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THE CHLOROFLOUROCARBON OZONE THEORY
ASSESSMENT OF NEW SCIENCE - 1981

Submitted by

Flourocarbon Program Panel
Chemical Manufacturers Association
Washington, DC

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SUMMARY

- Statistical trend analyses of Dobson total ozone measurements indicate slight increases during the decade of the 70's, with a trend detection threshold of 1 - 2%/decade. Trend analysis of ozone measurements detects net overall change in ozone. It has been structured to filter out natural variations and serve as a monitor for possible man-made changes.
- Ground-based observations of ClO illustrate its large variability and provide data which will be a critical check on the validity of the theory.
- Ethane measurements in the lower stratosphere imply a much lower concentration of chlorine atoms than that calculated by the models.
- The incorporation of new chemistry into the models has improved the comparison between the calculated concentrations of critical species and actual atmospheric measurements. However, significant discrepancies remain for several key NO_x and ClX species. The new chemistry has reduced the calculated steady state depletion from about 10% to about 6% in the last year.
- Concentration profiles of important temporary sink species, such as $ClONO_2$, HOCl and HO_2NO_2, have yet to be measured. Uncertainties, such as pressure and temperature dependencies and experimental identification of reaction products, remain.
- Two-dimensional models provide a more realistic basis for comparison of theory with measurement, but, at present, a shortage of latitudinal and seasonal measurement data limits such comparisons.

- Calculations of combined perturbations by CO_2, CFCs, and jet aircraft indicate no significant ozone change until after the year 2000. Other effects such as N_2O need to be taken into account.
- Two-dimensional calculations of ozone depletion show faster CFC photolysis and hence lower steady-state depletion than comparable 1-D models.

OZONE TREND ANALYSIS

Statistical analysis of Dobson total column ozone measurements have been continually refined during the past year with the object of both understanding and reducing uncertainties related to the method. Three independent groups at the University of Wisconsin,[1] Princeton University,[2] and Du Pont[3] have updated their results to include the 1979 measurements. They find long-term trends (with 2σ uncertainties) of $+0.8\pm1.35\%$, $+1.7\pm2.0\%$, and $+1.0\pm1.2\%$, respectively, for the period 1970-1979. The results are in substantial agreement. The differencies in the results are related to the specific data sets analyzed and variations in the method of analysis.

The Wisconsin and Du Pont studies treat time series of the measurement sets, and their estimates of uncertainties include all factors related to individual stations and local geographic groupings of station. The Princeton work involves a transform to the frequency domain by which uncertainties of a global nature (ie common to all stations) can be estimated. Hence, uncertainty estimates from Du Pont and Wisconsin are similar, and they are somewhat smaller than that from Princeton. The uncertainties quoted by the Wisconsin and Du Pont groups refer to the detection threshold for a ten-year trend in the ozone data from any natural or man-made cause. The Princeton value of $\pm2.0\%$ is more broadly interpreted as the threshold for a trend of man-made origin, or a trend not ascribable to natural causes.

All three groups have examined their work for the influence of atmospheric nuclear testing during the 1960's[5]. Models indicate some decrease in ozone due to testing in the early 1960's, followed by a recovery during the remainder of the decade. It has been argued that this known increasing trend in the data could bias statistical analyses such that they over-estimate increasing ozone in the 70's. They fi that including this additional variable does not significantly change either the accuracy of detecting a long-term ozone change or the observed trend[5].

The Wisconsin group has examined data obtained with the Nimbus 4 satellite to determine how well the locations of their chosen 36 Dobson stations represent a truly "global" ozone sample. They examined satellite data for the immediate geographical region of their 36 Dobson stations for a trend. They then compared that trend with the trend determined from the entire set of satellite data. Since the results do not differ significantly, the smaller set is found to be representative of global data for purposes of determining long-term trend. Since the comparison is made between a small set of satellite data and the entire satellite set, but not directly with ground-based data, the known degradation in the satellite itself is not relevant to this comparison.

At the May 1981 NASA/WMO stratospheric Workshop, fruitful discussions took place between the statisticians and the meteorologists who are familiar with the Dobson measurements. Continued collaboration should allow the statisticians to identify additional explanatory variables and thus lead to further refinements to the statistical models. The accuracy of the trend models improves with time as additional measurements are added to the data set. Given the continuing uncertainties associated with the model calculations, ozone trend analysis serves as an important independent constraint on both the structure and the data base used in the models, as well as an increasingly accurate monitoring tool.

The key conclusion, however, is that the trend detection threshold is already quite small -- 1 to 2% -- so that ozone trend analysis provides an early warning system for monitoring changes in atmospheric ozone.[1, 2, 3] This capability allows regulatory decisions to be delayed until either the theory of atmospheric processes is well enough established to permit confident predictions of man-made influences, or a measured significant negative trend in ozone is identified.

TROPOSPHERIC PROCESSES

It is obviously of great importance to understand how much of the CFC-11 and CFC-12 released into the troposphere reaches the stratosphere and hence could potentially affect stratospheric ozone. The Atmospheric Lifetime Experiment[28] is designed to answer this question by accurately monitoring the tropospheric concentrations as a function of time. By comparing changes in concentration with changes in emissions, the total lifetime for restrictive loss processes can be determined. Preliminary analysis of the initial two years' data suggests that the lifetime of CFC-11 may be only half that (75 years) calculated in the current models, which assume that stratospheric photolysis is the only sink. This result would mean that only about half of the CFC-11 reaches the stratosphere and, therefore, that its calculated ozone-depleting potential would be half that currently calculated. The error limits on the lifetimes, however, are currently very large. At least 3 years' data will be necessary to reduce the uncertainties and establish any firm conclusions.

Information is also accumulating about a possible removal process for CFC-11 in the troposphere. Considerably elevated concentrations

of CFC-21 have been observed in air which has passed over arid or desert areas.[7] It is well known that CFC-11 is susceptible to attack by electrons. An expected product of such attack on a sand surface in the presence of a source of protons, such as water, would be CFC-21. It is also known that silica is a source of electrons when exposed to UV, so the existence of a desert sand sink mechanism is chemically possible.[8-12] Experiments are under way to quantify the importance of this sink mechanism in the Sahara Desert.

ATMOSPHERIC MEASUREMENTS

As observations of stratospheric trace species accumulate, intercalibration of measurements made with different techniques becomes an important goal. Variation among various measurements may be related to measurement error, methods of data analysis, local variability in the atmosphere, or seasonal and latitudinal variations.[13] Separation of these effects can be a difficult process.

Technique-related differences can be investigated by intercomparison flights and data analysis workshops, both of which are being pursued by such funding organizations as NASA and CMA. Subsequently, greater latitudinal and seasonal coverage with individual techniques can provide information on the associated variations.

Ground-based techniques are best suited to record frequent measurements and to examine the temporal variability of atmospheric species. Accordingly, CMA is placing special emphasis on the ground-based millimeter wave measurements of

ClO.[14] This important species has exhibited considerable day-to-day variability in both total column and altitudinal distribution. Neither effect can be duplicated in current models, which implicitly assume averaged transport in the atmosphere. Another aim of the ground-based effort is to extend the technique to other important species, including simultaneous measurements of ClO and O_3, to look for correlations in their changing concentrations. This is needed to provide an answer to the critical question "When Cl is added to the real stratosphere, does it increase, decrease or not affect the net concentration of ozone?".

Several independent measurements of ClO in the stratosphere (14, 31, 32, 33) lead to the conclusion that the mixing ratio for this key intermediate to ozone depletion is significantly reduced in the lower stratosphere (at 25 Km) relative to model calculations the same measurements indicate that the mixing ratio for ClO is substantially greater above 40 Km than that of the model calculations.

Ground-based measurements of the stratospheric profiles of HCl have shown greater concentrations of this compound at high altitude than the models predict.[30] Several of the critical temporary sink species, such as HO_2, NO_2, $ClONO_2$, and HOCl have not been measured in the stratosphere.[13] Given the very uncertain chemistry of these chemical compounds, their measurement is critical in assessing the validity of current models.[15]

One of the chemicals controlling the concentration of ethane in the lower stratosphere is active chlorine since these species react at a rapid rate. However, the measured concentration of ethane in this region implies that the ambient chlorine concentration is actually lower by a factor of three than the model-calculated value.[16]

A further test of the theory is the reel-down technique of Anderson, which will allow repeated sampling of the same air mass by raising and lowering a set of instruments from a balloon platform at high altitude.[17] Correlations among the varying concentrations of several species, in the region above 30 Km where chemistry dominates, will provide a direct and essentially model-independent test of the stratospheric chemistry scheme.

ATMOSPHERIC CHEMISTRY

The most significant recent development in atmospheric chemistry has been increased awareness of the uncertainty associated with the chemical scheme in current atmospheric models. The rates of several important chemical reactions have been remeasured and are considerably different from the previously recommended values (NASA 1049). These important changes in several recommended reaction rates have increased the models' sensitivity to those rates. Several new values represent major adjustments to the reaction rates and fall well outisde the range of errors estimated in the NAS 1979 report leading to a substantial reduction in calculated ozone depletion.

Last year, revisions in odd hydrogen chemistry were anticipated based on preliminary work. The recommended rates of the reactions $OH + HNO_3$, $OH + HO_2NO_2$, and $OH + HO_2$ have now all been increased.[18] The effect was to reduce calculated OH and HO_2 concentrations, especially in the lower stratosphere. This leads to smaller calculated depletion from chlorofluorocarbons, through both direct effects and indirect coupling of HO_x with ClO_x and NO_x chemistry.

$ClNO_3$ remains a very important species whose formation and destruction have not been conclusively identified.[18]

Several research projects in progress are directed to the pressure dependence and product identification for important atmospheric reactions. The sensitivity of perturbation calculations to minor product "branches" is a matter of concern since in most studies to date the products of the reactions are assumed rather than measured.

ATMOSPHERIC MODELS

1 Comparison with Observations

The continued development of two-dimensional (2-D) models provides the ability for comparing model calculations to actual atmospheric measurements for a particular latitude and season.[20, 21] The agreement between model and measurement for odd nitrogen species has been significantly improved by recent revisions in chemistry. The overall features of the vertical profiles and the latitudinal and seasonal variations for the major NO_x species are now fairly well modeled. However, major discrepancies remain, including the models' overestimate of total odd nitrogen (and particularly HNO_3) at high altitudes.[21]

Chemistry changes have also improved the comparison between calculated and measured ClO profiles in the lower stratosphere, but models still appear to underestimate ClO at high altitudes ($\sim$40 Km). The effect of these changes has been to shift the region of calculated ozone depletion to higher altitudes and to reduce overall ozone depletion. Above 40 Km the complexities of coupled chemistry and transport are not present. This could simplify the model calculations by removing a source of ambiguity and lead to a more meaningful comparison between measured and theoretical values. Models appear to overestimate HCl below $\sim$20 Km, especially at high latitudes, leading to speculation that there may be a lower stratospheric chemical sink for chlorine not included in the models.[20, 21] In the upper stratosphere, the models calculate $\sim$ 2 ppb total chlorine, while the observations indicate a higher value ($\sim$ 3 ppb).[22] The calculated atmospheric lifetime of CFC-11 is somwehat shorter (20-30%) in 2-D than in 1-D models. The 2-D models calculate a faster rate of photolysis because the CFC-11 concentration in the tropics and the incident UV flux are both largest near the equator.[23, 24] Although the use of 2-D models to analyze these latitudinal covariance effects has just recently begun, such claculations are expected to provide new insight into the seasonal and latitudinal influences on stratospheric chemistry.

2 Perturbation Calculations

The most striking development during the last two years is the dramatic reduction in calculated ozone depletion due to CFCs. For constant mid-1970's CFC releases indefinitely into the future, with no other perturbations included, both 1-D and 2-D models now calculate 5 - 7% depletion in ozone at steady state.[24, 25, 26] Depletion through 1980, based on historical CFC release, is calculated to be 0.5 - 0.8%. For comparison, the

1979 NAS report[27] found 16.5% at steady state and 2.1% to date, respectively, for these two calculations. Significant uncertainties in the chemical data base remain, and further changes in either direction can be expected.

Two-dimensional models provide additional information on the distribution of the calculated depletion over latitude, altitude, and season. Except near the winter pole, the entire lower stratosphere now shows a net increase in calculated ozone as a result of CFC release.[24, 25] This contrasts with the large lower stratospheric depletion characteristic of models in 1979.[13] The calculated annual average depletion in total column ozone is relatively constant with latitude, but seasonal variations increase with increasing latitude such that polar winter is the time and location of maximum depletion.

It is now recognized that, if model calculations of stratospheric ozone change are to describe the real environment, they must take into account the coupled effects of all sources of chlorine, nitrogen and hydrogen trace constituents, as well as the CO_2 effect. This has not yet been accomplished although individual calculations have been made including the simultaneous effect of (1) CFC's, NO_x from subsonic aircraft and the documented buildup of atmospheric CO_2[4, 26] as well as (2) ClX, N_2O and NO_x.[30]

In these publications the calculated effects on total ozone column through 1980 result in a decrease of less than 0.5%. In the former calculation essentially no net change in ozone results through the year 2000. Although error limits have not been assigned in the model calculations, it is evident that this range of values overlaps that of the measured trend in ozone concentration. The latter is an observational constraint against which the perturbation calculations can be tested.

A calculated present day ozone depletion greater than 1% would conflict with current measurements.

BIOLOGICAL EFFECTS OF OZONE DEPLETION

Concern over calculated future depletion of stratospheric ozone develops from concern over the terrestrial effects of the anticipated increase in UV-B should ozone depletion actually occur. The concerns involve human skin cancer incidence, possible effects on crops and on marine life forms important to the marine food chain, and climatic effects. A commentary on the biological concerns has been prepared for a CMA-participating member company by a panel of independent authorities in the fields of plant, aquatic and radiation biology, as well as human skin cancer.

POTENTIAL HUMAN SKIN CANCER EFFECTS

Concern has been expressed that the incidence of the two types of skin cancer (melanoma and nonmelanoma) might increase as a result of a substantial increase in UV-B.

On malignant melanoma, a rare but often fatal type, the review shows that, for most forms, medical data do not support a cause and effect relationship between incidence of melanoma and accumulated damage from repeated overexposure to sunlight. A real worldwide increase in melanoma incidence has occurred in the absence of any ozone depletion. It occurs primarily in males and females who are not habitually or occupationally exposed to sunlight.

The review acknowledges that most nonmelanoma skin cancers (the most treatable form of cancer) do show a relationship to solar UV exposure. However, the present methods of estimating effects clearly overestimate them and need considerable refinement before realistic estimates of changes in nonmelanoma incidence can be made for hypothesized depletions of ozone.

NONHUMAN EFFECTS

The commentary emphasizes that the research on crops and marine effects is preliminary and necessarily of a scouting and exploratory nature and is not adequate to predict in any quantitative manner what the effects of ozone depletion would be. Further research is needed, and there is no reason to anticipate any imminent serious problem.

NATURAL VARIATIONS IN UV-B

There is already a natural variation in UV-B with latitude that greatly exceeds the change which would occur due to calculated steady state ozone depletion. Thus, meaningful comparisons could be made under controlled-environment conditions at different latitudes.

Such facilities, using greenhouses and natural sunlight would avoid the experimental difficulties encountered in the simulatio of sunlight.

POTENTIAL CROP EFFECTS

Growth chamber studies at the present time cannot be used to predict yields under field conditions. There is no data base to predict that catastrophes would result from depletion calculated to occur from continued CFC release.

A basic problem in research designed to study UV effects on crop is the effective simulation of sunlight. Growth chambers are unreliable as a means to estimate effects quantitatively. Plants grown under growth chamber conditions are typically much more sensitive to changes in UV than is the case for the sa plant under field conditions.

The differences between results from growth chambers and field experiments can be at least partly explained. Plants have natural mechanisms to minimize and repair damage from UV-B. The conditions in the growth chambers retard natural repair processes and thus exaggerate the effects of an increase in UV-B

While growth chambers are valuable for field study design and for anticipating the type of damage, reliance must be placed on the field studies themselves for estimates of real world effects.

POTENTIAL MARINE LIFE EFFECTS

Close analogies exist between studies of the effect of increased UV on marine larvae and the corresponding studies on crops. Experimentation in the ocean itself is extremely difficult, and studies under simulated ocean conditions in aquaria face problems in terms of realistic simulation of sunlight. Additiona concerns over the "naturalness" of the conditions in a laboratory aquarium stem from the limitations on the depth to which the organisms can move, temperature control, and the control, measurement, and calculation of the actual UV-B doses used in experiments.

The concerns over retarding natural repair mechanisms in aquarium experiments also apply to marine organisms.

The natural variability in aquatic ecosystems, particularly large natural mortalities, make it very difficult to measure fluctuations caused by UV-B. Much more research would be n before the extent of these effects can be determined.

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Human Effects

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Nonhuman Effects

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