✓
MASTER

PREPRINT UCRL- 82556

CONF-790858--2

Lawrence Livermore Laboratory

MAN'S EFFECT ON STRATOSPHERIC OZONE

Hugh W. Ellsaesser

August 1979

This paper was prepared for presentation at the 4th International Symposium on Environmental Biogeochemistry, August 26-31, 1979, Canberra, Australia.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MASTER

MAN'S EFFECT ON STRATOSPHERIC OZONE

Hugh W. Ellsaesser

Lawrence Livermore Laboratory, University of California,
P. O. Box 808, Livermore, CA 94550

ABSTRACT

Since McDonald, at the beginning of this decade, first proposed that water vapor from SST exhaust would lead to increases in skin cancer, about a dozen man-induced mechanisms have been suggested as threatening to modify our stratospheric ozone uv-shield. Possible thinning of the ozone layer has been attributed to one or more of the catalytic ozone destroyers, water vapor (HO_x), oxides of nitrogen (NO_x), chlorine (ClX) or bromine (BrX). The original catalyst, HO_x , rather quickly lost its role to NO_x . In an almost unique evolution, computed sensitivity of stratospheric ozone to NO_x progressively declined until a reversal of effect occurred. Models now compute a thickening of the ozone layer for any but high level or very massive injections of NO_x . Meanwhile, computed sensitivity to ClX has fluctuated widely and in 1978 models increased to the point where comparisons with observations were becoming an embarrassment. The potential role of BrX has also increased but awaits a credible source of stratospheric bromine to bring it center stage. More recently the atmospheric build-up of carbon dioxide, by cooling the stratosphere and increasing the chemical equilibrium level of ozone, has also been recognized as a potential modifier of the ozone layer.

INTRODUCTION

Less than a decade has passed since McDonald in November 1970 (Dotto and Schiff, 1978) suggested to the U.S. Congress that H_2O released in the stratosphere in

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

SST exhaust would, by destroying O_3 , lead to an increase in skin cancer. Since then the list of potential modifiers of our uv-screen has grown to include NO_x (Crutzen, 1970; Johnston, 1971), Cl (Hoshizaki et al., 1973; Stolarski and Cicerone, 1974), Br (Wofsy et al., 1975), bremsstrahlung x-rays from relativistic electron precipitation events (Thorne, 1976) and modifiers of stratospheric temperature (Blake and Lindzen, 1973; Boughner and Ramanathan, 1975). While cosmic ray produced negative ions (Ruderman et al., 1976) and stratospheric particles (Cadle et al., 1974) had been proposed as possible destroyers of O_3 , these threats now appear to have been eliminated (Fehsenfeld et al., 1976; Olszyna et al., 1979).

Through these agents man is now presumed capable of modifying his uv-screen by any of the following mechanisms:

1. Operation in the stratosphere or mesosphere of aircraft and rockets exhausting H_2O (Harrison, 1970), NO_x (Johnston, 1971) or Cl (Hoshizaki et al., 1973).
2. Detonation of nuclear devices such that their debris clouds can produce or carry NO_x into the stratosphere or mesosphere (Foley and Ruderman, 1973).
3. Stimulation of N_2O production by addition of fixed nitrogen to the biosphere whether through nitrogen fertilizer, animal wastes, combustion produced NO_x , expanded growth of legumes, infection of non-leguminous plants with nitrogen fixing bacteria or by green mulching (Crutzen, 1974).
4. Atmospheric release of stable Cl containing compounds such as chlorocarbons in general and chlorofluoromethanes in particular which can penetrate the stratosphere before decomposing (Molina and Rowland, 1974).
5. Atmospheric release of stable Br containing compounds such as the CH_3Br now used as a soil fumigant which can penetrate the stratosphere before decomposing (Wofsy et al., 1975).

6. Stimulation of N_2O production by denitrifying bacteria through increased acidity of precipitation from atmospheric release of oxides of sulfur and nitrogen (McElroy, 1976).
7. Operation of the space shuttle or similar programs with frequent ballistic return of orbiting vehicles to the atmosphere where they produce NO_x by compressional heating (Park, 1976).
8. Atmospheric release of stable IR absorbing gases such as CO_2 , chlorofluoromethanes, etc. which radiatively cool the stratosphere and thus shift the chemical equilibrium concentration of O_3 . In contrast to the other mechanisms cited, this one is expected to lead to a thickening rather than a thinning of our uv-screen.

THE NO_x CYCLE

When efforts were first made to estimate the effect of O_3 on the NO_x exhausted by SST's in the stratosphere, there were many unknown and poorly known factors; the natural level of NO_x , its sources and sinks, with what other species did it react, how rapidly was it transported vertically and how should diurnal variations be accounted for. By field observations, laboratory measurements, model experiments and plain trial and error, carried out principally under the auspices of CIAP (1974), COMESA (1975) and COVOS (1976), our knowledge of these factors slowly grew.

N_2O has been accepted as the major natural source of stratospheric NO_x . This stable gas is produced by soil and ocean bacteria and, being nearly uniformly mixed through the troposphere, ascends with the upwelling tropical Hadley flux into the stratosphere where over 90% of the net upward flux is photolyzed and the remainder reacts with $O(^1D)$. Somewhat more than half of these later reactions lead to the production of NO.

NO_x was also found to interact with the HO_x and ClX cycles isolating significant fractions of all three catalysts as inactive compounds such as HNO_3 , ClONO_2 , etc.; short circuiting the catalytic loops and even establishing new cycles which generated odd oxygen. In what Dotto and Schiff (1978) describe as a "peculiar anomaly . . . like tossing fifty heads in a row" each new piece of the puzzle resulted in a progressive decline in the calculated O_3 depletion. Figure 1 shows in chronological sequence the decrease in O_3 depletion for an NO_x injection estimated originally as equivalent to ~ 500 SST's operating at 17 and 20 km calculated for significant evolutionary stages of the Lawrence Livermore Laboratory (LLL) one-dimensional model.

It is interesting, that after announcement of the aerosol spray threat to O_3 by Molina and Rowland (1974) and model estimates of the amount of O_3 destruction by chlorofluoromethanes began to appear, it was found that the rate constant being used for the $\text{OH} + \text{HO}_2$ reaction was up to an order of magnitude slower than had been used during CIAP. This slower rate increased the O_3 destruction by ClX; but as can be seen in Fig. 1, sharply reduced O_3 destruction by NO_x . The eventual reversal of the SST effect from O_3 destruction to augmentation occurred when Howard and Evenson (1977) measured the $\text{NO} + \text{HO}_2$ reaction to be about 40 times faster than previously accepted. This faster rate enhanced NO_x interference with the HO_x catalytic cycle, the dominant destroyer of O_3 in the lower stratosphere. Note that the almost monotonic progression in the calculated response of O_3 to NO_x appears to have reversed within the past year. (While Fig. 1 is now widely referred to as the Broderick Diagram, it was originally prepared by my colleague, Donald J. Wuebbles, who also helped with this update.)

O_3 augmentation due to NO_x injection is restricted to levels below about 25 km; with sufficient NO_x the effect saturates and the NO_x catalytic destruction cycle becomes dominant. Another development has been the disappearance of the scaling

FIGURE 1 Percentage reductions in total O₃ computed for a standard NO_x injection (2 × 10⁸/cm² sec reduced to 1 × 10⁸/cm² sec after 1977 at 17 km (open circles); at 20 km (filled circles)) with different evolutionary stages of the LLL one-dimensional model. NASA 1010 and JPL chemistry refers to reaction rates in Hudson (1977) and NASA Panel for Data Evaluation (1979) respectively.

relationship between NO_x injection and O_3 destruction. This is because NO_x destruction of O_3 is now restricted to levels above about 25 km while below this level O_3 increases due to NO_x interference with the HO_x catalytic cycle. It is the net sum of these two different effects which determines the change in the O_3 -column or total O_3 .

Man can also put NO_x in the stratosphere by the detonation of nuclear bombs. Figure 2 shows calculations with 1976, 1977 and 1979 versions of the LLL model for the atmospheric nuclear tests of 1956 to 1962. Again, the abrupt decline in NO_x destruction of O_3 is apparent in the 1977 chemistry. The 1978 calculations (not shown) showed even larger increases in O_3 . The heights at which the nuclear clouds stabilized remains an additional uncertainty; the higher the cloud the greater the O_3 destruction, at least for yields up to about 25 MT. Note that the positive excursions in total O_3 are delayed several months after injection until the NO_x diffuses back to the lower stratosphere.

The fact that the chemical destruction of O_3 by NO_x is dependent on both the altitude and magnitude of the injection is shown graphically in Fig. 3. This shows time histories of total O_3 after NO_x injections corresponding to detonation of total nuclear yields of 100, 1000, 5000, and 10000 megatons but made up of individual bombs of 0.25, 1 or 4 MT each. These sizes correspond to injection altitudes (nuclear cloud heights) of 9.5-16.5, 12.5-21.5 and 17.5-28.5 km, respectively. Note that the smallest bombs always cause O_3 increases (although 10,000 MT is enough to cause a small initial reduction) and that the largest bombs always cause O_3 decreases — over 55% in the 10,000 MT case.

Supplying additional fixed nitrogen to the biosphere in fertilizer or by the growing of legumes, etc. was also suggested by Crutzen (1974) as a threat to the O_3 layer. Until recently it was believed that soil bacteria, in the absence of oxygen,

FIGURE 2 Time dependent changes in total O_3 due to NO_x from the 1956 to 1962 atmospheric nuclear tests computed by LLL one-dimensional model. 1979 results provided by William H. Duewer.

FIGURE 3 Time dependent calculations of change in total O_3 following nuclear detonations of 100, 1000, 5000 and 10,000 MT made up of individual bombs of 0.25, 1.0 or 4.0 MT each. From Luther (1978).

turned to nitrate as a source of oxygen and in the process of denitrification released a few percent of the nitrogen as N_2O . It was generally assumed that the natural N_2O production would be augmented in proportion to the amount of added fixed nitrogen. Since the fraction of the reduced nitrogen released as N_2O increases as pH is lowered, McElroy (1976) suggested that increased acidity of rain resulting from release of pollutant forms of sulfur and nitrogen would also cause increased production of N_2O and destruction of stratospheric O_3 . These were rather simplistic views. According to Johnston's (1977) summary of our understanding of N_2O production, lowered pH increases the fraction of reduced nitrogen released as N_2O but at the same time reduces the overall rate of denitrification. In fact, denitrification is inhibited completely below a pH of about 5.5. Since this is the normal pH for raindrops in equilibrium with the atmospheric concentration of CO_2 ; any additional lowering of the pH of rain would more likely prevent denitrification from occurring at all rather than increase the total output of N_2O . Also soil scientists have been complaining for years about agricultural practices causing loss of top soil, humus and fixed nitrogen from the soil. And to prevent anaerobic conditions, we drain and aerate the soil, particularly that soil to which we add fertilizer. I have argued earlier (Ellsaesser, 1977) that these practices appeared more likely to decrease, rather than increase, N_2O output, in view of our understanding at that time of the factors favoring N_2O production (Johnston, 1977). However, it now appears that most N_2O is produced under oxidizing conditions as a product of nitrification and that denitrification is a minor source at most (Elkins et al., 1978).

Presuming that atmospheric N_2O is increased by some mechanism, the resulting effect on the O_3 -layer can be calculated. Figure 4 shows changes in the O_3 layer computed by recent versions of the LLL one-dimensional model for large increases in the tropospheric concentration of N_2O . For small increases the layer was computed to

FIGURE 4. Computed steady state changes in total O_3 for multiples of present tropospheric concentration of N_2O . Solid line is for natural levels of stratospheric chlorine, dashed lines are for computed Cl levels due to CFM's. 1979 results provided by William H. Duerwer and Donald J. Wuebbles.

thicken in the 1978 model, particularly for high concentrations of Cl, but the effect become saturated at about 2 times the present N_2O level. However, William H. Duewer and Donald J. Wuebbles provided me with recent unpublished results which again show a monotonic decline in O_3 with increasing N_2O .

Operation of a continuing space shuttle program will involve releases of Cl and H_2O on the outbound flights. On return to the atmosphere, heating will produce an amount of NO_x equivalent to about 20% of the mass of the reentering vehicle, mostly between 50 and 70 km (Park, 1976 and private communication). Since the reentries are expected to occur at low latitude, most of the NO_x is expected to be photolyzed before it can reach the main O_3 layer. Accordingly, no currently foreseeable program is expected to have an appreciable effect on O_3 due to NO_x so produced.

Similarly, future hypersonic aircraft may have a significant effect on O_3 but no calculations are likely until better information becomes available on engine design, operating parameters and fleet size.

RELEASE OF IR ABSORBING GASES

According to current wisdom, man can also influence the depth of his uv-screen by increasing the atmospheric concentration of stable IR absorbing gases such as CO_2 . By increasing the optical depth of the atmosphere in the so called window region between 4 and 12 microns, such gases both warm the lower troposphere and cool the upper stratosphere, the latter temperature change being several times larger than the former as well as of opposite sign. Since the chemical equilibrium level of O_3 is negatively correlated with temperature (Blake and Lindzen, 1973), the stratospheric cooling will lead to an increase in O_3 concentration. Initial calculations by Boughner and Ramanathan (1975) of the effect of doubling the CO_2 concentration (or 600 ppm)

gave an increase of about 2%. Later calculations have given increases in O_3 concentration near 40 km of 16 to 27% and increases in total O_3 of 2.9% (Luther et al., 1977), 1.2-2.5% (Boughner, 1978), 4.7% (Groves et al., 1978) and 7% (Haigh and Pyle, 1974). The last result was with a two-dimension dynamical model which gave a latitudinal variation of < 2 to $> 14\%$, being greatest in high latitudes in winter. A recent unpublished recalculation by my colleague, Frederick M. Luther, gave a decrease of 5%.

THE CLX CYCLE

Interest was initially focused on the effect of Cl on stratospheric O_3 by HCl in the exhaust of the the space shuttle. CIAP funded Hoshizaki et al. (1973) to investigate the possible effect of the space shuttle on stratospheric O_3 . Meanwhile NASA had funded Stolarski and Cicerone (1974) to look into this problem. According to Dotto and Schiff (1978), original NASA estimates in January 1974 were that 60 space shuttles a year might cause a 1 or 2% O_3 depletion and as much as 5% in the launch corridor. Initial model calculations by several groups gave O_3 depletions of 0.15 to 0.2%. However, Howard and Evenson's (1977) 40-fold faster rate for the $NO + HO_2$ reaction (which had reversed the SST effect) also had the effect of doubling O_3 destruction by ClX. The most recent calculations for the effect of 60 shuttles a year is about 0.3% and the corridor effect has disappeared (R. C. Whitten, private communication).

As mentioned previously, at the time initial estimates of the O_3 destruction by CFM's (chlorofluoromethanes) began to appear, modelers began to prefer the 10-fold slower estimate for the $OH + HO_2$ reaction rate. This increased the effect of CFM's and decreased that of NO_x . This and other developments led to a growing appreciation

of the uncertainties in stratospheric model results, an appreciation which was all too lacking during CIAP.

The U. S. National Academy of Sciences study (NRC CISC, 1976; NRC PAC, 1976) put considerable effort into evaluating these uncertainties. They concluded that continued release of CFM's at the 1973 rate would take 100's of years to reach equilibrium, at which time the depth of the O_3 layer would have been reduced by 6 to 7.5%. The actual reduction was estimated, with 95% confidence, to lie between 2 and 20%. In addition to the quantifiable 8- to 10-fold uncertainty in this figure (kinetic rates 6-fold, transport 3-fold, alternate sinks 1.2-fold) several unquantifiable uncertainties were also listed. Issuance of the reports themselves were delayed several months by the uncertainties concerning the effects of $ClONO_2$.

The January 1977 NASA Workshop at Airlie House in Virginia (Hudson, 1977) estimated the uncertainties to be even greater. Nine groups with one-dimensional models and presumably using standardized input parameters, computed the steady state O_3 reduction from continued CFM release at the 1975 rate (essentially the same as the 1973 rate). Their results ranged from 5 to 9% reduction in O_3 . At a smaller follow-up NASA Workshop at Goddard Space Flight Center in July 1977, the Howard and Evenson (1977) 40-fold faster rate for $NO + HO_2$ was the major of several new bits of information considered. Recomputation of the steady state effect of CFM's at the 1975 rate by eight modeling groups gave O_3 reductions of 10.8 to 16.5%.

Since July 1977, the calculated sensitivity of O_3 to ClX has continued to vary inversely with that due to NO_x , as shown in Fig. 1. The calculated O_3 destruction by CFM's continued to rise until 1978 and has since declined. Interestingly, both the computed O_3 destruction and the estimates of the range of uncertainties are now essentially unchanged from the initial estimates of Molina and Rowland (1974).

My colleagues recently used the current LLL one-dimensional model to recalculate the CFM problem using the 1976 CFM release rates and the thermo-chemical reaction rates appropriate for 1976, 1977 and 1979. The results (made available by Joyce E. Penner) are listed in Table 1. Notice that the changes in chemistry result in different depths for the unperturbed O_3 column as well as different percentage reductions at steady state — which is only reached after about 300 years. The Howard and Evenson (1977) 40-fold faster rate for $NO + HO_2$ increased the unperturbed O_3 column to 341 m. atm-cm, which is at least 10% high for a global average. This computed O_3 column was 374 m. atm-cm if diurnal variations in solar flux were not included. Subsequent changes in chemistry have alleviated this problem somewhat. Current chemistry differs from JPL 79-27 (NASA Panel for Data Evaluation, 1979) mainly in forming $ClONO_2$ about 4 times faster. It computes that CFM's have already (1978) reduced the O_3 column by about 1.5% and will reduce it about 5% by the year 2000. Steady state changes in O_3 concentration for continued CFM release at the 1976 rates are shown in Fig. 5. At 40 km, the level of maximum change, the reductions with the current LLL chemistry are 4.5, 8.2, and 11.2% in 1980, 1990 and 2000.

Since Angell and Korshover's (1978) analysis of the Umkehr data suggests a 6% increase in northern hemisphere O_3 between 1957 and 1976 (8% 1962 to 1973) in the 32-46 km layer, the computed decline in O_3 at 40 km due to CFM's ($\sim 4\%$ in 1978) should give us cause for caution in interpreting current model results. If nothing else, such unexplained variations in the O_3 record will delay the point at which we can hope to confirm the effect of CFM's on O_3 observationally.

TABLE 1. Recent LLL one-dimensional model calculations of the effect of continued release of CFM's at the 1976 rate. Data supplied by J. E. Penner.

Model Chemistry	Unperturbed Total O ₃ c. 1950 (m atm cm)	Δ O ₃ (%)	
		In 1978	At Steady State
1976 NBS 866	278	-0.4	-4.2
1976 Old NO Photolysis	285	-0.6	-5.8
1976 Non-Diurnal	316	-0.0	-1.3
1977 NASA 1010	341	-1.2	-11.2
1977 Non-Diurnal	374	-0.1	-4.7
1979 JPL 79-27	328	-1.5	-14.0
1979 JPL less OH + ClO			-19.4
1979 Current LLL	327	-1.3	-14.2

FIGURE 5 Computed percentage change in O_3 concentration as a function of altitude for continued CFM release at the 1976 rate. NBS 866, NASA 1010 and JPL 79-27 refer to reaction rates in Hampson and Garvin (1975), Hudson (1977), and NASA Panel for Data Evaluation (1979) respectively. 1976 production rates for CF_2Cl_2 and $CFCl_3$ differ from their 1973 rates by -3.2% and +2.9% respectively. Computations performed by W. H. Duewer, J. E. Penner and D. J. Wuebbles.

THE BRX CYCLE

Aside from McElroy's "bromine bombs" (see Dotto and Schiff, 1978) Br has received little attention, principally because no one has suggested a credible Br source. Concentrations of Br detected in the stratosphere are about 20 pptv or 100-fold less than those of Cl. Thus, even though Br has been estimated to be about 10 times more effective than Cl in destroying O_3 , its effect remains small. However, CH_3Br is used as a soil fumigant and other compounds of Br are used as fire retardants and in gasoline. If these uses grow, or additional uses of Br are introduced, Br may become cause for concern.

LESSONS OF "THE OZONE WAR"

Since MacDonald's dramatization of the O_3 layer by tying it to skin cancer we have made rapid strides in increasing our knowledge of the stratosphere and of atmospheric chemistry in particular. However, there has been another result which may prove of greater consequence. "The Ozone War", as it was called by Dotto and Schiff (1978), has again revealed for the world that scientists are mere humans — with sometimes only a thin veneer of objectivity. I would like to believe that it has served a larger role by also bringing this point home to each of us scientists, thereby causing each of us to quietly resolve to ourselves to strive that much harder to retain our objectivity in the future.

During the course of "The Ozone War" I saw evidence which suggested to me that even the scientists involved were not above engaging in advocacy; emotionalizing by emphasizing and exaggerating the possibilities for deleterious consequences and by dismissing, downplaying and ignoring possible beneficial consequences of SST's and O_3

change; dismissing or disregarding observational data as inferior to the model results with which they conflicted; and, worst of all, attempting to discredit or label as biased those few individuals who sought to keep the record straight by presenting divergent views.

Eventually it became clear that even in the role of the U.S. Government in funding and directing the CIAP study there were built-in, albeit subconscious, decision-determining biases (Ellsaesser, 1978). As an example, several projects were funded to study and quantify the relation between total O_3 and skin cancer, a clearly deleterious consequence; but I am aware of no comparable effort to study and quantify the relation between total O_3 and rickets where the presumed effect of the SST might well have been beneficial. Skin cancer afflicts primarily light-skinned humans while cutaneous generation of vitamin D via uv exposure appears to be a problem which must be surmounted by almost all terrestrial vertebrates.

To claim that the rickets problem can be solved by food additives is less justifiable in my opinion than to claim that the skin cancer problem can be solved by education and letting each individual control his exposure to sunlight through life style, sunshades, clothing and skin creams. I think this view will become acceptable to most when they consider the populations at risk and the principle of freedom of choice. But this is certainly not the impression conveyed by most of the news and literature generated by this problem to date. If the taxpayer is going to be asked to support the work of scientists, I believe he has the right to expect and to demand greater objectivity than he has so far received during "The Ozone War".

ACKNOWLEDGMENTS

Advice, assistance and the sharing of unpublished results by my colleagues William H. Duewer, Frederick M. Luther, Joyce E. Penner and Donald J. Wuebbles are gratefully acknowledged. The author also profited from attendance and participation in the NASA Stratospheric Workshop at Harpers Ferry, WV, June 4-8, 1979. This work was performed in part under the auspices of the U. S. Department of Energy by the Lawrence Livermore Laboratory under contract No. W-7405-Eng-48, with support by the High Altitude Pollution Program of the Department of Transportation, Federal Aviation Administration and its delivery at ISEB4 was made possible by partial support by the Australian Academy of Science.

REFERENCES

- Angell, J. K. and Korshover, J., 1978. Global ozone variations: An update into 1976. *Monthly Weather Review*, 106:725-737.
- Blake, D. and Lindzen, R. S., 1973. Effect of photochemical models on calculated equilibria and cooling rates in the stratosphere. *Monthly Weather Review*. 101:783-802.
- Boughner, R. E., 1978. The effect of increased carbon dioxide concentrations on stratospheric ozone. *Journal of Geophysical Research*. 83:1326-1332.
- Boughner, R. E. and Ramanathan, V., 1975. Climatic consequences of increasing CO₂: A study of the feedback mechanisms between CO₂ concentrations and the atmospheric ozone, water vapor, and thermal structure balance. In: *Second Conference on Atmospheric Radiation*, October 29-31, 1975, Arlington, VA. American Meteorological Society, Boston, MA. pp. 153-157.
- Cadle, R. D., Danielsen, E. F., Lazrus, P. L., Schuster, B. G., and Shedlovsky, J. P., 1974. Recent studies of the stratospheric aerosol layer. In: J. H. Derco and E. J. Truhlar (Editors), *Proceedings of the International Conference on the Structure, Composition, and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations*. Vol. 1. Atmospheric Environment Service, Downsview, Canada. pp. 161-173.

CIAP, 1974. Report of Findings. The effects of stratospheric pollution by aircraft. DOT-TST-75-50, U. S. Department of Transportation, Washington, D. C.

Cicerone, R. J., Stolarski, R. S., and Walters, S., 1974. Stratospheric ozone destruction by man-made chlorofluoromethanes. *Science*, 186:1165-1167.

COMESA, 1975. The Report of the Committee on Meteorological Effects of Stratospheric Aircraft (COMESA) 1972-1975. U. K. Meteorological Office, Bracknell.

COVOS, 1976. Committee for the study of the consequences of stratospheric flight (COVOS) - Activities, 1972-1976. Translated for HAPP, U.S. Department of Transportation FAA Office of Environmental Quality, Washington, D. C. (unpaginated).

Crutzen, P. J., 1970. The influence of nitrogen oxides on the atmospheric ozone content. *Quarterly Journal of the Royal Meteorological Society*, 96:320-325.

Crutzen, P. J., 1974. Estimates of possible variations in total ozone due to natural causes and human activities. *Ambio*, 3:201-210.

Dotto, L. and Schiff, H., 1978. *The Ozone War*. Doubleday, Garden City, NY. 342 pp.

Elkins, J. W., Wofsy, S. C., McElroy, M. B., Kolb, C. E. and Kaplan, W. A., 1978. Aquatic sources and sinks for nitrous oxide. *Nature*, 275:602-606.

Ellsaesser, H. W., 1977. Has man increased stratospheric ozone? *Nature*, 270:592-593.

Ellsaesser, H. W., 1978. A reassessment of stratospheric ozone: Credibility of the threat. *Climatic Change*, 1:257-266.

Fehsenfeld, F. C., Ferguson, E. E., Streit, G. E., and Albritton, D. L., 1976. Stratospheric ion chemistry and the 11-year variation in polar ozone. *Science*, 194:544-545.

Foley, H. M. and Ruderman, M. A., 1973. Stratospheric nitric oxide production from past nuclear explosions and its relevance to projected SST pollution. *Journal of Geophysical Research*, 78:4441-4450.

Groves, K. S., Mattingly, S. R., and Tuck, A. F., 1978. Increased atmospheric carbon dioxide and stratospheric ozone. *Nature*, 273:711-715.

Haigh, J. D., and Pyle, J. A., 1979. A two-dimensional calculation including atmospheric carbon dioxide and stratospheric ozone. *Nature*, 279:222-224.

Hampson, R. F., Jr. and Garvin, D., 1975. *Chemical Kinetics and Photochemical Data for Modeling Atmospheric Chemistry*, NBS Technical Note 866, U. S. National Bureau of Standards, Washington, D. C.

Harrison, H., 1970. Stratospheric ozone with added water vapor: Influence of high-altitude aircraft. *Science*, 170:734-736.

Hoshizaki, H., Meyer, J. W. and Redler, K. O., 1973. Study of high altitude aircraft wake dynamics, Interim Report, Task VII: Problem definition advanced aircraft and fuels, Section 4: Potential destruction of ozone by HCl in rocket exhausts. Report LMSC-D354204, Lockheed, Palo Alto, CA.

Howard, C. J. and Evenson, D. M., 1977. Kinetics of the reaction HO_2 with NO. Geophysics Research Letters, 4:437-440.

Hudson, R. D. (Editor), 1977. Chlorofluoromethanes and the stratosphere, NASA Reference Publication 1010, NASA Goddard Space Flight Center, Greenbelt, MD, 266 pp.

Johnston, H. S., 1971. Reduction of stratospheric ozone by nitrogen oxides catalysts from supersonic transport exhaust. Science, 173:517-522.

Johnston, H. S., 1977. Analysis of the independent variables in the perturbation of stratospheric ozone by nitrogen fertilizers. Journal of Geophysical Research, 82:1767-1772.

Luther, F. M., Wuebbles, D. J., and Chang, J. S., 1977. Temperature feedback in a stratospheric model. Journal of Geophysical Research, 82:4935-4942.

Luther, F. M., 1978. Annual Report of Lawrence Livermore Laboratory to the FAA on the High Altitude Pollution Program - 1978, UCRL-50042-78 Lawrence Livermore Laboratory, Livermore, CA, 50 pp.

McElroy, M. B., 1976. Chemical processes in the solar system: A kinetic perspective. MTP International Reviews of Science, 9:127-211.

Molina, M. J. and Rowland, F. S., 1974. Stratospheric sink for chlorofluoromethanes: chlorine atom-catalyzed destruction of ozone. Nature, 249:810-812.

NASA Panel for Data Evaluation, 1979. Chemical Kinetic and Photochemical Data for Use in Stratospheric Modeling. JPL Publication 79-27, Jet Propulsion Laboratory, CIT, Pasadena, CA, 124 pp.

National Research Council Committee on Impacts of Stratospheric Change, 1976. Halocarbons: Environmental Effects of Chlorofluoromethane Release. U.S. National Academy of Sciences, Washington, D.C.

National Research Council Panel on Atmospheric Chemistry, 1976. Halocarbons: Effects on Stratospheric Ozone. U.S. National Academy of Sciences, Washington, D.C.

Olszyna, K., Cadle, R. D., and DePena, R. G., 1979. Stratospheric heterogeneous decomposition of ozone. Journal of Geophysical Research, 84:1771-1775.

Park, C., 1976. Estimates of nitric oxide production for lifting spacecraft reentry. Atmospheric Environment, 10:309-313.

Ruderman, M. A., Foley, H. M. and Chamberlain, J. W., 1976. Eleven-year variation in polar ozone and stratospheric-ion chemistry. Science, 192:555-557.

Stolarski, R. S. and Cicerone, R. J., 1974. Stratospheric chlorine: A possible sink for ozone. *Canadian Journal of Chemistry*, 52:1610-1615.

Thorne, R. M., 1976. Energetic radiation belt electron precipitation: A natural depletion mechanism for stratospheric ozone. *Science*, 195:287-289.

Wofsy, S. C., McElroy, M. B., and Yung, Y. L., 1975. The chemistry of atmospheric bromine. *Geophysical Research Letters*, 2:215-218.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

Technical Information Department

LAWRENCE LIVERMORE LABORATORY

University of California | Livermore, California | 94550