Chemical Events in the Atmosphere and their Impact on Environment
Pontifical Academy of Sciences, *Scripta Varia* 56, Vatican City 1985
www.pas.va/content/dam/accademia/pdf/sv56/sv56-rowland.pdf

INCREASING CONCENTRATIONS OF PERHALOCARBONS, METHYLCHLOROFORM AND METHANE IN THE ATMOSPHERE

F.S. ROWLAND, D.R. BLAKE, S.C. TYLER and Y. MAKIDE (*)
Department of Chemistry, University of California
Irvine, California 92717, U.S.A.

Introduction

The total concentration of organically-bound chlorine in the troposphere now exceeds 3,000 parts per trillion by volume (1 pptv = 10^{-12}), an increase of at least a factor of two during the time period from 1970-1983. The major components include CCl_2F_2, CCl_3F, CCl_4, CH_3CCl_3 and CH_3Cl, with lesser contributions from numerous other chlorinated chemical species. The potential environmental importance of ultraviolet photodissociation in the stratosphere of the chlorofluoromethanes CCl_3F (Fluorocarbon-11) and CCl_2F_2 (Fluorocarbon-12) [Molina and Rowland, 1974a; Cicerone *et al.*, 1974; Crutzen, 1974; Rowland and Molina, 1975a; W.M.O.-N.A.S.A., 1982; N.A.S., 1976, 1979, 1982, 1984] was recognized soon after the detection of CCl_3F in tropospheric air in both the northern and southern hemispheres [Lovelock *et al.*, 1973]. Atomic chlorine released by photolysis of CCl_3F and CCl_2F_2, as shown in (1) for the former, initiates the ozone-depleting ClO_x stratospheric chain of (2) and (3) [Stolarski and Cicerone, 1974; Crutzen, 1974]. The most effective altitudes for ClO_x-chain removal of ozone lie between 30-45 km because the O atoms required for (3) are much less abundant in the lower stratosphere and below 30 km the alternative reaction of (4) becomes dominant in completing the cycle returning ClO to Cl.

(*) Present address: *University of Tokyo*, Tokyo, Japan.

$$CCl_3F + u.v. \rightarrow Cl + CCl_2F \tag{1}$$

$$Cl + O_3 \rightarrow ClO + O_2 \tag{2}$$

$$ClO + O \rightarrow Cl + O_2 \tag{3}$$

$$ClO + NO \rightarrow Cl + NO_2 \tag{4}$$

Compounds released in the troposphere are usually removed by rainout, by solar photolysis in the visible or near ultraviolet wavelengths, or through chemical attack by reactive species such as HO radicals. These processes are not important for perhalo fluorocarbons such as CCl_3F and CCl_2F_2 because they lack solubility in water droplets, are transparent to solar radiation with wavelengths longer than 295 nm, and have no available chemical reaction channels with common atmospheric reactants such as HO and atomic O [Rowland and Molina, 1975a]. Without tropospheric removal, the atmospheric lifetimes for CCl_3F and CCl_2F_2 were estimated to be 40-150 years, as controlled by stratospheric decomposition processes [Molina and Rowland, 1974a]. For similar reasons, the atmospheric lifetime for carbon tetrachloride, CCl_4, was calculated to be 30-50 years and assumed to be controlled by stratospheric processes as well [Molina and Rowland, 1974b].

Some of the common anthropogenic chlorinated molecules such as CH_3CCl_3 (Methylchloroform) and $CHClF_2$ (Fluorocarbon-22) are not fully halogenated, and contain C-H bonds which are susceptible to reaction with tropospheric HO radicals. The most abundant of these in its present atmospheric concentration is CH_3CCl_3 which is decomposed by reaction (5).

$$HO + CH_3CCl_3 \rightarrow H_2O + C_2H_2Cl_3 \tag{5}$$

The high concentration of CH_3CCl_3 makes it useful as a monitor for the rate of removal of similar molecules from the atmosphere [Rowland and Molina, 1975b; Singh, 1977; McConnell and Schiff, 1978; Singh *et al.*, 1979; Makide and Rowland, 1981; W.M.O.-N.A.S.A., 1982]. We have estimated an atmospheric lifetime of 6 to 7 years for CH_3CCl_3 from a comparison of its measured absolute concentrations versus total emissions [Makide and Rowland, 1981] and from its observed hemispheric concentration gradient [Rowland *et al.*, 1984a]. The measured laboratory reaction rate of $CHClF_2$ with HO is less than half as large as k_5, leading to an estimated atmospheric lifetime more than twice as long (17 years) as for CH_3CCl_3.

Methane is found throughout the troposphere in concentrations now exceeding 1.6 parts per million by volume (1 ppmv = 10^{-6}), and is the most abundant source of C-H bonds in the atmosphere. Its primary atmospheric removal process is also reaction with HO radicals, as in (6). The atmospheric lifetimes for CH_4 and CH_3CCl_3 can be connected through the relative rates of reactions (5) and (6), and the value observed in the laboratory

$$HO + CH_4 \rightarrow H_2O + CH_3 \tag{6}$$

for k_5/k_6 of 1.5 leads to an estimate of 9 to 10 years for the lifetime of methane [Mayer *et al.*, 1982]. The major sources of methane in the atmosphere involve anaerobic biological processes occurring in swamps, rice paddies, ruminant mammals, etc. [Ehhalt, 1978]. With an atmospheric burden of about 4500 megatons and a ten-year lifetime, the emissions of methane to the atmosphere must be in the range of 450-500 megatons per year. The world-wide concentration of methane has been observed to be increasing from 1978-1981 at a rate of about 0.02 ppmv per year [Rasmussen and Khalil, 1981; Blake *et al.*, 1982; Khalil and Rasmussen, 1983; Rowland *et al.*, 1984b], implying a current imbalance between sources and sinks for methane of about 50 megatons per year.

Methyl chloride is now present in the atmosphere at about 600 pptv, and was probably also there in comparable concentrations in the year 1900 and before. Very likely CH_3Cl was then the only major organochlorine compound because all of the others now present in large concentrations have been introduced in 20th century technological uses. Although the emission sources for CH_3Cl have not been quantitatively established, the major current release to the atmosphere is believed to come from natural sources such as the oceanic chlorination of methyl iodide released from kelp beds [Watson *et al.*, 1980; Singh *et al.*, 1983]. From the inverse ratio of HO reaction rates vs. CH_3CCl_3, we have estimated the atmospheric lifetime of CH_3Cl as 1.6 years [Makide and Rowland, 1981].

The first anthropogenic compound to be released to the atmosphere in important quantities was CCl_4 which began to be manufactured industrially about 70 years ago. Although CCl_4 was formerly used in major quantities as a cleaning agent, its major current use on a world-wide basis is as the synthetic precursor of CCl_3F and CCl_2F_2. The perhalo fluorocarbons were developed about fifty years ago as a class of chemical compounds suitable for use as refrigerants, and CCl_2F_2 has been for many years the standard refrigerant gas in most applications. Home air-conditioning, however, has been developed with $CHClF_2$ as the working fluid.

The same properties of chemical inertness and volatility make these chlorofluorocarbons useful for many other purposes, including the major one as propellant gases for aerosol spray devices. Other important uses are found as solvents and as the expansion gas in the blowing of polyurethane foams. Manufacture of CCl_3F and CCl_2F_2 doubled every 5 to 7 years through the 1950s and 1960s, reaching in 1974 world-wide yearly production levels of about 370 kilotons for CCl_3F and 470 kilotons for CCl_2F_2 as tabulated by the Chemical Manufacturers Association [C.M.A., 1982, 1983]. Methylchloroform is widely applied as a solvent, especially for grease removal, and is currently at a world-wide level of about 500 kilotons per year.

The exponential increases in yearly production for CCl_3F and CCl_2F_2 continued until the scientific connection to potential ozone depletion became apparent in the mid-1970s. These environmental concerns have led to consideration of national and/or international regulations for the production and release of these compounds to the atmosphere. A ban on the usage of CCl_3F and CCl_2F_2 as propellant gases for aerosol sprays was announced in late 1976 by three U.S. government agencies, and similar prohibitions are in effect in Canada and several Scandinavian countries. No regulations are in effect in most other countries, although a voluntary reduction in use as aerosol propellants has been agreed upon in several European countries. No regulations applicable to other important uses are in force in any country, and some of the production formerly intended for aerosol propellant use has been shifted to other end uses.

Most of the applications for all of these compounds, except that of CCl_4 as synthetic precursor for CCl_3F and CCl_2F_2, involve eventual release to the atmosphere unchanged, usually within a few months. Analysis of the data on the yearly production and atmospheric release for CCl_3F and CCl_2F_2 shows that the cumulative release of each to the atmosphere has at all times in the past two decades exceeded 85% of its cumulative manufacture [C.M.A., 1983]. Most of the residual amount not yet emitted to the atmosphere is held either in refrigerators or in "closed-cell" polyurethane foams.

Possible tropospheric sinks for chlorofluoromethanes

As the importance of atmospheric accumulation of CCl_2F_2 and CCl_3F was realized, many suggestions were offered of possible alternative reactions which might result in the removal of these compounds from the atmosphere. Such searches for "tropospheric sinks" for chlorofluoromethane compounds can be carried out by testing individually proposed removal mechanisms, or by looking for changes caused by the combined effects of all such processes [Rowland and Molina, 1975a, 1976; N.A.S., 1976, 1979, 1982, 1984; Cunnold *et al.*, 1978]. All specifically identified removal mechanisms (e.g. freezing out into Antarctic snow [N.A.S., 1976]; decomposition on desert sand [Alyea *et al.*, 1978; Lovelock and Simmonds, 1980; Lovelock, 1982]) have been judged to be unimportant relative to stratospheric removal [N.A.S., 1976, 1979, 1982, 1984; W.M.O.-N.A.S.A., 1982].

The other possibility for the discovery of such tropospheric sinks, either singly or in combination, lies through comparisons of the total amounts of CCl_3F and CCl_2F_2 found in the atmosphere with the amounts expected still to be there if stratospheric photodecomposition is the only important removal process [Rowland and Molina, 1976]. An alternative to this integral approach is the differential, "trend analysis" method in which incremental changes in atmospheric burden are compared with incremental emissions to the atmosphere over a particular period of time. The most complete application of the trend analysis procedure has been carried out through the Atmospheric Lifetime Experiment (ALE) sponsored for its first several years by C.M.A. and now by N.A.S.A. [Cunnold *et al.*, 1978, 1983a,b; Prinn *et al.*, 1983; Simmonds *et al.*, 1983].

In the past, the atmospheric accumulations of CCl_3F and CCl_2F_2 have been frequently stated to be much smaller than expected for stratospheric loss alone, indicative of tropospheric sinks capable of removing CCl_3F and CCl_2F_2 in time periods as short as 10 years [Jesson *et al.*, 1977; Jesson, 1980, 1982; Miller *et al.*, 1981]. The basis for the estimate of chlorofluoromethane atmospheric lifetimes as short as ten years has usually been the claim that a substantial fraction of the CCl_3F or CCl_2F_2 emitted to the atmosphere is no longer there, and by inference must have been removed by some not yet identified atmospheric process. The calculation of such "missing" CCl_3F has often been based upon tropospheric concentrations measured in the north temperate region, e.g. at 52°N, together with a "weighting factor" determined from the north/

south concentration gradient of a factor of two reported for 1971-2 by Lovelock *et al.* [1973]. Other measurements made in 1972 failed to confirm these large latitudinal gradients in CCl_3F [Wilkniss *et al.*, 1973, 1975], and extensive measurements during the past few years have shown CCl_3F gradients no larger than 15% between the northern and southern temperate zones [N.A.S. 1979, 1982; Cunnold *et al.*, 1983a]. The measured atmospheric burdens are then approximately in agreement with the amounts expected to remain if stratospheric losses represent the only important sink for CCl_3F.. The atmospheric lifetime for CCl_3F has been estimated as 78 years from its observed concentrations during 1978-1981 in the ALE program [Cunnold *et al.*, 1983a], while that for CCl_2F_2 has been given as > 80 years [Cunnold *et al.*, 1983b]. Both lifetimes are consistent with negligible loss to all tropospheric sinks combined, and stratospheric decomposition is now confirmed as the only important sink for either molecule.

Increasing tropospheric concentrations of chlorinated compounds

The tropospheric concentrations of CCl_3F in 1971 as reported by Lovelock *et al.* [1973] ranged from 80 pptv at 50°N latitude to about 40 pptv in the southern temperate zone. Since that time, measurements have been made by several research groups with increasing frequency over the past decade, including the multiple assays made since mid-1978 by the several stations in the ALE program [Cunnold *et al.*, 1983a,b]. Our own measurements have been taken during various seasons by collecting air samples in remote locations and returning them to the laboratory for analysis. Our data collected around July 1979 are illustrated in Figure 1, and in January 1980 in Figure 2. These distributions show varying latitudinal gradients in different seasons, while clearly demonstrating that CCl_3F is present in approximately equivalent concentrations in all remote locations throughout the world. In 1984 the tropospheric concentration of CCl_3F is about 200 pptv, an increase of a factor of 3 over that reported by Lovelock for 1971. The input of CCl_3F to the atmosphere continues at approximately 270 kilotons per year, and the observed concentrations continue to rise steadily [Cunnold *et al.*, 1983a; N.A.S., 1984]. If its atmospheric lifetime is 78 years and atmospheric release continues at the yearly rate of 270 kilotons, the eventual steady-state amount CCl_3F can be expected to increase by another factor of 4.7 to approximately 1000 pptv.

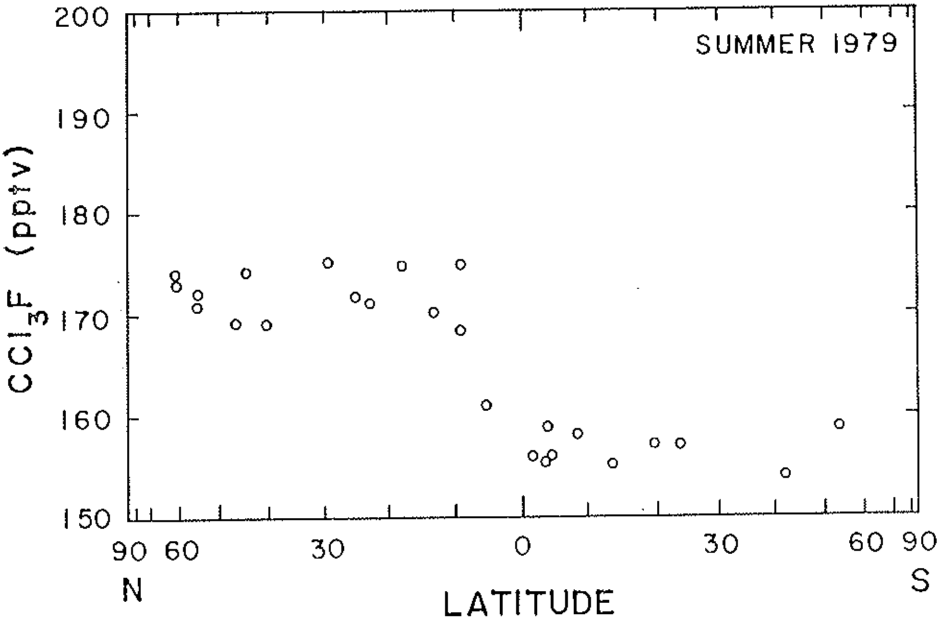

Fig. 1. Tropospheric Concentrations of CCl_3F Measured in Remote Locations during Summer 1979.

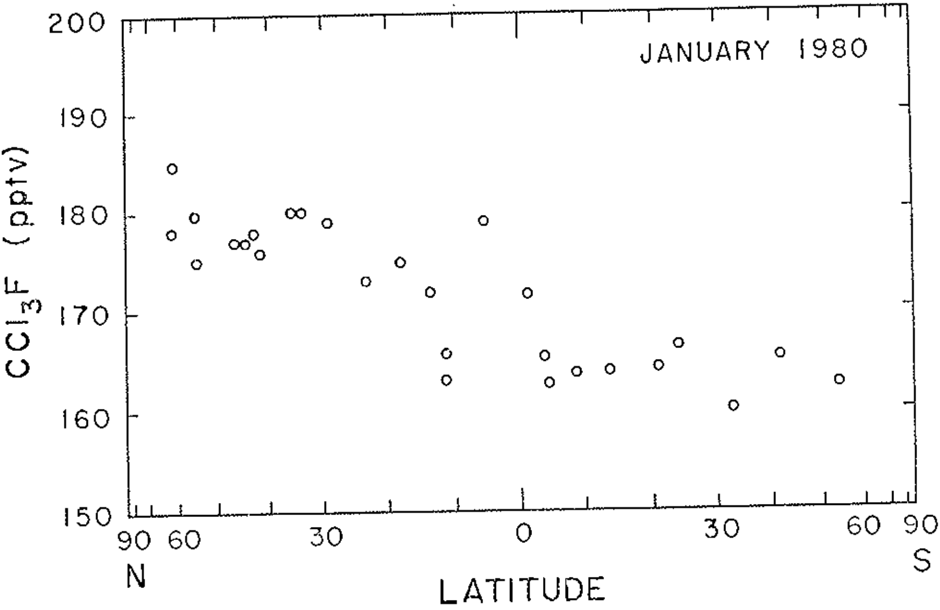

Fig. 2. Tropospheric Concentrations of CCl_3F Measured in Remote Locations during January 1980.

The tropospheric concentrations of CCl_2F_2 have also been increasing steadily during the entire period of its measurements, and are now approaching 400 pptv in the northern hemisphere. These concentrations are also about three times larger than those present in 1970. The emissions estimates for CCl_2F_2 made earlier by the Chemical Manufacturers Association [1981] showed a consistent decrease from 1974 through 1980, but the atmospheric measurements of CCl_2F_2 were not in agreement with these estimates [Rowland *et al.*, 1982; Gidel *et al.*, 1983]. Most of this discrepancy has now been removed with the substantial increase in the revised C.M.A. estimates [1982, 1983], which now show CCl_2F_2 emissions of 392.5, 412.2, and 422.8 kilotons per year estimated for 1980-1982, in contrast to the earlier value of 333.7 kilotons per year for 1980 [C.M.A., 1981]. A major uncertainty remains in the origin of these increased emissions of CCl_2F_2 because much of the expressed basis for the revised calculations has been the attribution by C.M.A. of an 18% yearly growth in releases from the Soviet Union and other eastern European countries from 1975 onward. No direct estimates of CCl_3F or CCl_2F_2 releases in these countries have been published for any year after 1975 [Borisenkov and Kazakov, 1977], and an 18% yearly increase amounts to a factor of 4 increase in less than 9 years. Such a rapid production increase clearly requires a very large development of manufacturing capacity, and the assumption now attributes more than 20% of the world production of CCl_2F_2 to the Soviet Union. Despite the uncertainty in the actual origins of the CCl_2F_2 now being released to the atmosphere, the concentrations definitely are rising steadily, consistent with the very long atmospheric lifetimes calculated from current atmospheric models, now as long as 150-200 years [Cunnold *et al.*, 1983b]. The atmospheric concentration of CCl_2F_2 at steady-state with yearly emissions of 422 kilotons can be expected to increase by a factor of 7 for an atmospheric lifetime of 120 years and a factor of 11 if the lifetime is 200 years. The expected eventual accumulation of CCl_2F_2 at current emission rates would then be 3000-4000 pptv.

Measurements made in our laboratory have shown slowly increasing concentrations of CCl_4 versus time to the present level of about 115-120 pptv in the northern hemisphere, with concentrations only a few pptv lower in the southern hemisphere. The latitudinal distribution in December 1980 is shown in Figure 3. This gradient in concentration is substantially smaller than that found with CCl_2F_2 and CCl_3F, consistent with the fact that widespread industrial use of CCl_4 began much earlier

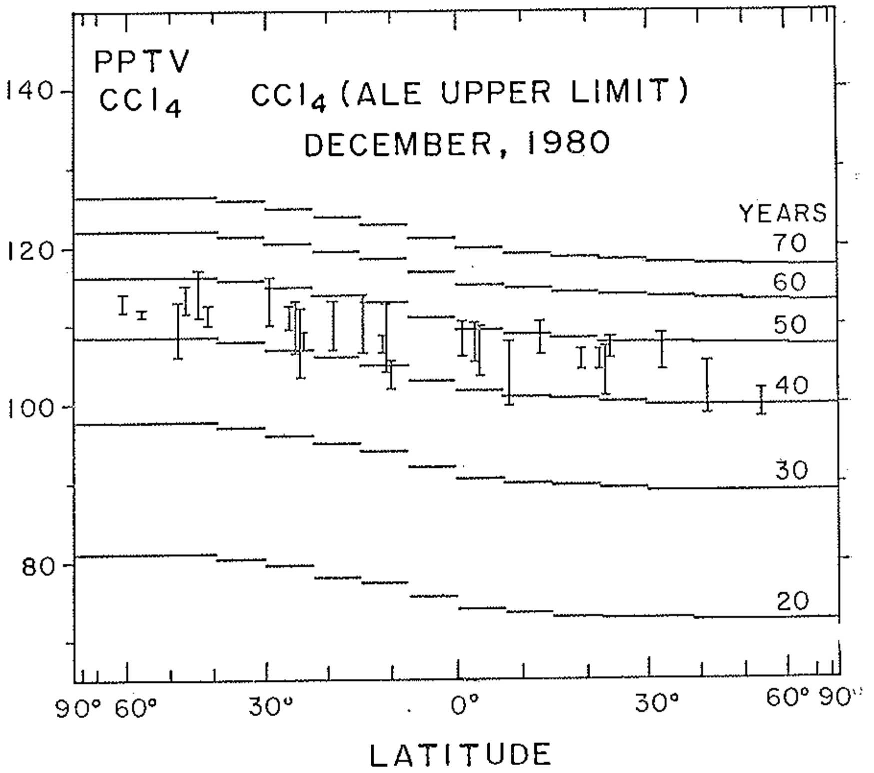

FIG. 3. Tropospheric Concentrations of CCl_4 Measured in Remote Locations during December 1980. Calculated concentrations for various postulated atmospheric lifetimes in combination with the upper limit estimated for atmospheric emissions by Simmonds *et al.* (1983).

than for the chlorofluorocarbon compounds. All of the anthropogenic halocarbons are produced and used almost entirely (about 95%) in the northern hemisphere, and consequently are found in higher concentrations in the north. We have evaluated north/south transport parameters from the observed gradient in concentrations for CCl_3F, as in Figures 1 and 2, and have then applied them with a plausible emission pattern versus time for CCl_4 [Simmonds *et al.*, 1983]. The amounts of CCl_4 and the latitudinal gradient in concentrations is quite satisfactorily reproduced, as shown in Figure 3, lending plausibility to the assumption that all of the CCl_4 in the atmosphere can be satisfactorily attributed to anthropogenic origins. Some previous evaluations of tropospheric concentrations for CCl_4 have indicated levels as high as 150-160 pptv [N.A.S., 1982; W.M.O.-N.A.S.A., 1982]. However, new absolute calibrations for measurements made by some of the research groups involved have resulted in downward revisions [Simmonds *et al.*, 1983] in the estimated tropospheric concentrations until the remaining disagreement with the data of Figure 3 is probably within tbe respective experimental accuracies.

Our measurements and those of others indicate a slow increase (about 2% per year) in the tropospheric concentrations of CCl_4, consistent with a yearly emission rate of 100-150 kilotons/year and an atmospheric lifetime of 45-70 years. Such an atmospheric emission rate is higher than expected from the frequent statement that the current major use as precursor molecule for the production of CCl_3F and CCl_2F_2 accounts for about 95% of the total CCl_4 production. On the other hand, experimental observations of tropospheric concentrations of CCl_4 in some urban locations routinely show excess amounts relative to simultaneous measurements in remote locations at the same latitude, indicating that urban releases of CCl_4 are occurring in substantial quantities during the 1980s. The present magnitude of estimated releases for CCl_4, 100-150 kilotons/year, corresponds to about half as much chlorine being added to the troposphere in the form of CCl_4 as in being added for CCl_3F. An atmospheric lifetime of 70 years for CCl_4 and continued emissions at 150 kilotons/year would result in a further increase in CCl_4 concentration by a factor of about 3, toward a steady state concentration of about 350 pptv.

Concentrations exceeding 100 pptv in the northern hemisphere have also been observed for methylchloroform, with an excess of 35-40% in the north temperate zone relative to the south temperate zone, as shown in Figure 4. As with CCl_4, substantially higher concentrations have also been reported earlier for CH_3CCl_3 by other research groups [W.M.O.-N.A.S.A., 1982; N.A.S., 1982; Prinn *et al.*, 1983] but new absolute calibrations have lowered most of these measurements into reasonable consistency with the data of Figure 4. Comparisons of the amounts remaining in the atmosphere with the estimates of total release to date show that only about $50 \pm 5\%$ still remains there, indicative of appreciable loss already through tropospheric decomposition processes.

The only important contributor to these processes is reaction (5) with HO radicals. Comparison of the integrated emissions with the observed atmospheric concentrations led to an estimate of 6.9 ± 1.2 years for the atmospheric lifetime of CH_3CCl_3 [Makide and Rowland, 1981]. Although atmospheric concentration data are now available for

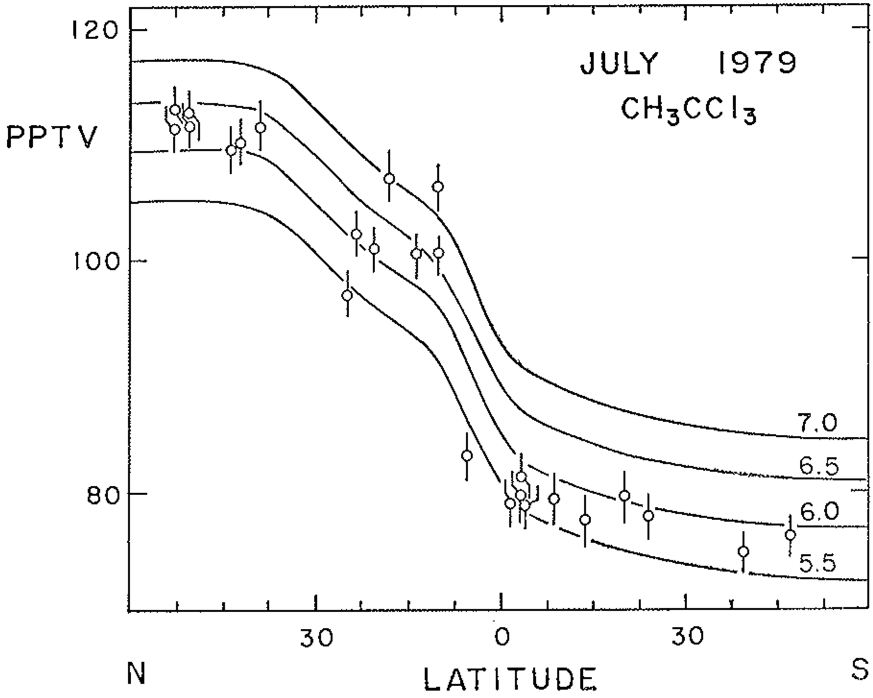

FIG. 4. Tropospheric Concentrations of CH_3CCl_3 Measured in Remote Locations during Summer 1979. Calculated concentrations for various postulated atmospheric lifetimes. Assumed hydroxyl sinks of equal magnitude in both hemispheres; primary losses in tropics.

an additional five years, there has been no appreciable improvement in the estimates of environmental release and therefore no better check on the actual atmospheric lifetime for CH_3CCl_3. The world-wide production has not been rising during the last several years, and the atmospheric concentrations appear to be leveling off as would be expected with nearly-constant emission and an atmospheric lifetime of only about 7 years. The expected latitudinal dependence of CH_3CCl_3 concentrations has been simulated with transport parameters fitted to the CCl_3F gradient, and various assumed atmospheric lifetimes for loss by reaction (5). The results are shown in Figure 4 and demonstrate reasonable agreement both in absolute magnitude and in latitudinal gradient for lifetimes of about 6 ± 1 years. The simulation in Figure 4 has assumed equal losses in the northern and southern hemispheres, with 80% of all losses by HO radical reaction occurring between 30°N and 30°S.

The five most abundant organochlorine compounds in the troposphere in 1984 are CCl_2F_2, CCl_3F, CCl_4, CH_3CCl_3 and CH_3Cl. The organochlorine content in the troposphere includes approximately 600 pptv from CCl_3F (3 × 200 pptv), 700 pptv from CCl_2F_2 (2 × 350 pptv), 480 pptv from CCl_4 (4 × 120 pptv), 420 pptv from CH_3CCl_3 (3 × 140 pptv) and 600 pptv from CH_3Cl, for a total of 2800 pptv. Other chlorocarbon molecules such as $CHClF_2$, CCl_2FCClF_2, $CClF_2CClF_2$, $CH_2{=}CHCl$ and $CCl_2{=}CCl_2$ contribute another 300 pptv or more in the northern hemisphere for a present total in excess of 3000 pptv Cl. Methyl chloride is the only one of these molecules not almost entirely of anthropogenic origin, and was probably therefore the chief contributor of organochlorine content in the atmosphere in the year 1900 and earlier. If its concentration at the beginning of the century was about equal to its present value, the total organochlorine content in 1900 was probably around 600-700 pptv.

The atmospheric concentrations of anthropogenic molecules such as CCl_4 first became appreciable in the 1940s, and the concentrations of the other chlorofluorocarbons in the 1950s and 1960s. The total concentration of organochlorine compounds probably reached 1500 pptv about 1970, and 3000 pptv early in the 1980s. The concentrations of chlorine in the stratosphere must inevitably follow these tropospheric concentrations, with allowance for the time delay in upward transport. One clear implication of these estimated increases in the tropospheric concentrations of organochlorine compounds during the 20th century is that a change in stratospheric inorganic chlorine concentrations must already have occurred relative to that which existed during the 19th century [Wuebbles, 1983]. However, because full equilibration of the chlorine concentration up to the stratopause lags behind tropospheric concentrations by a decade or more, the present upper stratosphere does not yet accurately reflect the changes in tropospheric organochlorine content which have already occurred during the 1970s.

Estimates of future concentrations of organochlorine compounds in the troposphere are basically dependent upon the projected yearly anthropogenic releases to the atmosphere, coupled with the individual atmospheric lifetimes of the chemical species involved. The concentration of relatively short-lived CH_3CCl_3 will probably not increase too much beyond the present values unless there are substantial increases in the yearly production and release. However, the increases in CCl_3F and CCl_2F_2 observed during the past ten years are likely to he repeated in the next decade and longer because the observed atmospheric lifetimes are in the range of many decades to centuries. A total organochlorine content of about 4000 pptv Cl in the troposphere is a reasonable prediction for 1990, with continued increases of about 1000 pptv Cl per decade into the 21st century unless there is a major change in the release patterns for the perhalo chlorofluorocarbons.

Some indication of concentrations of organochlorine compounds to be expected in the more distant future can be calculated from the extrapolations to steady state described above. With 1000 pptv of CCl_3F, 3000-4000 pptv of CCl_2F_2, 350 pptv of CCl_4, 150 pptv of CH_3CCl_3 and 600 pptv of CH_3Cl, plus an estimated 800 pptv in now-minor compounds, a tropospheric organochlorine concentration of 12,000-14,000 pptv can be reached. These steady-state concentrations are only approached for the longer-lived compounds over a period of several centuries, and a more directly pertinent indication of future concentrations can be found from a projection to 2084 A.D. With atmospheric lifetimes of 120, 80, 70 and 7 years for CCl_2F_2, CCl_3F, CCl_4 and CH_3CCl_3, respectively, the factors of concentration growth over the next 100 years at present emission rates will be about 4.4, 3.5, 2.6 and 1.3, to about 3000, 2000, 1300 and 500 pptv of Cl, and a total of 6800 pptv Cl bound in these four organochlorine compounds. With the addition of 600 pptv for CH_3Cl and 600 pptv for the minor compounds, the total Cl content of the troposphere would then be 8000 pptv in carbon containing compounds alone. Of course, an increase in yearly emissions for the longer-lived compounds would result in substantially greater total atmospheric burdens of organochlorine compounds. A relatively small CCl_2F_2 increase of 12 kilotons per year, comparable to the CMA estimated [1983] increases for 1981 and 1982 of 19.7 and 10.6 kilotons would cause CCl_2F_2 with a 120-year lifetime to reach the factor of 4.4 increase in about 45 years, and a factor of about 11 by 2084 A.D. If the lifetime were actually 200 years, then the concentration increases by 2084 A.D. would be considerably higher for either steady emissions at 422 kilotons per year or for a linear increment of 12 additional kilotons per year.

Environmental consequences from increasing chlorocarbon concentrations

The growths in the tropospheric concentrations of several organochlorine compounds, and in the stratospheric release of atomic Cl from their decomposition has a variety of potential environmental consequences. One of these is the direct physicochemical effect of Cl upon the ozone content of the stratosphere; others arise as indirect responses because of the importance of (a) the heating effect in the upper stratosphere from the absorption of u.v. radiation by ozone; and (b) the partial absorption by O_3 of u.v. radiation with wavelengths between 290-320 nm, and thereby the prevention of its transmission to biological species at the earth's surface.

Molecules with atmospheric lifetimes exceeding one year generally exhibit a negligible vertical gradient in mixing ratio within the troposphere. Ultimately, the stratospheric mixing ratios are controlled by these mixing ratios at the tropopause, and an increase in average tropospheric concentration for organochlorine compounds is followed inexorably by an increase in their stratospheric concentrations. Furthermore, stratospheric decomposition then inevitably causes increases in the concentrations of the chlorinated compounds formed following photodecomposition of the organic species. These include not only Cl and ClO, but also HCl, $ClONO_2$ and HOCl formed by reactions such as (7) to (9). The

$$Cl + CH_4 \rightarrow HCl + CH_3 \tag{7}$$

$$ClO + NO_2 + M \rightarrow ClONO_2 + M \tag{8}$$

$$ClO + HO_2 \rightarrow HOCl + O_2 \tag{9}$$

measured growth in the tropospheric organochlorine content is necessarily followed by an increase in Cl/ClO content at 40 km, and the chain reaction of (2) and (3) then leads directly from photochemical theory to a diminished average concentration of ozone at that altitude.

The concerns for changes in atmospheric ozone can be divided into two major categories: changes in total column of ozone, and changes in the concentrations at particular altitudes. The penetration of ultraviolet radiation to the surface of the earth is determined almost entirely by the total amount of ozone in the atmospheric column, with very little dependence on the altitude distribution of this ozone. However, if the prime concern is with processes such as the conversion of ultraviolet energy into heat after absorption by ozone (i.e. with the temperature structure of the stratosphere), then a redistribution of ozone to different altitudes is extremely important.

Measurements of the total amounts of ozone in a vertical column of the atmosphere can be made with a Dobson spectrometer from the penetration of 300-320 nm ultraviolet radiation to the earth's surface.

An alternate technique uses the back-scattered solar ultraviolet (BUV) radiation reflected into space and measured outside the atmosphere from an orbiting satellite. The vertical distribution of ozone within this total column can be measured with the ground-based Dobson instrument through the "umkehr" technique, which depends upon the variation in ultraviolet penetration versus solar zenith angle over a period of several hours. The vertical distribution of ozone can also be determined from the wavelength dependence of the BUV signal.

Statistical analysis of the world-wide umkehr data has shown significant loss (about 3%) of ozone at 40 km over the past decade in amounts consistent with the expectations from photochemical theory [Reinsel *et al.*, 1984]. This conclusion is contrary to that stated in an earlier paper in which no such diminution was found [Reinsel *et al.*, 1983], but which had no corrections for the well-known perturbation of umkehr results by light-scattering from volcanic particulates. Angell and Korshover [1983a] have also interpreted the umkehr data to indicate ozone depletion in the upper stratosphere over the past decade. They avoided any correction for light-scattering from volcanic dust by choosing an overall time interval straddling the large volcanic eruption of Fuego in 1974. Analysis of the BUV data from the satellites Nimbus-4 and Nimbus-7 has likewise shown evidence for ozone depletion at 40 km over the decade of the 1970s [Heath, 1981].

Calculations of the aeronomic consequences of the depletion of ozone at 40 km altitude indicate an expected decrease in atmospheric temperatures between 40-50 km [N.A.S., 1979]. Separate evaluations of the atmospheric effects from increasing concentrations of CO_2 have also predicted a decrease in upper stratospheric temperatures. An approximate 5°C decrease in average temperature at the stratopause has been reported during the 1970s [Angell and Korshover, 1983b], but the observed decrease is larger than that generally calculated for the combined effects from ClO_x-induced ozone decreases at 40 km plus increased CO_2 concentrations throughout the stratosphere. One recent report, however, has indicated calculated temperature changes of the same magnitude as actually observed over the past decade when the two effects are considered together [Brasseur *et al.*, 1983]. Close comparisons between this calculation and others indicating lesser temperature changes have not yet been carried out to determine the origin of these discrepancies among atmospheric models.

The predictions of the extent of future diminution with increasing atmospheric chlorine content of the total vertical column content of ozone have fluctuated considerably over the past decade as further information has become available about the chemistry of the troposphere and lower stratosphere [N.A.S., 1976, 1979, 1982, 1984]. The current estimates are substantially lower than the 15 ± 5% depletions calculated about five years ago [N.A.S., 1979]. Some of these re-evaluations have been caused by improved accuracy in measurements of chemical or photochemical reaction rates, or by the inclusion as very important to the overall calculation of additional chemical reactions and reactants (e.g. $ClONO_2$, HOCl, HO_2NO_2). Other changes have been brought about by the recognition that the concentrations of many trace species are increasing significantly with time, in addition to the well-established increases for CO_2 and the chlorofluoromethanes. Among the other species which are changing are CH_4, N_2O, and tropospheric O_3 [N.A.S., 1982, 1984], while an increase has been postulated for NO_x which has not yet been confirmed in the atmosphere itself. Predictions of future changes in the concentrations of O_3 and other stratospheric species now require simultaneous inclusion of future growth rates for many molecules.

With the chemical understanding of early 1984, predictions of future ozone depletions from increasing ClO_x content generally indicate an eventual average loss of about 3-5% of total stratospheric ozone over the next century. This change is accomplished by much larger decreases (35-50%) around 40 km, combined with an increase in ozone concentrations near 20 km altitude. In these model calculations, the diminution in ozone at 40 km is a direct photochemical consequence of increasing ClO_x concentrations, and the operation of the ClO_x chain of reactions (2) and (3). At the same time, the increased chlorine content interferes in the lower stratosphere with ozone depletion by the NO/NO_2 catalytic chain through the formation of $ClONO_2$, leaving higher ozone concentrations there as a result. Such calculations indicate that $ClONO_2$ should be a major chlorine containing species in the 20-30 km region, accounting for as much as 40-50% of total Cl at some altitudes. Confirmation in the atmosphere of the presence of $ClONO_2$ and of the existence of these calculated large abundances for it would be an important step in validation of the current predictions of future effects from increasing ClO_x concentrations.

Changes in total ozone column concentrations can also arise from changes in other trace species, including N_2O, CH_4, NO_x and CO_2. The growth in the use of subsonic jet aircraft during the past 25 years has led in most atmospheric calculations to steady increases in the amounts of ozone predicted to be present in the upper troposphere and lower stratosphere. Measurements there generally confirm such an increase, without necessarily establishing its mechanistic origin. A less direct effect on total ozone columns can result from the steady increase in tropospheric methane [Rasmussen and Khalil, 1981; Blake *et al.*, 1982; Khalil and Rasmussen, 1983; Rowland *et al.*, 1984b] which slowly lessen the catalytic efficiency of the stratospheric ClO_x chain by increasing the rate of diversion of atomic Cl into less reactive HCl by reaction (7). Methane is also involved in tropospheric reaction sequences which can increase ozone concentrations there. Combinations of such simultaneous changes for each of several trace species can readily lead to predictions of negligible total ozone column changes over the next two or three decades, as well as in the recent past [N.A.S., 1984]. However, all of these calculations are in agreement that none of the projected scenarios for concentration growths in N_2O, NO_x, CO_2 and CH_4 alters the expectation that the increasing content of ClO_x in the upper stratosphere will lead in the next few decades to large losses of ozone in a band centered around 40 km altitude.

Multi-decade observations of total ozone concentrations and trends are necessarily limited to the Dobson spectrophotometer ground stations around the world because satellite observations of ozone only began about 1970. The stations are not distributed equally among all geographic areas and tend to be found in the relatively well-developed countries of the north temperate zone. The quality of the data from these stations is quite variable and a program of calibration of the Dobson instruments has shown errors in the 5-10% range upon recalibration, making extraction of trends in the 1%-3% range over one or two decades very difficult to detect. Komhyr [1982] has reported an overall decrease of about 1% in the average amount of total ozone over North America for the period of 1961-1980, the combination of an average increase during the 1960s and a slightly larger decrease in the 1970s. Small increases in average ozone levels have been reported for other regions of the earth over the same time interval [Angell and Korshover, 1983a], and the overall estimation of changes in the world-wide average ozone content has a substantial statistical margin of error. The limits of statistical detectability of total ozone change on a world-wide basis are less sensitive than the predicted changes for almost all hypothetical scenarios tested in model calculations and no total ozone column change has been established from the data [N.A.S., 1984].

Biological consequences from a decrease in total column ozone can follow through increased penetration to the earth's surface of ultraviolet radiation with wavelengths between 295-320 nm. These wavelengths have the capability of causing deleterious effects for many biological systems, with an increased incidence of skin cancer the primary effect in humans [N.A.S., 1982, 1984]. Such effects are of course contingent on changes in the average total ozone content of the atmosphere, and any such changes to date are within the statistical error of measurement.

The accumulation of chlorofluorocarbons in the troposphere can have physical atmospheric consequences for at least two reasons. As discussed earlier, a decrease in ozone concentration around 40 km can have a direct effect on upper stratospheric temperatures because energy input there is dependent almost entirely on absorption of ultraviolet radiation by ozone. Changes in the ozone concentration at any altitude will affect the energy absorption at that altitude, but these effects are generally more important for ozone in the upper stratosphere than at lower altitudes. The second influential effect of chlorofluorocarbons arises from their direct absorption of outgoing infrared radiation from the earth. The absorption bands in the infrared for molecules containing C-F bonds frequently fall into wavelength regions not strongly absorbed the more abundant polyatomic molecules, chiefly O_3, H_2O and CO_2 [Ramanathan, 1975; Wang *et al.*, 1976; Lacis *et al.*, 1981; N.A.S., 1983, 1984]. The escape of infrared radiation from the earth is necessary to maintain a terrestrial energy balance with the incoming visible solar radiation, and this energy loss in the infrared can be hindered through absorption in the vibrations of polyatomic molecules such as CCl_3F, CCl_2F_2, etc. When the average infrared escape probability is thus reduced, a higher surface temperature is required for the earth in order to increase the probability of energy escape through those wavelength bands still transparent to infrared. The infrared absorption characteristics of CCl_3F, CCl_2F_2 and CCl_4 all add significantly to the greenhouse effect expected from the increasing CO_2 concentrations in the atmosphere. One estimate of the various contributions to the greenhouse effect for the chlorocarbons is, per each 1000 pptv increase: CCl_3F, 0.15°C; CCl_2F_2, 0.13°C; CCl_4, 0.14°C [N.A.S., 1983].

Increasing concentrations of tropospheric methane

The availability of tropospheric air samples from 55°N to 53°S latitudes obtained for halocarbon analysis [Makide and Rowland, 1981] has permitted an extension of our measurements of the world-wide distribution of trace atmospheric species to methane [Mayer *et al.*, 1982]. Only about a dozen air samples were available for our initial latitudinal sequence in early 1978, but subsequent collections have provided much larger numbers of samples, as shown in Figures 5 and 6 for two collection periods during 1982 and 1983. From 1978-1981 most of our southern hemisphere sample collections were made at coastal sites in Brazil and Chile. However, comparisons were made of the relative latitudinal behavior of CH_3CCl_3 and CH_4, based on the assumption that both are chiefly removed

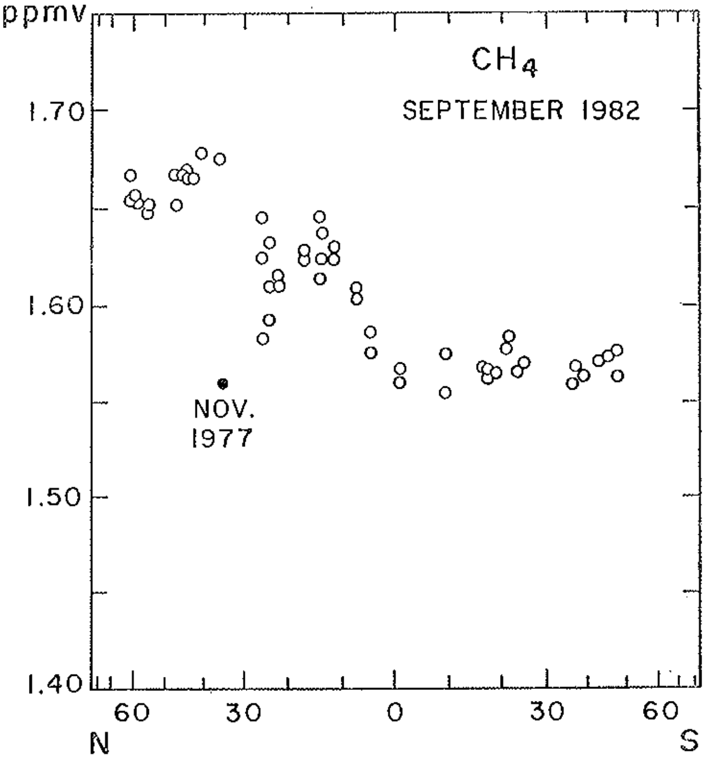

Fig. 5. Tropospheric Concentrations of CH_4 Measured in Remote Locations during September 1982. Solid circle indicates concentrations in secondary standard collected in California desert, November 1977.

from the atmosphere by HO radicals in reactions (5) and (6). Correlations of these two yields as in Figure 7 led us to conclude that about 10% of the earth's CH_4 was being emitted in the Amazon region [Mayer *et al.*, 1982], and that air samples collected in coastal sites in northeast Brazil did not contain actual background levels for CH_4 but were elevated because of emissions from local sources. Our major latitudinal collections below 20°N have been made since 1982 in Pacific island locations.

The latitudinal distributions for CH_4 shown in Figures 5 and 6 are quite different from each other, reflecting as with CCl_3F in Figures 1 and 2 appreciable seasonal changes in the transport of trace species from one latitude to another. Measurements at specific sites have shown variations of 3% in the monthly means in northern hemispheric locations [Khalil and Rasmussen, 1983], which complicate estimates of longer

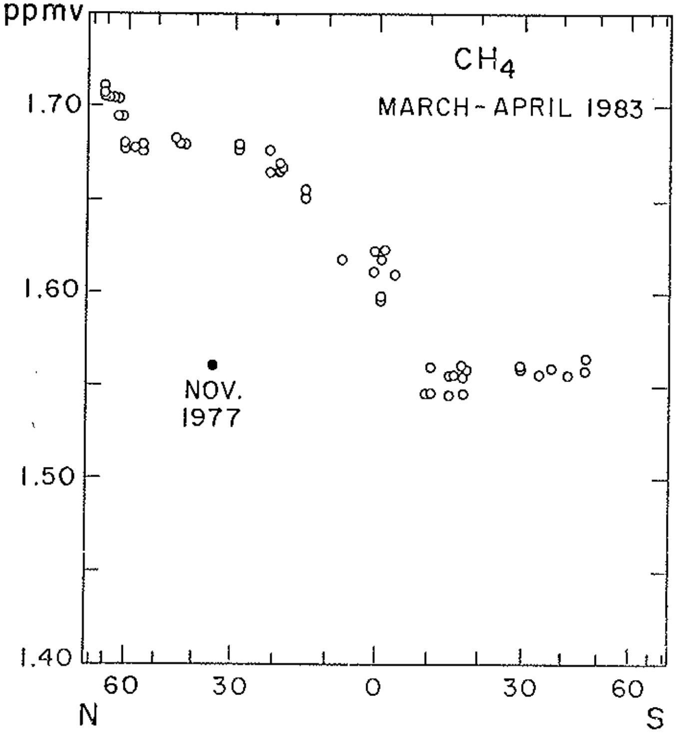

FIG. 6. Tropospheric Concentrations of CH_4 Measured in Remote Locations during March/April 1983. Solid circle indicates concentration in secondary standard collected in California desert, November 1977.

term trends. We have therefore divided the surface area of the earth into sixteen segments of equal surface area (divisions at the equator, and at 7°, 14°, 22°, 30°, 49°, and 61° in each hemisphere) and calculated the average concentration of methane for each segment in each of eight collection periods beginning in January 1978. Air samples from the Amazon region, as illustrated in Figure 7, have been excluded, as have a few which simultaneously showed elevated levels for several of the halocarbons symbolic of recent urban emissions. Segments in the southern hemisphere left without valid samples have been filled by extrapolation from measurements made between 10°S-53°S. Average world-wide concentrations ob-

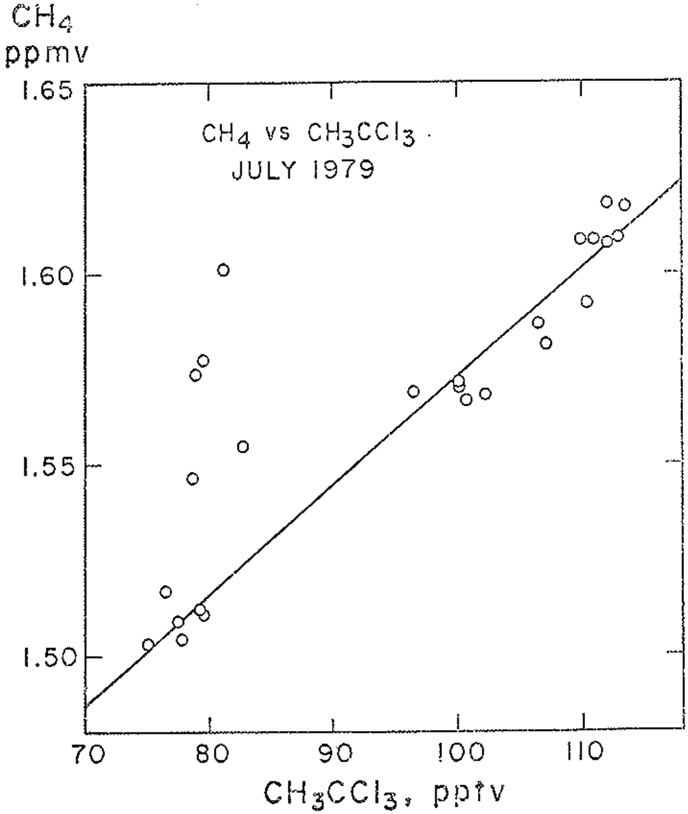

FIG. 7. Correlation of Concentrations of CH_4 and CH_3CCl_3 Measured in the Same Tropospheric Air Samples Collected in Remote Locations during Summer 1979. The points not fitted by the correlation represent samples collected in the Amazon region of South America.

tained from the sixteen segment averages are graphed in Figure 8 for these eight time periods.

The world-wide tropospheric CH_4 concentration has increased steadily during the time period since 1978, and this increase is well represented by the solid line in Figure 8 which corresponds to a rate of increase of 0.018 ppmv per year. The two dashed lines demonstrate increases of 0.018 ± 0.002 ppmv per year, providing outer limits for the observed rate of change in concentration. These values correspond in the early 1980s to an increase of 1.1 ± 0.2% per year, in general confirmation of the increases derived from shorter time series, although slightly less than the 1.4% per year calculated by Khalil and Rasmussen [1983]. The data are satisfactorily fitted with a straight line, and there is no indication

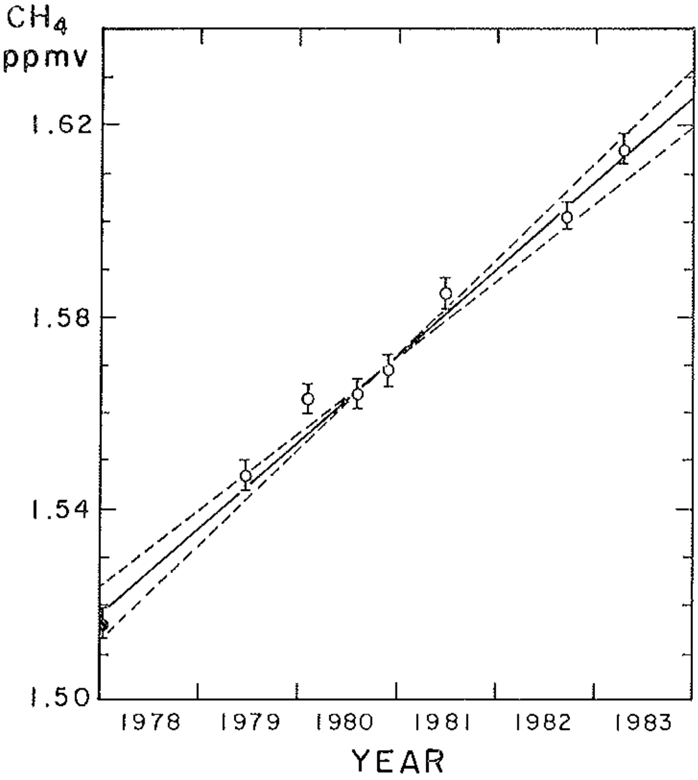

FIG. 8. World-wide Average Tropospheric Concentrations of CH_4 Measured in Remote Locations, 1978-1983.

of any important change in the yearly rate of increase over the six-year period of measurement.

The atmospheric lifetime for CH_4 can be estimated from that for CH_3CCl_3 through the reaction rate constant ratio $k_5/k_6 = 1.5$, leading to an estimate of 9 to 10 years. We have calculated the expected latitude distribution for CH_4 using (a) the transport parameters evaluated from the latitudinal distribution of CCl_3F; (b) the latitudinal distribution of HO sinks from the distribution fitted to CH_3CCl_3 in Figure 4; (c) an estimate that 72% of all CH_4 is emitted in the northern hemisphere; and (d) assumed atmospheric lifetimes for CH_4 of 7, 9, 10 and 13 years. These distributions are shown in Figure 9 in comparison with the CH_4 concentrations

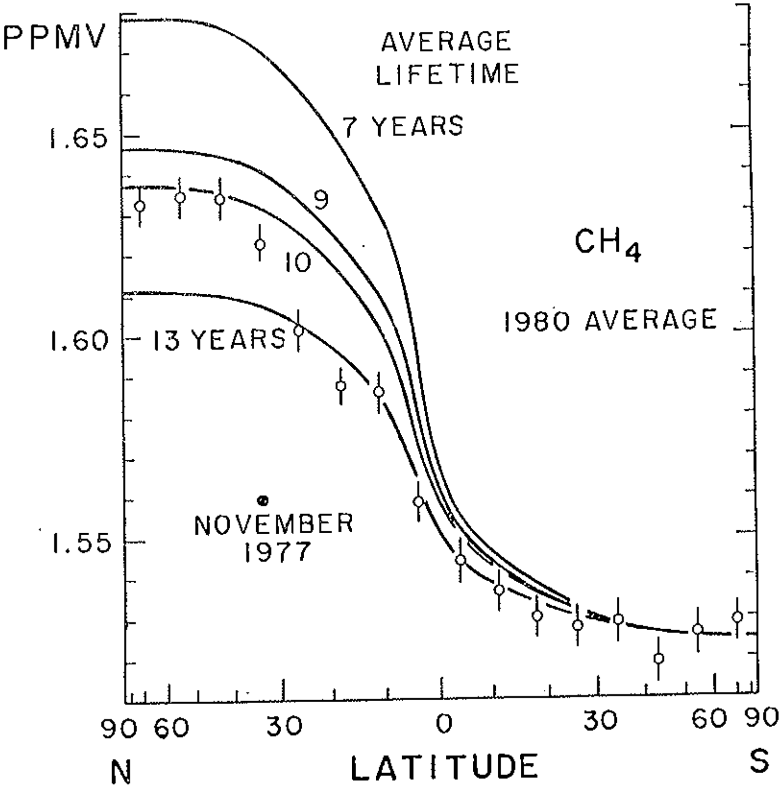

FIG. 9. Year-long 1980 Averages of CH_4 Tropospheric Concentrations versus Latitude Compared with Various Postulated Atmospheric Lifetimes. Northern hemisphere emissions: 72%. Otherwise as in Figure 4.

have any evidence of olefins produced by other plants? Are they in such concentrations that can be interesting or not? We know that many fruits produce a great amount of ethylene.

Rowland

I think I'll defer this to Paul Crutzen. Paul, would you like to answer? He has considered this in more detail than we have.

Crutzen

There definitely are very large emissions of higher hydrocarbons from plants, including ethylene. This has been definitely discovered above the tropical forests in Brazil. The most active emissions are actually isoprene and the terpenes, but there are many other hydrocarbons which are chemically very reactive.

Liberti

I wish to add the following to what Professor Crutzen was saying. There are large amounts of terpenes which are emitted. However, they are terrifically reactive, especially with ozone, so that in order to measure them particular care has to be taken.

Anderson

I would like to resurrect the question that Dr. Chameides raised about the changing rate of oxidation in the troposphere. That to me is the central issue, and if we cannot partition this point between increasing production and decreasing rate of oxidation, what do you think is the approach that should be taken in order to determine what that spot is.

Rowland

The question is whether there is a measurement separate from the increasing concentration of methane that bears on this situation. I am not sure that the accuracy is sufficient to give information. Measurements have been made in Paul Crutzen's group in Mainz by Wolfgang Seiler. He has been measuring the concentration of carbon monoxide over an extended period of time, of the order of a dozen years. The statement which he has made is that he has not observed a change in the carbon monoxide concentration. This is a very difficult statement to make with any accuracy because it is averaged over very substantial variations from one season to another every year. The concentration of carbon monoxide is also controlled by chemical reaction with hydroxyl radical. If the hydroxyl radical concentration has been reduced, then one should see an increase in carbon monoxide concentration that would parallel this increase in methane concentration. It is Seiler's view that his measurements on carbon monoxide do not show evidence for such a change. On the other hand, Rasmussen and Khalil have a paper in press — I received a copy about two months ago — in which they report that they are seeing an increase in carbon monoxide concentrations. Such an increase in carbon monoxide might be an indication of a reduced oxidative capability of the atmosphere.