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Possible Variations in Atmospheric Ozone
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Abstract

Changes in ozone, temperature, and other minor constituents resulting from eleven year variations in the solar flux between 180 and 340 nm are presented. Results were computed using a one-dimensional time dependent model that allows for all major feedbacks and time delays which may result from changing photolysis rates in the $O_3 - NO_x - HO_x - ClO_x$ system.

Since the 1950's the chlorine content of the stratosphere has been increasing. The effect of this increase on ozone variability during the last two solar cycles is analyzed. Expected variations in O_3 and temperature resulting from changes in the uv flux are compared to available measurements.

1. INTRODUCTION

The suggestion of a relationship between ozone and the solar cycle dates back to at least 1910 (Humphreys, 1910), and various researchers have found correlations of sunspot number with total ozone (Willet, 1962; Paetzold, et al., 1972; Christie, 1973; Angeli and Korshover, 1976). Researchers studying total ozone fluctuations for the period from 1958 to the present have in general found less evidence to support an ozone-solar correlation (Angeli and Korshover, 1978a, London and Oltmans, 1977), but the period over which ozone was studied may not have been long enough to properly establish a long term cycle. Several plausible mechanisms linking the hypothesized ozone variations with the solar cycle have been suggested. Ruderman and Chamberlain (1975) first proposed that solar modulation of the source of nitric oxide produced by galactic cosmic rays might explain the ozone record, since the cosmic ray source of NO is approximately 30% smaller at solar maximum than at solar minimum. A subsequent study by Crutzen (1975) failed to support this mechanism (see also Ruderman, et al., 1976). Zerefos and Crutzen (1975) suggested that solar proton events may also provide a link between ozone variations and the solar cycle, but the study was not conclusive. Since solar proton events are localized and of short duration (Heath, et al., 1977), it is not clear how they may affect global ozone concentrations or even mid latitude ozone concentrations.

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Variations in the solar uv flux provide a third mechanism of potentially much greater significance for ozone variability in a global sense. The case for solar uv variability is, as yet, not completely established. We have only a few sets of measurements which suggest there may be a significant variation in the solar flux between 180 and 340 nm from solar maximum to solar minimum (Heath and Thelakakara, 1977). In view of the possible importance of the proposed variability on ozone, we shall attempt in this paper to estimate the effects this variability would have had on the ozone record to date. We are particularly concerned with the ozone record near 40 km where both the proposed variability, and chlorine increases due to past fluorocarbon release should have had their greatest effects. The effect of long term solar uv variability on ozone and temperature was first studied by Callis and Nealy (1975). Their model treats the atmosphere in steady state and does not include chlorine chemistry. Our time dependent model includes a full set of chlorine chemistry reactions and can be operated in a mode which calculates temperature self-consistently. As we shall see, our calculated ozone and temperature response differs significantly from that calculated by Callis and Nealy.

The radiative transfer model for the temperature calculation used in this study is described in Luther, et al. (1977). The full set of chemical reactions are given in Chang, et al. (1977). The rate constants and absorption cross sections were those recommended in NASA (1977), except that the absorption cross section for H_2O_2 has been updated to reflect new measurements (Molina, et al., 1977). Calculated species include O_3 , $O(^3P)$,

Explorer 55 in November, 1975. The measured variability below 255 nm depends on only three photometric observations taken near 180 nm in 1965, 1969, and 1970. The flux variation measured with these instruments at longer wavelengths overlaps the region measured by the double monochromators. The photometers show about a 15% larger variation than the double monochromators. We have chosen to accept the double monochromator measurements at these wavelengths as being the more nearly correct, since they were made with identical instruments. Since there are no monochromator data below 255 nm, we applied a correction of about 15% to the average of the photometric measured flux variation near 180 nm. The curve in Figure 1 marked "B" thus represents what we consider the largest probable variation. The curve marked "A" gives more weight to the measured variation near 255 nm and is also consistent with balloon measurements which indicate that the flux variation between 200 and 220 nm was not larger than 10% from 1972 to 1976 (Simon, 1976). The curve marked "C" represents an intermediate case and is used for most of the calculations shown in the following sections.

The calculated ozone response in our model depends fairly critically on the relative flux variation above and below 255 nm. Photons with wavelengths less than 255 nm can add to the total atmospheric reservoir of odd oxygen according to the reaction

Photons in the entire range of wavelengths considered here are able to

III. EFFECTS OF TEMPERATURE FEEDBACK

The primary source of heating for the upper stratosphere is the absorption of solar photons in the Hartley (200-300 nm) and Huggins (> 300) bands of ozone. We use the method of Lindzen and Will (1973) for the treatment of the heating rate from these bands. The heating rate is computed by using the average solar energy flux and ozone absorption cross section in the wavelengths between 237.5 and 275 nm and between 275 and 340 nm. Very little heating results by ozone absorption of the solar energy flux outside this wavelength interval because the solar flux and ozone cross sections are small below 237.5 nm and because the ozone absorption cross section is small above 340.0 nm.

Figure 3 shows the calculated change in temperature and ozone when the solar flux is perturbed from minimum conditions by the amount shown by curve B in Figure 1. (The average flux used in the Lindzen and Will parameterization was perturbed by the average change in each band.) Our calculations show a temperature increase of no more than about 13 degrees near 45 km. The Lindzen and Will parameterization ignores flux perturbations below 237.5 nm, but since these wavelengths contribute no more than about 10% of the ambient heating rate at 45 km our calculated temperature change should be correct to within 10%. The left panel of Figure 3 shows the effects of including temperature feedback on calculated O_3 concentrations. With temperature feedback the peak response of ozone is reduced due to the temperature dependence of the reactions,

IV. COMPARISON TO OZONE AND TEMPERATURE RECORD

The calculations described thus far were performed using a steady state version of our model. It is of interest to examine the atmospheric response to a time varying solar flux, and to allow for emissions of CFCl_3 and CF_2Cl_2 in order to compare our calculated response to available compilations of the ozone and temperature record. In the calculations which follow we used the emission rates for release of CFCl_3 and CF_2Cl_2 given by McCarthy, et al. (1977) and the solar flux variation shown in Figure 1 curve C, to calculate a time history for ozone over the past 47 years. The flux variation followed a sinusoidal eleven year cycle with maximum and minimum corresponding to the years 1936, 1947, 1958, 1969 and 1942, 1953, 1964, 1975, respectively. The calculation included all of the feedback mechanisms discussed above and simulated average conditions for 30° latitude.

The calculated percentage deviation of total ozone from the mean is shown in Figure 4 for the period 1957 to 1978 along with the total ozone record for 11 stations in North America and 14 stations in Europe as presented by Angell and Korshover (1978a). Angell and Korshover have smoothed the ozone data from "Ozone Data for the World" by averaging over each season and then applying a 1-2-1 weighting twice to the seasonal values. They have plotted the resulting deviation of total ozone for each season from the mean seasonal value over the period. Our plotted curves have not been smoothed and we estimate that a similar smoothing of our calculated ozone would change the peak variation by about .4%. The

Thus, the apparant discrepancy between theory and observation after 1972 does not necessarily invalidate the background ozone cycle caused by solar uv flux variations and chlorine changes and its true significance can only be determined with data from the next solar cycle.

The calculated ozone deviation for the levels 32-46 km is compared to the Unkehr measurements presented by Angell and Korshover (1975) for this same period in Figure 5. Again, the two regions with the largest number of stations were chosen for comparison. Unkehr measurements are much more difficult to make than measurements for total ozone. The observations should accordingly be viewed with caution, (see discussion in Dütsch and Ling, 1973). Angell and Korshover estimate there was an 8% increase in north temperate latitudes between 1962 and 1973, and a slight decrease after 1974. They believe the observed decrease may be fictitious, however, due to the presence of aerosols in the stratosphere after the eruption of Fuego in 1974. We calculate a 5.8% increase for this layer from the solar minimum in 1964 to the solar maximum in 1969, and an 8.2% decrease from 1969 to 1975. This may be compared to an increase of 5.8% from solar minimum to solar maximum and a decrease of 6.4% from solar maximum to solar minimum for the pre-CFM atmosphere. As shown in Figure 5, our calculated decrease begins earlier and is larger than the observed decrease. We believe this difference between the model and observation may be indicative of the presence of other physical processes controlling the local ozone concentrations which are not included in this model. (see London et al, 1977.)

in temperature from 1969 to 1975 of 8.5° K, 6.5° K, and 3.1° K for layers 46-55 km, 36-45 km and 26-35, respectively, in reasonable agreement with Angell and Korshover's estimate of about a 5° K decrease for the middle and upper stratosphere after 1970.

V. SUMMARY

The ozone response to a variety of solar conditions was examined and shown to depend on the relative ratio of uv variability above and below about 255 nm. We find that the increased temperature expected in the stratosphere due to increased heating by ozone in the Hartley and Huggins bands significantly reduces the total ozone variation above 30 km.

We used what we consider to be the most reasonable variation in the solar uv flux consistent with available data to calculate a time history for ozone and temperature dating from before the fluorocarbon releases starting in 1950, up until the present time. We conclude that the ozone record as published by Angell and Korshover (1978 a,c) is apparently consistent with solar flux variations of the magnitude used, although more data are required to fully establish this relationship. Some of the less satisfactory results above 37 km requires further analysis and more quantitatively reliable data. We calculate an ozone decrease for the 32-46 km layer from solar average conditions in 1966 to average conditions in 1977 of 3.6%, consistent with current calculations for the decrease in ozone concentration at these levels due to the release of CfO_x from fluorocarbons using average solar conditions for the full period. In our view this decrease

REFERENCES

1. Angell, J. K. and J. Korshover, "Global Analysis of Recent Total Ozone Fluctuations," *Mon. Wea. Rev.* 104, 63-75, 1976.
2. Angell, J. K., and J. Korshover, "Global Ozone Variations: An Update into 1976," *Mon. Wea. Rev.* 106, 725-737, 1978a.
3. Angell, J. K. and J. Korshover, "Recent Rocketsonde-Derived Temperature Variations in the Western Hemisphere," *J. Atmo. Sci.*, in press, 1978b.
4. Angell, J. K. and J. Korshover, "Comparison of Ozone Variations Derived from Ozonesondes, and Umkehr and Total Ozone Measurements, for Period 1967-1976," submitted to *Mon. Wea. Rev.*, 1978c.
5. Callis, L. B., Jr. and J. E. Nealy, "Solar UV Variability and its Effect on Stratospheric Thermal Structure and Trace Constituents," *Geoph. Res. Lett.* 5, 249-252, 1978.
6. Chang, J. S., W. A. Dwyer, and D. J. Whiebbles, "The Atmospheric Nuclear Tests of the 50's and 60's: A significant Test of Ozone Depletion Theories," submitted to *J. Geophys. Res.* (1977), Lawrence Livermore Laboratory Report UCL-80246.
7. Crutzen, P. J., "A Two Dimensional Photochemical Model of the Atmosphere below 55 km: Estimates of Natural and Man-Caused Ozone Perturbation Due to NO_x ," in *Proceedings of the Fourth Conference on the Climatic Impact Assessment Program*, ed. by T. M. Hard and A. J. Broderik, 264-279, 1975.

16. McCarthy, R. L. F. A. Bower and J. P. Jesson, "The Fluorocarbon Ozone Theory - I, Production and release - World production and release of CCl_3F and CCl_2F_2 (Fluorocarbons 11 and 12) through 1975," Atmos. Env. 11, 491-497, 1977.
17. Molina, L., S. D. Shinke, and M. Molina, "Ultraviolet Absorption Spectrum of Hydrogen Peroxide Vapor," Geophys. Res. Lett. 4, 580-583, 1977.
18. NASA Reference Publication 1010, "Chlorofluoromethanes and the Stratosphere," ed. by R. D. Hudson, August 1977.
19. Paetzold, H. K., F. Piscalar, and H. Zschornner, "Secular Variation of the Stratospheric Ozone Layer Over Middle Europe During the Solar Cycles From 1951 to 1972," Nature Physical Sci. 240, 106-107, 1972.
20. Ruderman, M. A. and J. W. Chamberlain, "Origin of the Sunspot Modulation of Ozone: Its Implications for Stratospheric NO Injection," P.S.S. 23, 247-268, 1975.
21. Ruderman, M. A., H. M. Foley and J. W. Chamberlain, "Eleven Year Variation in Polar Ozone and Stratospheric-ion Chemistry," Science 192, 555-557, 1976.
22. Simon, P., private communication, 1978.
23. Willet, H. C., "The Relationship of Total Atmospheric Ozone to the Sunspot Cycle," J. Geoph. Res. 62, 661-670, 1957.
24. Zerefos, C. S. and P. J. Crutzen, "Stratospheric Thickness Variations Over the Northern Hemisphere and Their Possible Relation to Solar Activity," J. Geoph. Res. 80, 5041-5043, 1975.

Fig. 4 Comparison of calculated ozone deviations to the analysis of the observed ozone variations for Europe and North America by Angell and Korshover (1978a).

Fig. 5 Comparison of calculated layer-mean ozone variations to the analysis of the Umkehr measured variations for Europe and Japan by Angell and Korshover (1978a).

Fig. 7
Comparison of calculated layer-mean temperature changes to the analysis of rocketsonde measured temperature changes for the Western hemisphere north subtropics by Angell and Korshover (1978b).

$\text{O}(^1\text{D})$, NO , NO_2 , H_2O , HNO_3 , N , OH , HO_2 , H_2O_2 , H , HCl , ClONO_2 , ClO , CH_4 , OCCO , CH_3Cl , ClNO_2 , HCl , NO_3 , N_2O_5 , CFCl_3 , CF_2Cl_2 , and CCl_4 . Since H_2O is not calculated in our model we expect that our total HO_x at solar maximum and minimum is somewhat over- and under-estimated respectively. The effects should not seriously alter our main results, since the calculated local variation for HO_x in our model is at most 20% and should be even less in a fully coupled calculation.

The following section reviews the measured variation in solar flux and describes our model's response to a number of prescribed solar conditions. Section 3 examines the stratospheric temperature and ozone response to increased heating from solar photon absorption by ozone. Finally, Section 4 presents a time history for ozone for the last few solar cycles in light of the fluorocarbon releases since 1950. The calculation is compared to the analysis of the ozone and temperature record by Angell and Korshover (1978a,b,c).

II. VARIABILITY IN SOLAR FLUX AND ITS EFFECT ON OZONE

Figure 1 shows the ratio of the uv flux at solar minimum to the uv flux at solar maximum as a function of wavelength (Heath and Thekaekara, 1977; NASA, 1977). The measurements shown by Δ and $\square$ taken during 1966, 1969, and 1970 represent broad band photometric observations from a rocket flight in August 1966 and from satellites Nimbus 3 and 4 launched in April 1969 and April 1970. Those shown by $\bullet$ were obtained using identical double monochromators flown on Nimbus 4 in April 1970 and

shift the balance between atomic oxygen and ozone according to

but by far the most efficient are those with wavelengths longer than 255 nm. The point is illustrated in Figure 1. The curves marked A1 and B1 show the calculated ozone increase when the solar flux is only varied below 255 nm by the amounts indicated in curves A and B of Figure 1, respectively. A larger flux at these wavelengths produces more ozone. The curves marked A2 and B2 show the ozone response to flux variations above 255 nm. (The portion of curves A and B of Figure 1 above 255 nm.) A large flux at these longer wavelengths shifts the balance of odd oxygen in favor of atomic oxygen so that ozone is decreased. The net result for flux variations over the entire wavelength range is to increase ozone over most altitudes, as shown by the curves marked B1 + B2 and A1 + A2, and for these models the calculated ozone response is approximately the sum of the variations calculated separately. These considerations demonstrate the need for a precise determination of the relative flux variations in these wavelength bands. Since the net ozone response depends on the superposition of two effects of opposite sign, it is clear that the altitude of the maximum response depends on this relative flux variation.

and

and the altitude above which ozone decreases is lowered from 50 km to 41 km.

Our calculated temperature increase at solar maximum is significantly smaller than that calculated by Callis and Nealy (1978). This remains true even for flux perturbations as large as their case 1. We believe their primary thermal response is due to heating by wavelengths below 210 nm since an examination of their calculated temperature response for case 3 (symbol Δ of their paper) shows a significant increase in temperature (20°K near 45 km) even though the solar flux is not perturbed above 210 nm and their calculated ozone concentration at that altitude is decreased. [Compare Figures 2 and 5 of their paper.] A detailed calculation of the ambient heating rate from O_3 absorption at 45 km shows that the heating by wavelengths below 210 nm is only .07% of that for the entire interval from 175 to 350 nm, so that flux perturbations in this region should not greatly affect stratospheric temperature. Figure 3 shows that temperature feedback is important for calculating the change in ozone above about 40 km, but the calculated temperature change is not nearly so sensitive to flux variations as that calculated by Callis and Nealy.

record from North America and Europe was chosen for comparison because these areas have the largest number of stations (other than Russia) and are considered to be the most accurate and reliable. The error bars for the observations are two standard deviations of the mean.

Clearly our calculated ozone variation for this period is at least not inconsistent with this record. The observed ozone increase during the late 1960's appears to be reasonably consistent with our assumed change in solar flux. We calculate an increase in total O_3 from the solar minimum in 1964 to the solar maximum in 1969 of 5.1%. For a similar variation in the solar flux before the introduction of CFM's, we obtain an increase of 5.5%. This may be compared to the observed 5% increase in total O_3 for the Northern Hemisphere from the early 60's to 1970 and a 2% increase for total O_3 for the Southern Hemisphere from 1960 to 1968, according to Angell and Korshover (1978a). We calculate a decrease from 1970 to 1972 of 2.5% which agrees well with the 1-2% decrease in the Northern Hemisphere estimated by Angell and Korshover. The decrease in observed ozone appears to have leveled off after 1972, but we calculate a further decrease through 1975. Our calculated decrease is primarily due to the solar flux variation since the 1975 minimum is only 1.3% smaller than that calculated without the influence of increasing chlorofluoromethanes.

Clearly there are local disagreements between theory and observation throughout the period shown. Evidently some processes which control ozone on shorter time scales (3-4 years) are not accounted for by the model, and the solar uv connection and the effects of increasing chlorofluoromethane will only be revealed by looking at the general long-term picture.

As Figure 6 shows, our calculated decrease after 1969 is consistent with the ground-based data for lower altitudes. The top panel of Figure 6 shows again the Unkehr data for 32-46 km for Europe. The lower 2 panels compare our calculated ozone variations to the ozonesonde record for the layers 24-32 km and 16-24 km as analyzed by Angell and Korshover (1978c). Our calculations agree fairly well with the record for Europe for these lower layers, though Angell and Korshover's analysis shows a slight increase for this period over Japan. Angell and Korshover estimate a 4% decrease in each of the 2 lower layers as an average for the north temperate latitudes as a whole. Our calculated ozone decreased from solar maximum in 1969 to solar minimum in 1975 by 7.8% and 4.8% for the 24-32 km and 16-24 km layer, respectively.

For the layers shown in Figure 6, we would calculate decreases of 6.4%, 6.9% and 4.6%, respectively, for the same solar flux variations from the maximum in 1969 to the minimum in 1975 without the influence of increasing chlorofluoromethanes. Changes in ozone resulting from the release of CFM's are apparently small compared to changes resulting from our assumed solar flux variation. Therefore any effort to detect a trend in ozone due to the CFM releases must take into account the effects of solar uv variability.

Finally Figure 7 compares our calculated temperature variations for the layers 26-35 km, 36-45 km and 46-55 km to the temperature data for the period 1965-1976 as analyzed by Angell and Korshover (1978b). It is notable that temperature maxima and minima appear to be nearly in phase with the solar cycle variation except for the highest layer before 1968. (Though the equatorial stations show a decrease through the entire time interval, see Angell and Korshover, 1978b). We calculate a decrease

would be difficult if not impossible to detect from the given ozone record if solar flux variations of the magnitude considered here were present during this period.

In so far as the present calculations should be considered tentative, a long time series of measurements of the ozone concentrations near 35 km in conjunction with measurements of the uv flux as a function of wavelength is needed to further establish the validity of these effects.

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8. Dutsch, H. U. and Ch. Ch. Ling, "Fourteen-Year Series of Vertical Ozone Distribution Over Arosa, Switzerland, from Umkehr Measurements," PAGEOPH, 106-108, 1139-1150, 1973.
9. Heath, D. T. and M. P. Thekaekara, "The Solar Spectrum between 1200 and 3000 Å," in The Solar Output and its Variation, ed. by O. R. White, Colorado Assoc. Univ. Press, Boulder, Colorado, 193-212, 1977.
10. Hill, W. J. and P. N. Sheldar, "Statistical Modeling of Total Ozone Measurements with an Example using data from Arosa, Switzerland," Geophys. Res. Lett. 2, 541-544, 1975.
11. Humphreys, W. J., "Solar Disturbances and Terrestrial Temperatures," Astrophys. J. 32 (2), 97-111, 1910.
12. Lindzen, R. S. and D. I. Will, "An Analytic Formula for Heating Due to Ozone Absorption," J. Stmp. Si. 30, 513-515, 1973.
13. London, J., J. E. Frederick and G. P. Anderson, "Satellite Observations of the Global Distribution of Stratospheric Ozone," J. Geophys. 82, 2243-2556, 1977.
14. London, J. and S. J. Oltmans, "The Global Distribution of Total Ozone Variations During the Fifteen Year Period 1957-72," paper presented at IAGA/IAMAP Joint Assembly, Seattle, Washington, August 22-September 3, 1977.
15. Luther, F. M., D. J. Wuebbles and J. S. Chang, "Temperature Feedback in a Stratospheric Model," J. Geoph. Res. 82, 4935-4942, 1977.

FIGURE CAPTIONS

Fig. 1 Ratio of solar flux. Data points are from Heath & Thekaekara (1977) and NASA (1977)

Fig. 2 Percent change in O_3 from solar minimum to solar ((max - min)/min $\times$ 100). Solar flux was varied by the amounts shown by curves A and B of Fig. 1. For curves A1 and B1 only the portion below 255 nm was varied. For A2 and B2 the portion above 255 nm was varied.

Fig. 3 Percent change in O_3 ((max - min)/min $\times$ 100) and temperature change from minimum to maximum. The change in slope of the temperature variation near 40 km is due to the simple band absorption model employed (see text) and the depletion of the uv flux for wavelengths less than 275 nm below 40 km.

Fig. 6

Comparison of calculated layer-mean ozone variations to the analysis of the Umkehr and ozoneonde measured variations for Europe by Angell and Korshover (1978C).