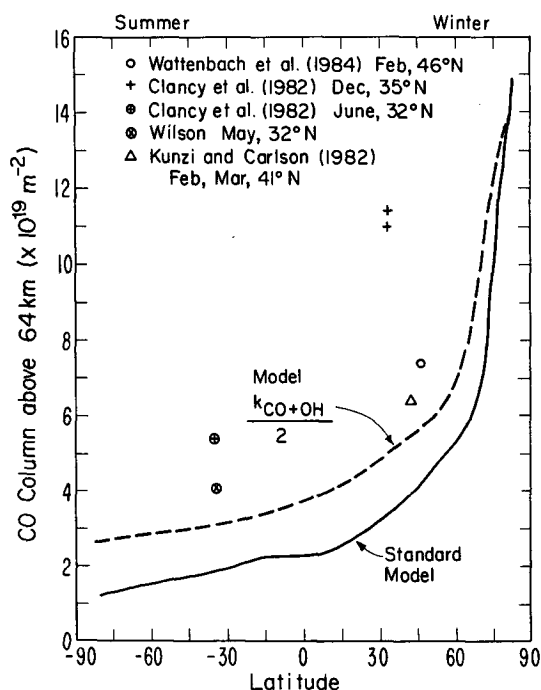


FIG. 5. Calculated CO column abundance above about 64 km compared to microwave observations for the standard model using recommended chemistry and that obtained using a reduced rate constant for the reaction between CO and OH (see text).

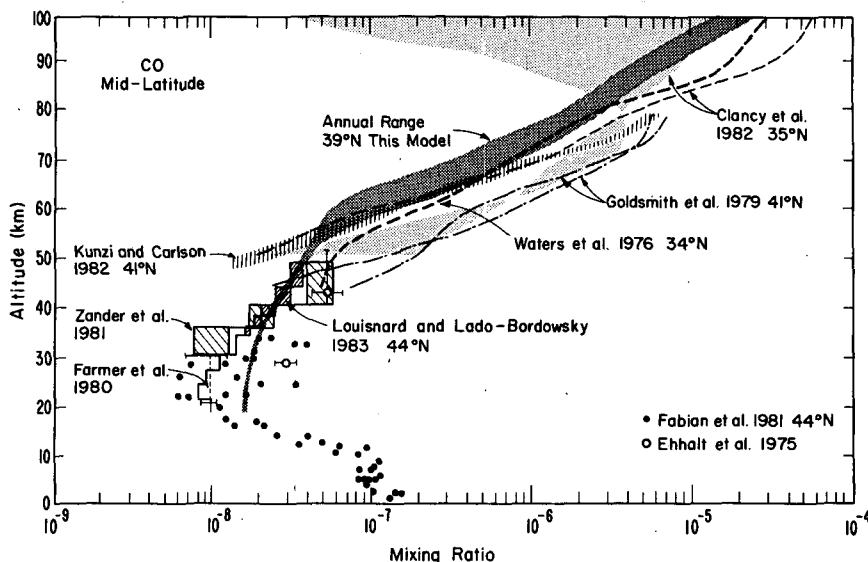


FIG. 6. Observed and calculated midlatitude CO profiles. The dark shaded area shows the model's annual range at 39°N, while the light shaded area from the study by Clancy *et al.* (1982) indicates an uncertainty estimate for mesospheric microwave CO observations. Stratospheric observations by infrared and cryogenic sampling methods are also shown.

attempted to produce agreement by arbitrary adjustment of the indicated model parameters, particularly since several different parameters could contribute to the differences.

In general, the calculated profiles compare reasonably well to the observed vertical distribution of CO, and the observed amplitude of the seasonal variations found at midlatitudes are similar to those predicted for zonally averaged conditions. In the next section, we explore the possible effects of zonal asymmetries on the distribution of CO.

5. The effects of zonal asymmetries

Our zonally averaged two-dimensional model cannot be used to quantitatively examine the local influence of zonally asymmetric motions (waves) on the distributions of photochemical constituents. However, based upon study of the distributions of chemical species in the zonal mean, we can attempt to estimate what the effects of certain wave disturbances might be. For example, large scale planetary waves can displace parcels of air meridionally (North-South) over large distances at particular longitudes, and any species having a latitude gradient should be influenced by such transport processes (e.g., see Schmidt, 1982; Solomon and Garcia, 1983b; Berrgren and Labitzke, 1968). The sharpness of the CO gradient in high latitude winter (Figs. 3 and 5) suggests that latitudinal displacements due to wave effects should dramatically affect its local densities.

Like CO, odd nitrogen is also theoretically expected to exhibit sharp gradients in the high-latitude winter

mesosphere (e.g., see Garcia and Solomon, 1983). It is interesting to note that satellite observations of odd nitrogen (Russell *et al.*, 1984), as well as the pattern of the sporadic "winter anomaly" in radio wave absorption (Kawahira, 1982) indicate that planetary wave transport of mesospheric NO can be quite important. Large local enhancements in odd nitrogen have been observed at mesospheric heights near regions of low geopotential height when large scale wave activity was present (Russell *et al.*, 1984).

Microwave observations of terrestrial constituents are generally obtained through sporadic use of microwave astronomy telescopes designed and principally devoted to astronomical applications; for example, Fig. 6 shows that only about ten CO profiles have been obtained over a period of perhaps eight years. In late January 1982, CO observations happened to be made nearly simultaneously at two observing sites. As we shall see, the times and locations of these observations were remarkably fortunate, and yield some unique and important information regarding the distribution and transport of CO.

Observations of mesospheric CO were obtained (Bevilacqua *et al.*, 1985) by microwave emission at Holmdel, New Jersey (40.4°N) on 28 January 1982 and by microwave absorption at Kitt Peak, Arizona (32°N; Clancy *et al.*, 1984) on 24, 25 and 29 January. The observed altitude profile from Holmdel on 28 January is shown in Fig. 7. This observation exhibits lower mesospheric abundances that are perhaps 10–100 times greater than other midlatitude winter observations (a profile obtained by Kunzi and Carlson, 1982, at the same site about four years earlier is

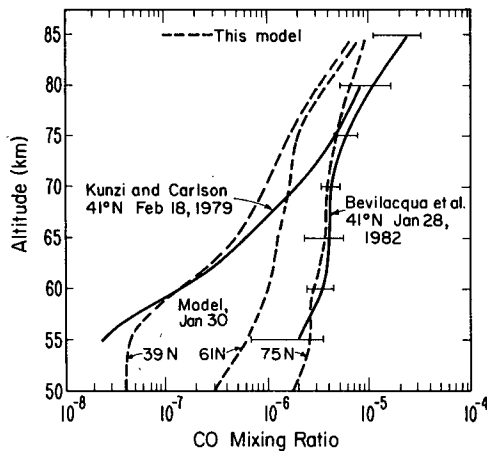


FIG. 7. Observed CO profile at Holmdel, N.J. during 28 January 1982, compared to model calculations in winter at several latitudes. The observation by Kunzi and Carlson obtained in February 1979 at the same site is also shown for comparison.

shown for comparison; see also Fig. 6). Such large CO mixing ratios near the stratopause are found in the model only in the polar night region. Indeed, Fig. 7 shows that the shape of the observed profile on 28 January is consistent only with our model profiles in the polar night region ($\sim 75^\circ$ latitude). The calculated polar night abundances at about 80 km are not much larger than midlatitude values because the lifetime of CO against photochemical loss is very long at this altitude, even in the sunlit atmosphere (Fig. 1), but the calculated gradient in mixing ratio is very large at lower altitudes where the lifetime is about a week in the presence of sunlight.

Measurements of the CO column abundance using the microwave technique at midlatitudes generally yield information about the column above about 64 km, because midlatitude CO densities are normally very small below that level. Due to the extremely large densities observed in the lower mesosphere, Bevilacqua *et al.* (1985) were able to derive a CO column abundance above about 55 km in this case. The observed column above 55 km was about $3.12 \pm 0.3 \times 10^{20} \text{ m}^{-2}$. (The column abundance measured above 64 km during the experiment was $1.3 \pm 0.16 \times 10^{20} \text{ m}^{-2}$; this can be compared to the column abundances above 64 km shown in Fig. 5.) Table 1 compares the column abundance above 55 km measured at Holmdel on this day and the model calculated column abundances. Again, it is clear that we can only explain these observations within the context of our model results if the mesospheric air over Holmdel came from high latitudes.

Figure 8 presents CO column abundances above about 64 km measured at Kitt Peak, Arizona on 24, 25 and 29 January. The observed column on 29 January is about twice as large as those obtained on the 24th and 25th. The Kitt Peak observations on

TABLE 1. CO column abundances above 55 km (molec m^{-2}).

Bevilacqua <i>et al.</i> 40.4°, 28 January 1982	$3.10 \pm 0.3 \times 10^{20}$
This model, 39°, January	0.44×10^{20}
This model, 54°, January	0.68×10^{20}
This model, 75°, January	2.9×10^{20}

the 29th yield a column abundance above 64 km that is nearly identical to that observed at Holmdel on the previous day, but do not yield as much information about the region from 55 to ~ 65 km as the Holmdel spectrum does. This difference is due to the instrument noise level of the two measurements in the extreme line wings, from which the information on CO below 65 km is derived. The ability to retrieve CO in the lower mesosphere can therefore vary from one instrument to another, and the Kitt Peak data yield good information on CO above about 64 km while those of Holmdel are appropriate for altitudes above about 55 km.

The Kitt Peak absorption spectrum of 29 January is unusual in that it was taken during a violent thunder/hailstorm. Although the tropospheric microwave optical path increased significantly due to the storm, the calibration of the absorption measurement proved to be remarkably consistent as indicated by spectra of Venus atmospheric CO taken before and during the storm. The depth and shape of the Venus line was essentially unchanged by the larger tropospheric opacity during the storm, giving strong confidence that the terrestrial mesospheric CO line was

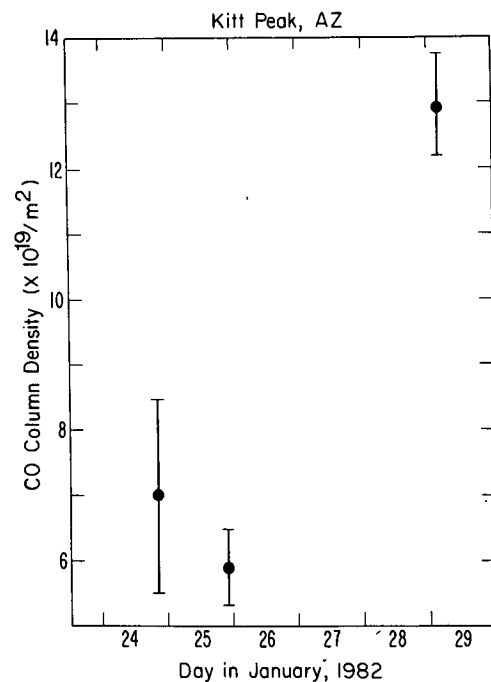


FIG. 8. Observed CO column above about 64 km at Kitt Peak, Arizona, for several days in January 1982.

not significantly affected by the change in tropospheric opacity. At the time, it was presumed that a large mesospheric cooling might have caused the observed changes in the terrestrial CO spectrum since the microwave spectrum is temperature dependent. An extremely large temperature change of about 50 K near 65 km during the period from 25 January to 29 January would be required to explain the Kitt Peak observations. The temperatures reported at the highest level of the National Meteorological Center (NMC) analysis (0.5 mb, or about 55 km) were no more than 15 K colder or 29 January over Kitt Peak than those reported on 24 and 25 January; therefore such a large temperature change near 65 km seems unlikely. Further, the Holmdel observation is an emission spectrum, while the Kitt Peak observation is an absorption spectrum, and it is important to note that

the emission method is only about half as sensitive to temperature as is the absorption method. Therefore, since the observed Holmdel spectrum is as intense as the Kitt Peak spectrum, even an extremely large temperature decrease does not provide a viable explanation of both observations. It seems more likely that the observed changes in the Kitt Peak spectrum, and the very large CO abundances suggested by the Holmdel spectrum, reflect real features in mesospheric CO densities. The sharp change in CO column observed on 29 January strongly suggests that the air observed over Kitt Peak on that day only had recently come from higher latitudes (see Fig. 5), as suggested above for Holmdel on 28 January.

Figure 9 presents geopotential height maps for 1200 UT at 0.4 mb (about 55 km) for selected days in late January 1982, obtained from the NMC anal-

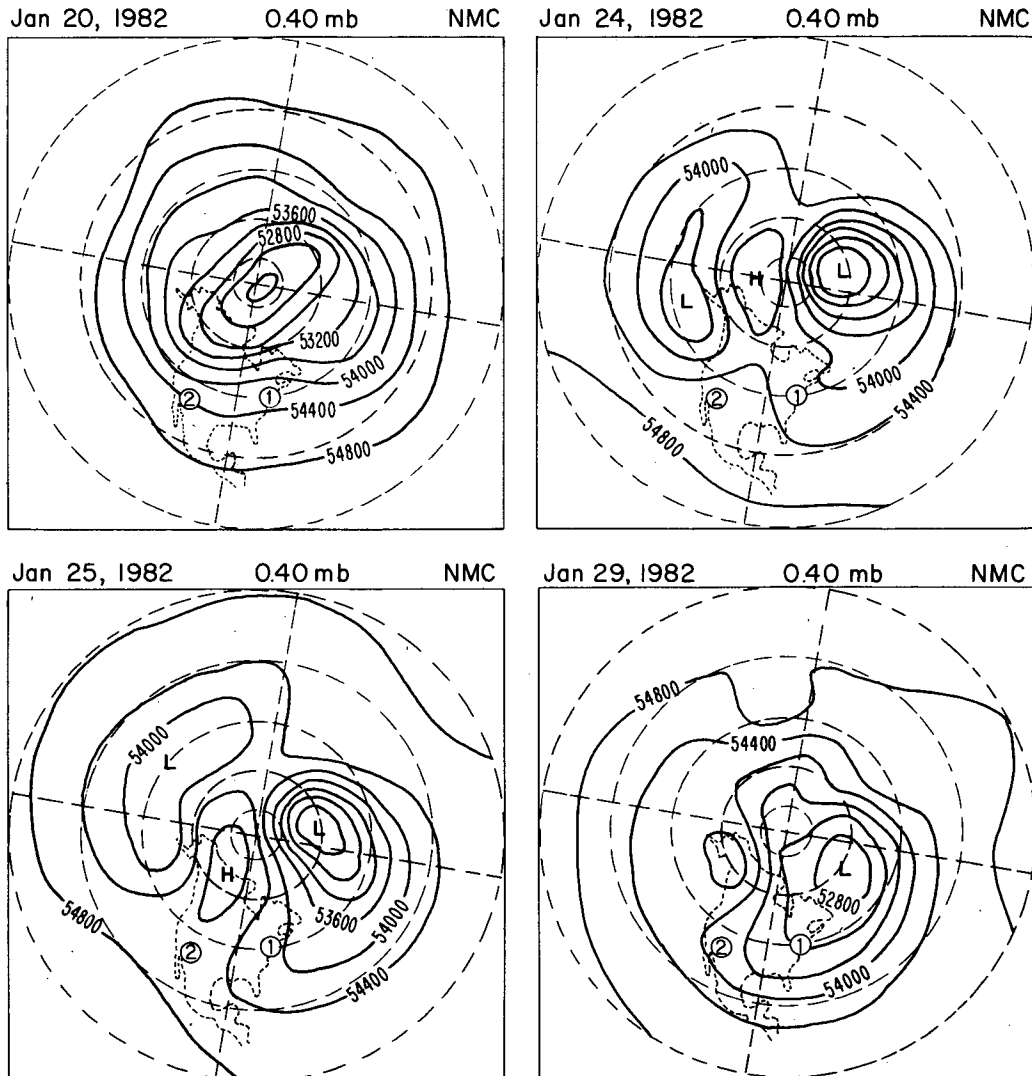


FIG. 9. Geopotential height maps (m) at 0.4 mb (about 55 km) for 20, 24, 25 and 28 January 1982. Large-scale wave activity is clearly present after the 24th.

yses. The 1.0 mb (50 km) and 2.0 mb (45 km) level maps were quite similar to those shown here. Holmdel and Kitt Peak are denoted by points 1 and 2, respectively. Flow patterns can generally be assumed to be parallel to geopotential height lines for geostrophic conditions (see also Fig. 10). The map shown in the upper left corner for 20 January is typical of observed structure throughout January before about 22 January. During the first 22 days of the month, the polar low pressure region (the vortex) was centered near the pole. Assuming geostrophic flow, the airflow over Holmdel and Kitt Peak was largely zonal (East-West) during this period, so that the air parcels passing over these observing sites probably had chemical "character" typical of mid latitudes (e.g., characteristic midlatitude abundances of species like CO and odd nitrogen). On 24 January the polar vortex split and was displaced from the pole. On the 25th the low near 0° longitude began to shift westward, so that Holmdel was moving into the polar flow, but Kitt Peak was still well outside of the vortex. By the 29th, both Holmdel and Kitt Peak were inside the vortex. They were therefore receiving airflow from the north, and the parcels reaching both points were very likely to be parcels which resided near the pole only a few days earlier. Thus they may be expected to contain elevated levels of CO, as shown in Figs. 7 and 8.

A more quantitative study of the recent origin of the mesospheric air reaching the observing sites can be provided by a trajectory analysis. Using the observed NMC height fields, we have constructed isobaric parcel trajectories for 25 and 29 January. It is well known that isobaric trajectories can deviate substantially from actual ones, particularly in the troposphere (e.g., Danielsen, 1961), and during unstable conditions such as those depicted in Fig. 9. Austin and Tuck (1985) have presented detailed

comparisons of isobaric and (more realistic) isentropic and quasi-isentropic trajectories for a variety of stratospheric conditions. These authors make the important point that the time evolution of the altitude of a given parcel can vary substantially depending upon which method is used. This has important effects on photochemically active species whose loss rate depends on altitude. However, the horizontal positions of the parcels studied by those authors were found to be generally similar regardless of which trajectory analysis method was used.

In this study, we will use an isobaric trajectory analysis to study the recent history of parcels arriving at the indicated sites. The justification of the use of the isobaric method in this case is partly that the photochemical loss rate of CO is rather insensitive to height from about 50–70 km, because the OH densities do not change much with altitude in that region. Therefore, errors in derived altitudes as a result of inaccuracies in the trajectories are not very important for CO. Further, the chemical lifetime of CO is of the order of a week or more near 50–60 km, so that a polar air parcel exposed continuously to sunlight for a week would lose about 60% of its CO. Since the high-latitude CO mixing ratios near the stratopause are as much as 10–100 times those at midlatitudes (Fig. 4), this chemical loss of 60% or so will not be very important; indeed the most important uncertainty becomes the complete history over time scales of at least a month. We cannot hope to resolve this definitively even with the most detailed trajectory analysis. Further, because of this very large gradient in lower mesospheric CO, substantial fluctuations in lower mesospheric CO densities might even be observed for long periods after irreversible wave events. Thus CO would probably serve as a good tracer for the mixing and dispersion associated with such processes at mesospheric altitudes, as is ozone at strato-

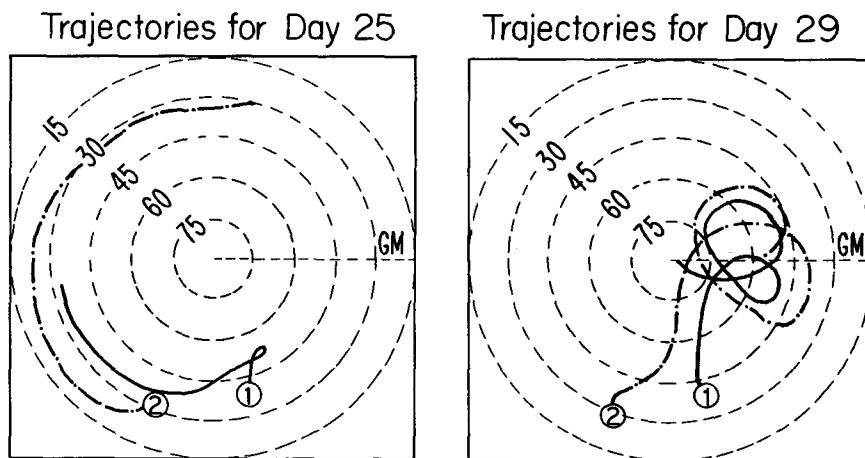


FIG. 10. Six-day backward isobaric parcel trajectories at 0.4 mb for Holmdel, N.J. (1) and Kitt Peak, Arizona (2) at 0800 CST 25 January 1982, and at 0300 CST 29 January 1982. Flow pattern changes from zonal to polar, as indicated by the maps in Fig. 9.

spheric levels (Leovy *et al.*, 1985). In view of these considerations, we only wish to determine whether a first order isobaric trajectory would yield parcel histories consistent with the observations presented in Figs. 7 and 8 and argued qualitatively based on the maps of Fig. 9; i.e., is it reasonable to suppose that Holmdel and Kitt Peak are receiving polar air on 28 and 29 January, respectively, and that Kitt Peak received "midlatitude" air on 24 and 25 January.

Austin and Tuck (1985) suggest that trajectory analyses are not generally reliable for time scales longer than about six days. Figure 10 presents 6-day back trajectory analyses for both points on 25 January at 0800 CST and for 29 January at 0300 CST. The trajectory for Holmdel on the 28th is very similar to that shown here early on the 29th. As indicated qualitatively based on the maps, airflow over Kitt Peak is largely zonal on the 25th, consistent with the relatively low CO abundances observed on that day. It is unfortunate that a CO measurement was not made on the 25th at Holmdel, for Fig. 10 suggests that typically small midlatitude CO abundances would have been obtained on that day in the mesosphere. In contrast, the trajectories for both Holmdel and Kitt Peak early on the 29th strongly suggest a polar origin for the air parcels, as do the CO observations themselves.

6. Summary

Coupled two-dimensional dynamical-chemical model calculations presented here indicate that the distribution of mesospheric and upper stratospheric CO exhibits considerable seasonal and latitudinal variations, primarily because of the competition between downward transport from the thermospheric production region and photochemical loss processes. In particular, larger CO abundances are predicted to be present at these altitudes in winter than in summer, especially in the polar night region, where the calculated latitudinal gradient in CO becomes very large. Similar seasonal variations are indicated on average for midlatitudes by a limited series of microwave observations.

The strong latitudinal gradient calculated near the polar night region suggests that mesospheric CO should be influenced substantially by large scale planetary waves. Two ground-based microwave observations in January 1982 are consistent with this suggestion.

A continuous midlatitude observing program for carbon monoxide could be expected to improve our knowledge of both the properties of this constituent and of middle atmospheric transport, particularly during the winter and spring seasons when planetary wave activity should often be present. Because water vapor provides the primary source of OH at mesospheric heights (which is the species responsible for

photochemical destruction of CO), and because water vapor is also sensitive to mesospheric transport processes, it would be very useful to couple observations of microwave observations of CO with water vapor observations. Even a limited series of observations of CO and water vapor at high latitudes as a function of season could also do much to clarify our understanding of mesospheric dynamics.

Acknowledgments. S. Solomon is partly supported by a grant from the Defense Nuclear Agency. We are grateful to J. M. Zawodny for use of his trajectory analysis program and to M. Gelman of NMC for kindly sending needed meteorological data tapes. We thank J. Kasting and two anonymous reviewers for their very helpful comments.

REFERENCES

- Allen, M., Y. L. Yung and J. W. Waters, 1981: Vertical transport and photochemistry in the terrestrial mesosphere and lower thermosphere. *J. Geophys. Res.*, **86**, 3617-3627.
- , J. I. Lunine and Y. L. Yung, 1984: The vertical distribution of ozone in the mesosphere and lower thermosphere. *J. Geophys. Res.*, **89**, 4841-4872.
- Austin, J., and A. F. Tuck, 1985: The calculation of stratospheric air parcel trajectories using satellite data. *Quart. J. Roy. Meteor. Soc.*, (submitted).
- Berggren, R., and K. Labitzke, 1968: The distribution of ozone on pressure surfaces. *Tellus*, **20**, 88-97.
- Bevilacqua, R. M., P. R. Schwartz and A. A. Stark, 1985: The variability of CO in the terrestrial mesosphere as determined from ground-based observations of the $J = 0 \leftarrow 1$ emission line. *J. Geophys. Res.*, (to be published).
- Clancy, R. T., D. O. Muhleman and G. L. Berge, 1982: Microwave spectra of terrestrial mesospheric CO. *J. Geophys. Res.*, **87**, 5009-5014.
- , — and M. Allen, 1984: Seasonal variability of CO in the terrestrial mesosphere. *J. Geophys. Res.*, **89**, 9673-9676.
- Danielsen, E. F., 1961: Trajectories: Isobaric, isentropic and actual. *J. Meteor.*, **18**, 479-486.
- Fabian, P., and Collaborators, 1981: The vertical distribution of stable trace gases at mid-latitudes. *J. Geophys. Res.*, **86**, 5179-5184.
- Farmer, C. B., O. F. Raper, B. D. Robbins, R. A. Toth and C. Muller, 1980: Simultaneous spectroscopic measurements of stratospheric species: O₃, CH₄, CO, CO₂, N₂O, H₂O, HCl and HF at northern and southern mid latitudes. *J. Geophys. Res.*, **85**, 1621-1632.
- Garcia, R. R., and S. Solomon, 1983: A numerical model of the zonally averaged dynamical and chemical structure of the middle atmosphere. *J. Geophys. Res.*, **88**, 1379-1400.
- , and —, 1985: Effect of breaking gravity waves on the dynamical and chemical structure of the mesosphere and lower thermosphere. *J. Geophys. Res.*, **10**, 3850-3868.
- Goldsmith, P. F., M. M. Litvak, R. L. Plambeck and D. R. Williams, 1979: Carbon monoxide mixing ratio in the mesosphere derived from ground-based microwave measurements. *J. Geophys. Res.*, **84**, 416-418.
- Hays, P. B., and J. J. Olivero, 1970: Carbon dioxide and monoxide above the troposphere. *Planet. Space Sci.*, **18**, 1729-1733.
- Hedin, A. E., C. A. Reber, G. P. Newton, N. W. Spencer, H. C. Brinton, H. G. Mayr and W. E. Potter, 1977: A global thermospheric model based on mass spectrometer and incoherent scatter data, MSIS 2, composition. *J. Geophys. Res.*, **82**, 2148-2156.

- Holton, J. R., 1982: The role of gravity wave induced drag and diffusion in the momentum budget of the mesosphere. *J. Atmos. Sci.*, **39**, 791-799.
- , 1983: The influence of gravity wave breaking on the general circulation of the middle atmosphere. *J. Atmos. Sci.*, **40**, 2497-2507.
- Kasting, J. F., and R. G. Roble, 1981: A zonally averaged chemical-dynamical model of the lower thermosphere. *J. Geophys. Res.*, **86**, 9641-9653.
- Kawahira, K., 1982: An observational study of the D-region winter anomaly and sudden stratospheric warmings. *J. Atmos. Terr. Phys.*, **44**, 947-955.
- Kunzi, K. F., and E. R. Carlson, 1982: Atmospheric CO volume mixing ratio profiles determined from ground-based measurements of the $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ emission lines. *J. Geophys. Res.*, **87**, 7235-7241.
- Leovy, C. B., C. R. Sun, E. E. Remsberg, J. M. Russell, L. L. Gordley, J. C. Gille and L. V. Lyjak, 1985: Transport of ozone in the middle stratosphere: Evidence for planetary wave breaking. *J. Atmos. Sci.*, (submitted).
- Lindzen, R. S., 1981: Turbulence and stress owing to gravity wave and tidal breakdown. *J. Geophys. Res.*, **86**, 9707-9714.
- Louisnard, N., and C. Lado-Bordowsky, 1983: Spectroscopic measurements of carbon monoxide in the stratosphere. *J. Geophys. Res.*, **88**, 3789-3797.
- Russell, J. M., S. Solomon, L. L. Gordley, E. E. Remsberg and L. B. Callis, 1984: The variability of stratospheric and mesospheric NO₂ in the polar winter night observed by LIMS. *J. Geophys. Res.*, **89**, 7267-7275.
- Schmidt, M., 1982: The influence of large scale advection on the vertical distribution of stratospheric source gases in 44° and 41° North. *J. Geophys. Res.*, **87**, 11239-11246.
- Solomon, S., and R. R. Garcia, 1983a: On the distribution of nitrogen dioxide in the high latitude stratosphere. *J. Geophys. Res.*, **88**, 5229-5239.
- , and —, 1983b: Simulation of NO_x partitioning along isobaric parcel trajectories. *J. Geophys. Res.*, **88**, 5497-5501.
- , D. W. Rusch, R. J. Thomas and R. S. Eckman, 1983: Comparison of mesospheric ozone abundances measured by the solar mesosphere explorer and model calculations. *Geophys. Res. Lett.*, **10**, 249-252.
- Trincks, H., and K. H. Fricke, 1978: Carbon dioxide concentrations in the lower thermosphere. *J. Geophys. Res.*, **83**, 3883-3886.
- Waters, J. W., W. J. Wilson and F. I. Shimabukuro, 1976: Microwave measurement of carbon monoxide. *Science*, **191**, 1174-1175.
- Wattenbach, R., E. J. Durwen, H. P. Roser and G. V. Schultz, 1984: Observation of the CO ($J = 6 \leftarrow 5$) rotational transition in the Earth's upper atmosphere. *J. Geophys. Res.*, **89**, 7285-7290.
- Weinstock, J., 1982: Nonlinear theory of gravity waves: Momentum deposition, generalized Rayleigh friction and diffusion. *J. Atmos. Sci.*, **39**, 1698-1710.
- Wofsy, S. C., J. C. McConnell and M. B. McElroy, 1972: Atmospheric CH₄, CO and CO₂. *J. Geophys. Res.*, **77**, 4477-4493.
- Zander, R., H. Leclercq and L. D. Kaplan, 1981: Concentration of carbon monoxide in the upper stratosphere. *Geophys. Res. Lett.*, **8**, 365-368.