

METHANE AND CHLOROCARBONS IN THE EARTH'S ATMOSPHERE

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Until the early 1970s my research group was largely concerned with laboratory studies of gas phase tracer chemistry, usually using molecules containing radioactive labels such as ^{14}C or tritium. A decade ago we expanded these tracer studies from the laboratory to the atmosphere, and began with an attempt to determine the eventual fate there of CCl_3F , trichlorofluoromethane, colloquially known as Fluorocarbon-11. This compound was discovered in the atmosphere in 1970 by Jim Lovelock, and shown by him in 1971 to be present everywhere in the troposphere [1]. I first heard of Lovelock's observations early in 1972 in the context of a proposal that this molecule could serve as a very useful tracer of atmospheric motions because of its chemical inertness. I found Lovelock's discovery intriguing, and began to consider the general problem of the possible atmospheric behavior of molecules which are not very chemically reactive under most circumstances. Fluorocarbon-11 has a companion molecule, CCl_2F_2 (Fluorocarbon-12), which is also produced industrially in substantial quantities and was soon found in the atmosphere as well. When Mario Molina joined my research group in 1973 as a postdoctoral associate, we began a systematic investigation of the possible chemical reactivity of CCl_3F and CCl_2F_2 in the atmosphere.

The three most important reaction routes which can remove gaseous organic molecules from the atmosphere are direct solar photolysis, solubility in rain, and reaction in the troposphere with free radicals such as hydroxyl. However, examination of these possibilities in 1973 led Molina and me to conclude that none of them would be effective for CCl_3F or CCl_2F_2 . They are transparent in the visible and near ultraviolet wavelengths, and therefore cannot be photolyzed in the troposphere. They are insoluble in water, and are therefore not removed by rain. And they do not react with hydroxyl radicals. Because none of these primary removal processes affects CCl_3F or CCl_2F_2 , they must have relatively long lifetimes in the atmosphere, and be removed by some secondary process which would be of only minor importance for reactive gaseous molecules. Our investigation settled on solar ultraviolet photolysis in the stratosphere as the major removal process for CCl_3F and CCl_2F_2 , as shown in reactions (1) and (2), [2, 3] and subsequent study has confirmed this dominant role.⁴⁻⁷



Both of these molecules will release chlorine atoms if photolyzed, but the process first requires absorption of ultraviolet radiation, and each is transparent even for wavelengths as short as 230 nanometers. Solar ultraviolet light shorter than 230 nanometers is found only in the middle stratosphere or higher because such radiation is strongly absorbed by O_2 and O_3 and does not penetrate down into the troposphere. Molecules such as CCl_3F and CCl_2F_2 can only be exposed to u.v. radiation in the 190–230 nm wavelength band if they have first risen high enough in the atmosphere to be above most of the O_2 and O_3 . At 30 km, for example, 99% of O_2 and about 80% of O_3 is at lower altitudes, and 190–230 nm radiation is still present in the incoming solar flux. Both Fluorocarbons–11 and –12 can be photolyzed near 30 km, and will release chlorine atoms through reactions (1) and (2). Such photolysis occurs increasingly rapidly as the altitude of exposure increases from 25 to 30 to 35 km, and little CCl_3F or CCl_2F_2 survives above 35 km. Because only 1% of the atmosphere lies above 30 km, almost all of the fluorocarbons are always found at considerably lower altitudes, protected from solar photolysis by the absence of 190–230 nm ultraviolet radiation. With stratospheric photodissociation as their only important removal process, these molecules must have very long average lifetimes in the atmosphere before undergoing reactions (1) and (2). In 1974 Molina and I estimated these atmospheric lifetimes as 40 to 80 years for CCl_3F and 75 to 150 years for CCl_2F_2 ; current estimates are in the 60 to 80 and 100 to 150 year ranges, respectively. [7–9] It is not just coincidence that the chlorine decomposition products from these compounds are found at the same altitudes with abundant ozone concentrations. After all, photolysis of the chlorofluorocarbons cannot occur except at altitudes higher than most of the ozone in the atmosphere, and the chlorine atoms released from (1) and (2) then have to pass back down through the major fraction of ozone before being removed (as HCl) in rain.

Fifty years ago Sydney Chapman explained ozone in the upper atmosphere using the four reactions shown in (3) to (6). In modern terms, this set of equations is usually described as the ‘Chapman reactions’, or the ‘pure oxygen reactions’. The rapid interchange between O and O_3 in reactions (4)



and (5) leads to another bit of useful terminology: ‘odd oxygen’, which refers to both O and O_3 , in contrast to the abundant O_2 . Note that the combination of O with O_2 in (4) does not alter the concentration of odd oxygen – there is one odd oxygen molecule on each side of the equation. One odd oxygen molecule is also on each side of equation (5). In the Chapman cycle, the only reaction which actually increases the concentration of odd oxygen is the direct photolysis of O_2 in (3), which increases odd oxygen by two molecules. The only process in this cycle which removes odd oxygen is the combination of O and O_3 in (6) which removes two molecules of odd oxygen. Sources which actually

increase total atmospheric ozone are basically limited to reactions which increase total odd oxygen, and ozone sinks capable of reducing total ozone are limited to those reactions which decrease total odd oxygen.

During the years from 1930 to about 1960, the four Chapman reactions provided a satisfactory semi-quantitative explanation for the observed amounts of ozone found in the stratosphere. Remember that actual measurements of solar ultraviolet fluxes for wavelengths shorter than about 295 nm were very scarce prior to the first orbiting satellites in the 1950s. Chemical kinetic measurements were also less precise then, especially over the lower temperatures and pressures characteristic of the stratosphere. By 1960, however, some scientists had realized that the Chapman cycle could not be the whole ozone story because the amounts of ozone actually found in the atmosphere were considerably less than the amounts expected from these four oxygen reactions alone. Either the source strength for formation of odd oxygen was being overestimated, or some undiscovered process was removing it. The missing component turned out to be an ozone sink, or rather several sinks, all of them involving free radical catalytic chain reactions.

In the past twenty years or so, the description of stratospheric ozone chemistry has been greatly altered by the inclusion of the chemistry of free radicals. The three most important families of free radicals in the stratosphere involve oxides of hydrogen, nitrogen and chlorine – the HO_x series of H, HO and HO₂; the NO_x family of NO, NO₂ and NO₃; and the ClO_x species Cl and ClO – colloquially, these are known as HO_x, NO_x and ClO_x. The most important NO_x reactions in the stratosphere are given in (7) and (8), and sum together to give the same result as in reaction (6). Both



(7) and (8) result in the removal of a single molecule of odd oxygen, but the combination leads an unchanged total concentration of NO or NO₂. With no permanent variation in NO or NO₂, these NO_x species play the role of catalysts and the pair of reactions is described as the NO_x catalytic chain reaction. A comparable ClO_x catalytic chain is shown in (9) and (10), while similar chains can be written for the HO_x family as well.



The chemical reaction rate constants corresponding to Equations (9) and (10) have been measured in the laboratory and are very rapid. Using the measured stratospheric concentrations of O and O₃ together with these reaction rate constants, the average rate of removal of a chlorine atom in the stratosphere by (9) can be calculated to require about one second, while the removal of ClO by reaction (10) takes about one minute. The net result is that the ClO_x cycle of reactions (9) and (10) is completed in one minute, with the removal of two odd oxygen molecules through conversion back to O₂. The

cycle then repeats itself the next minute, and the next, and so on until the catalytic chain is diverted by some other chemical reaction. The usual termination for the sequence of (9) + (10) occurs through the competitive reaction of Cl with CH_4 to form HCl, but on the average about 1000 ClO_x cycles are completed before being stopped. The formation of HCl is only a temporary relief from the chain reaction, however, for the chlorine is released again by HO attack on HCl, and about 100 cycles through HCl are completed before final removal through rainout from the troposphere. The ClO_x catalytic chain thus provides a very effective multiplier through which a single chlorine atom can eventually convert about 100 000 molecules of odd oxygen back into O_2 before being permanently removed from the atmosphere. The NO_x , ClO_x and HO_x catalytic chains supplement reaction (6) as additional channels for removal of odd oxygen from the stratosphere, and together provide a satisfactory quantitative explanation of the observed total concentration of ozone in the atmosphere. The possible influences of man on stratospheric ozone begin with the introduction into the atmosphere of additional sources of NO_x or of chlorine. If more chlorine compounds are in the atmosphere now or in the future than were present in the past, more chlorine atoms will be in the stratosphere to participate in reactions (9) and (10), and the total removal of ozone by the ClO_x catalytic chain will be larger, such that the average ozone concentration will be reduced. The amounts of relatively inert chlorofluorocarbon compounds introduced into the atmosphere reached one million tons yearly in the early 1970s and have remained at about that level for the past decade.

Atmospheric molecules can be conveniently separated into two groups: those which absorb radiation of wavelength longer than 295 nm, and those which do not. This dividing line is determined by the average concentration of ozone present in the atmosphere because of the decreasing absorption cross sections for ozone as the wavelength of ultraviolet radiation increases from 280 nm to 320 nm. Absorption by ozone at 280 nm is sufficiently strong that all such solar radiation is absorbed in the high stratosphere. Absorption at 320 nm is so much weaker that the major fraction of solar radiation at this wavelength passes through the entire atmosphere and reaches the Earth's surface. The crossover from strong absorption to weak is marked by the empirical observation of photon fluxes at the surface near 295 nm, and is often described as the 'ozone cutoff'. Those molecules whose absorption cross sections extend to wavelengths longer than 295 nm are exposed to energetic radiation which they can absorb at all altitudes down to the surface itself, and usually undergo rapid photodecomposition in the atmosphere. All of the permanent atmospheric gases such as N_2 , O_2 , CO_2 , N_2O , CH_4 , etc., are transparent in the near ultraviolet and visible wavelength regions. Molecules such as Fluorocarbons-11 and -12 which are also transparent at wavelengths longer than 295 nm are photochemically inert in the troposphere, protected from the shorter wavelength ultraviolet radiation by its absorption in stratospheric ozone.

The strength of absorption of radiation by ozone exhibits a peak between 250 nm and 260 nm, and declines on either side of this maximum. At wavelengths below about 190 nm absorption by O_2 becomes very strong, and such radiation is predominantly

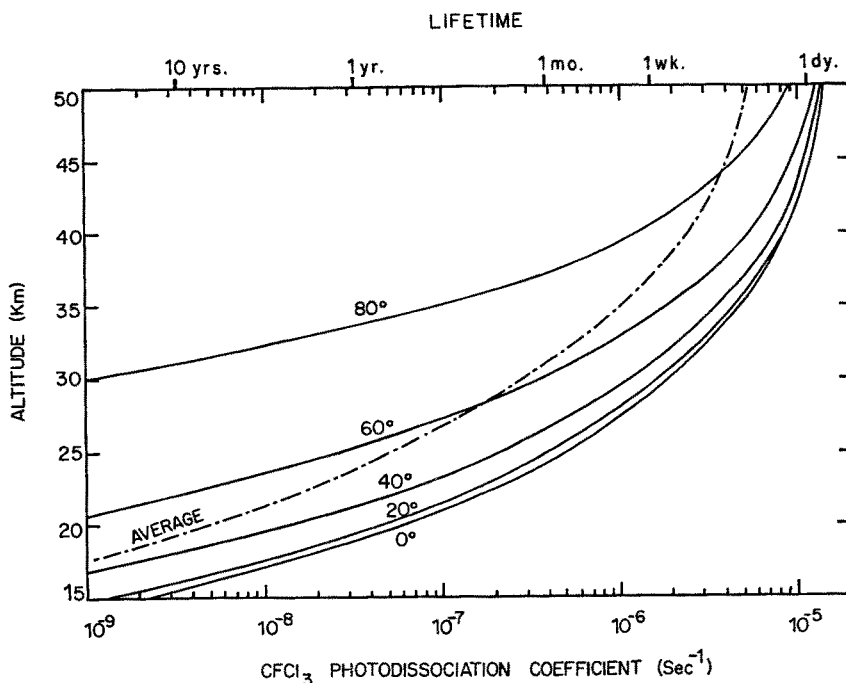


Fig. 1. Photodissociation rates for CCl_3F versus altitude.

removed by (3) rather than (5) because of the much higher concentrations of O_2 versus O_3 . For molecules transparent beyond 295 nm, the next wavelength region of importance for atmospheric photocomposition is in the partial 'window' of 190–230 nm, flanked below 190 nm by the strong absorption of O_2 and above 230 nm by the maximum in ozone absorption near 250 nm. The solar photon flux can be calculated at each altitude from the known flux outside the atmosphere, coupled with its progressive reduction at lower altitudes by absorption in O_2 and/or O_3 . These solar fluxes are also dependent upon the solar zenith angle because slanting sun angles provide longer pathlengths and increased probabilities for absorption. The total probability per second for photodecomposition can be calculated for each particular molecule as the cross-product of the photon absorption cross section times the available solar flux at that altitude and zenith angle, summed over all wavelengths. In the 190–230 nm region, the absorption cross sections for CCl_3F are larger than those of CCl_2F_2 by roughly a factor of ten, leading to an expectation of more rapid photodissociation for CCl_3F . The probabilities for photodecomposition of CCl_3F at each altitude for several zenith angles are shown in Figure 1, together with an instantaneous world average weighted over all zenith angles. The average photodecomposition rate for CCl_3F at 30 km in Figure 1 is $3 \times 10^{-7} \text{ s}^{-1}$, corresponding to an average lifetime at that altitude of about one month. The photodecomposition rate for CCl_2F_2 at 30 km is about $3 \times 10^{-8} \text{ s}^{-1}$, for an average lifetime there of about one year.

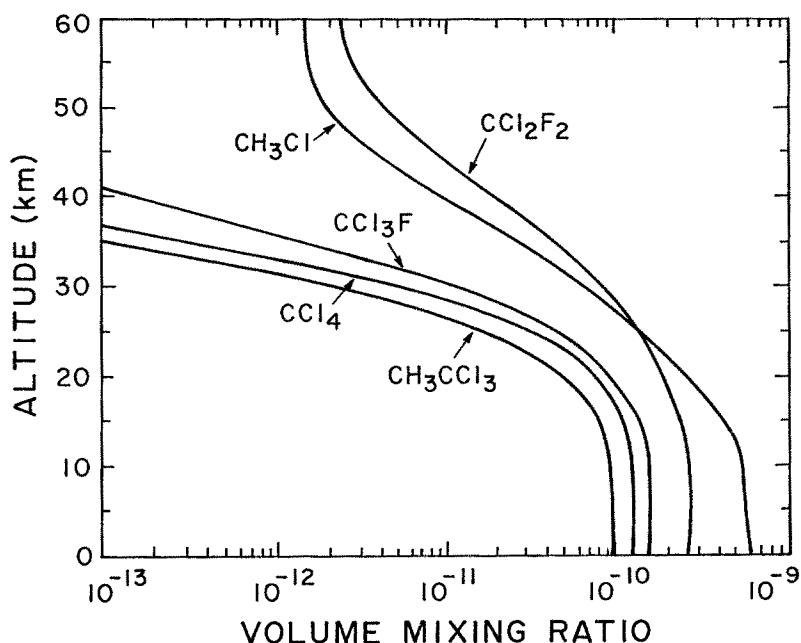


Fig. 2. Predicted vertical mixing ratio profiles for several chlorocarbon compounds.

The photodissociation probabilities for CCl_3F versus altitude can then be combined with a vertical eddy diffusion coefficient – a one-dimensional parameterization of the vertical component of the three-dimensional motions in the atmosphere – for a prediction of the altitude dependence of the CCl_3F mixing ratio. Basically, gases mix quite rapidly up to the tropopause, but the mixing processes are much slower in the stratosphere, and much steeper gradients are found for molecules which strongly absorb solar ultraviolet radiation. The averaged photon absorption cross sections decrease steadily in the series CCl_4 , CCl_3F , CCl_2F_2 , $\text{CClF}_2\text{CClF}_2$ and CClF_2CF_3 , and the predicted mixing ratio profiles with altitude are progressively less steep. Predicted profiles for several halocarbons are shown in Figure 2.

During the past few years the techniques for collection and measurement of trace concentrations of halocarbons in the stratosphere have been greatly improved, and simultaneous vertical profiles have now been measured for as many as a dozen different trace components. An extensive data set obtained up to 35 km altitude by Fabian and Penkett and their colleagues is shown in Figure 3. [10] Examination of this data shows a very steep gradient in the mixing ratio for CCl_3F , lesser gradients for CCl_2F_2 and $\text{CClF}_2\text{CClF}_2$, and essentially no gradient at all versus altitude for CClF_2CF_3 or CF_4 . Carbon tetrafluoride is exceedingly inert photochemically, with no absorption at wavelengths longer than 110 nm. Consequently, it has no photochemical interactions in the stratosphere, and no removal process there. It is undoubtedly subject to decomposition processes at much higher altitudes, but its atmospheric lifetime is believed to be in excess of 10 000 years because of the absence of tropospheric or

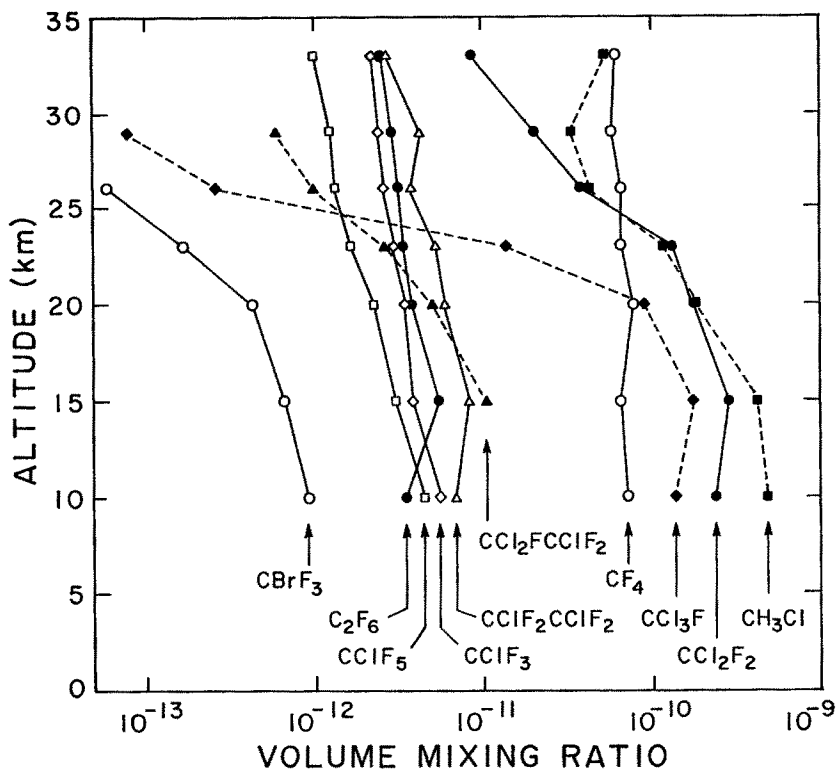


Fig. 3. Measured vertical mixing ratio profiles for several halocarbons.

stratospheric removal processes. [11] The observation of very little vertical gradient in the mixing ratio of CF_4 versus altitude illustrates the ready penetration into the upper stratosphere by such inert molecules released at the surface. In contrast, a steep gradient is found for CCl_3F – not because the stratospheric mixing process is different for it than for CF_4 , but because upward mixing is slower than the process of photodecomposition. The individual atoms carried upward initially as CCl_3F do continue to penetrate upward, but in other chemical forms such as ClO , HCl and HF .

My own research group initiated in 1977 a program of monitoring the concentrations of several halocarbon gases at various ground level locations around the world, and added measurements of methane to the list in early 1978. Many other research groups are also carrying out such measurements, usually with somewhat different procedures and motivations. Our approach has been to construct two-liter stainless steel canisters with a single stainless steel valve, avoiding as much as possible moving parts, stopcock grease, O-rings, auxiliary pumps, etc. We simply evacuate the canister in the home laboratory, transport it to a remote ground level location, open it to the ambient atmosphere, and return it to the laboratory for gas chromatographic assay of its contents.

The time-scale of interest in these experiments is very much shorter than that in most

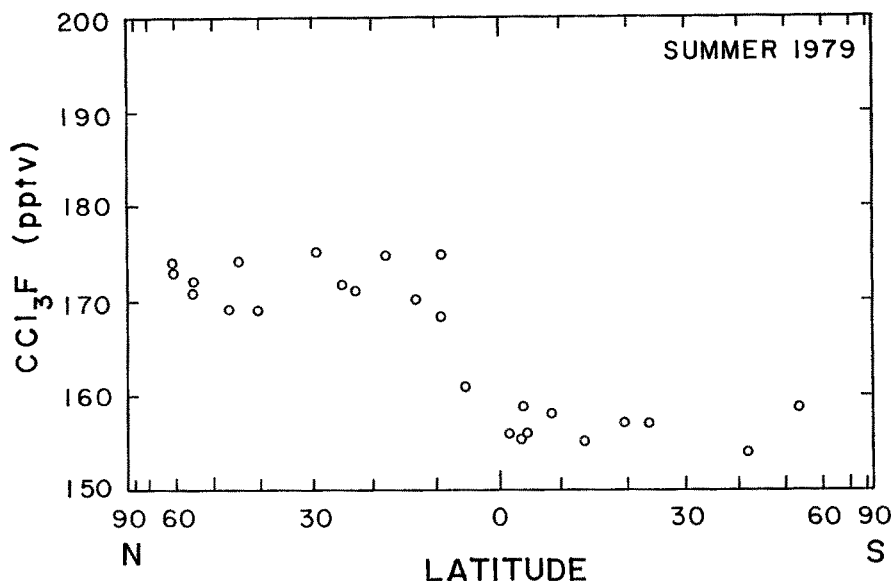


Fig. 5. Tropospheric concentrations of CCl_3F . Summer 1979.

of these canisters of tropospheric air are then analyzed by gas chromatography. One set is analyzed with an electron capture detector which has great sensitivity for chlorinated molecules, with typical results such as those illustrated in Figure 4. Our initial aim had been to make accurate measurements for methylchloroform, CH_3CCl_3 , but we obtain equally good data from the aliquot on the concentrations of CCl_2F_2 , CCl_3F and CCl_4 . During the summer of 1979 we obtained the concentration data on CCl_3F shown in Figure 5 on a scales given in parts per trillion by volume (pptv, 10^{-12}). That summer all of the data showed essentially the same concentration everywhere above 7°N latitude. All of the data from the equator south have another nearly constant concentration, lower than that in the north. The one intermediate concentration sample was picked up at 5°N in Surinam, which was at the time in the middle of the Intertropical Convergence Zone (ITCZ), the meteorological boundary between northern and southern hemisphere air. Gaseous exchange between the northern and southern hemispheres had not been extensive for the previous few months, and a very sharp gradient in CCl_3F concentration existed between the equator and 10°N . This condition is neither typical nor highly unusual. In some seasons there is a steady small north/south gradient covering the entire latitude range from about 35°N to 20°S , and in others the gradient is steep and confined to a much smaller latitude range, as in Figure 5.

Another facet of the summer 1979 data is illustrated in Figure 6 which shows them with the 1971 CCl_3F data of Lovelock. Our own data for the summers of 1980 and 1981 are shown in Figures 7 and 8, and by 1983 the northern hemisphere concentrations of CCl_3F had risen above the scale used in these figures. Clearly there has been a continuing substantial increase in the concentration of CCl_3F throughout the world

during the last dozen years. A very extensive program called the Atmospheric Lifetime Experiment (ALE) is monitoring the concentration of CCl_3F several times a day at four different stations, producing thousands of individual data points. The monthly averages of these ALE data from four stations are shown in Figure 9, and again exhibit this rapid buildup of CCl_3F concentrations at all latitudes. [8, 9] Over a period of time several different research groups have carried out absolute calibration experiments for CCl_3F at the 10^{-10} level in air, and the likelihood now is that the absolute concentration can be measured with an accuracy of $\pm 5\%$ or better.

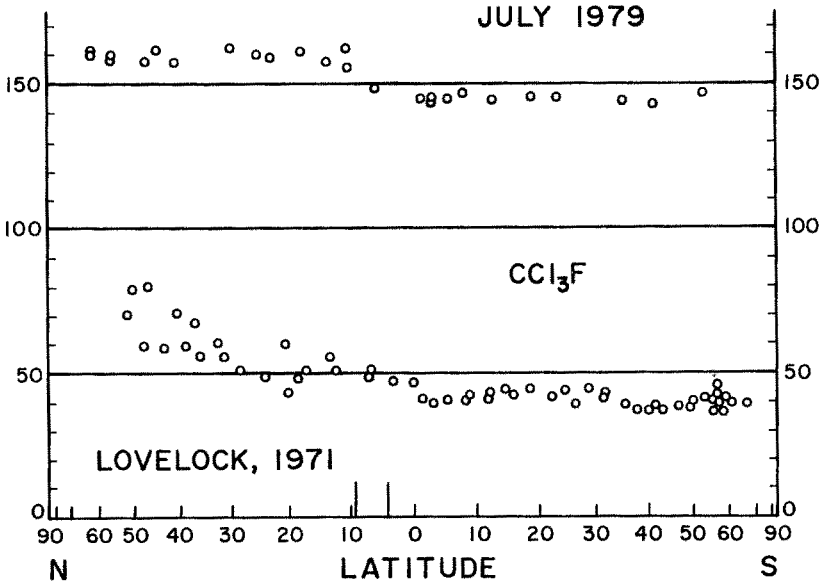


Fig. 6. Tropospheric concentrations of CCl_3F . 1971 versus 1979.

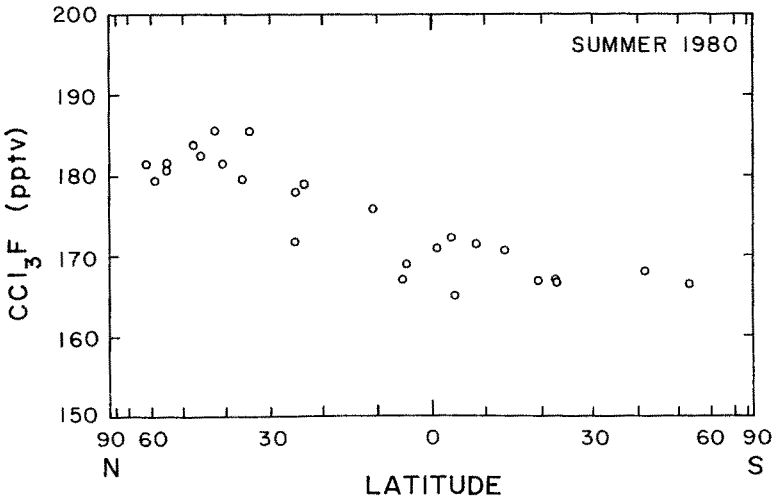


Fig. 7. Tropospheric concentrations of CCl_3F . Summer 1980.

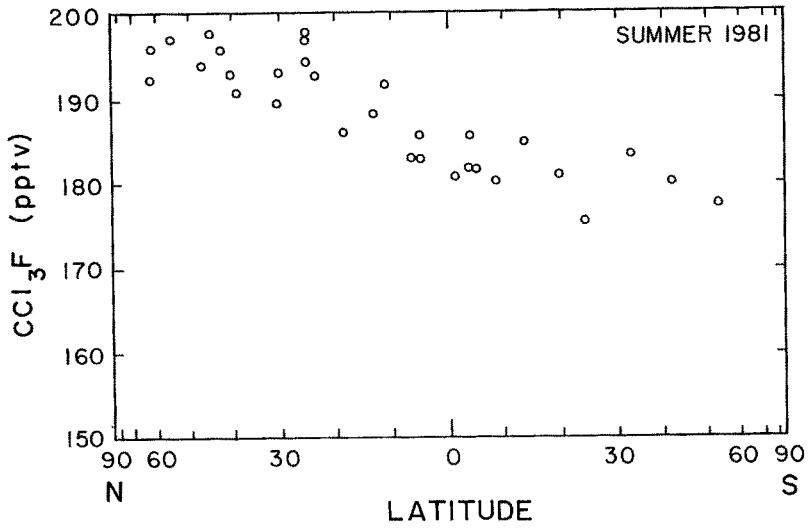


Fig. 8. Tropospheric concentrations of CCl_3F . Summer 1981.

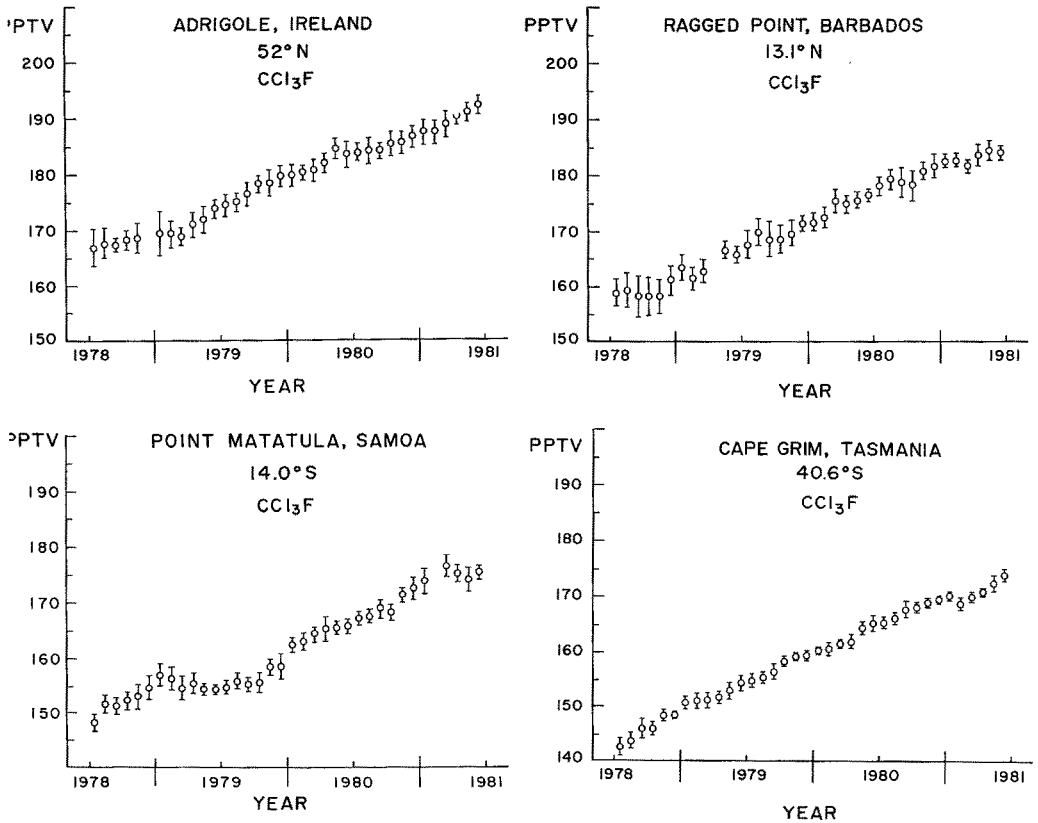


Fig. 9. Measured concentrations of CCl_3F at four locations, data of atmospheric lifetime experiment (See refs. 8, 9).

What is the cause of this steady increase in concentration for CCl_3F and for even larger increases found for CCl_2F_2 ? The explanation is simple and has two parts: (1) Fluorocarbons-11 and -12 continue to be manufactured in substantial quantities and eventually released to the atmosphere; and (2) no rapid atmospheric removal process exists for CCl_3F (fluorocarbon-11) or CCl_2F_2 (fluorocarbon-12). Two approaches can be taken to the quantitative question of the tonnage of CCl_3F and CCl_2F_2 being released to the atmosphere each year. One is to examine the yields in the manufacturing process. The other is to measure the actual concentration increase in the atmosphere. Most of the fluorocarbon manufacturers have grouped together under the auspices of the Chemical Manufacturers Association (C.M.A.) and have arranged for the accumulation of individual production data into world-wide totals. The manufacturing data from individual companies or countries have not been separately released, even – or rather especially – not to one another. Some of the major uses include automobile air-conditioning (Fluorocarbon-12); the blowing of polyurethane foam (Fluorocarbon-11); and as aerosol propellant gases (mixture of Fluorocarbons-11 and -12) in countries other than the United States, Canada and Scandinavia. The fractional release to the atmosphere and the time delays involved in such release have been evaluated separately for each specific end usage, and then applied to the production data to provide C.M.A. estimates of the yearly world-wide atmospheric release of Fluorocarbons-11 and -12 over the past half century. One important omission from the direct input is production data from the governments in eastern Europe, but these

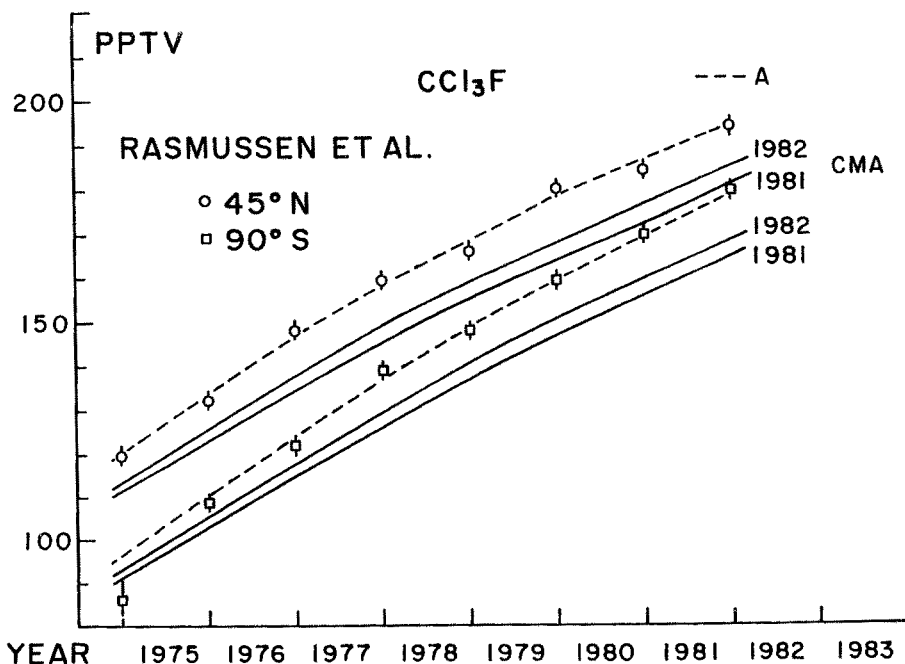


Fig. 10. Calculated time dependence of atmospheric concentrations of CCl_3F . Data of Rasmussen *et al.* (*Science* 211, 285, 1981).

contributions have been separately estimated by C.M.A. and included in their worldwide totals.

I have shown in Figure 10 our comparison of the measured CCl_3F atmospheric concentrations with the expectation from the C.M.A. emission estimates though 1980 as published in the summer of 1981, [12] and with their revision of these estimates published in 1982. [13] The fit could be improved, and we have made a separate estimate of the atmospheric release from the slope of the measured increases in absolute concentrations. The two C.M.A. estimates and our differential estimate are all shown in Figure 11. There are some differences – for example, the C.M.A. estimates place the maximum in yearly release in 1974, while our evaluation of the atmospheric measurements indicates a maximum in 1976, the year in which the U.S. government announced the forthcoming ban on Fluorocarbon-11 as a propellant gas for non-essential applications. For most purposes, however, these differences are not too large, for the accumulated totals are within about 10% of one another. The steady exponential increase in yearly emissions of CCl_3F from 1955 to 1974 was terminated in the mid-1970s, and has now leveled off into a more or less steady yearly release to the atmosphere of 250 to 300 kilotons of CCl_3F . The fit of our differential calculations of emissions to the ALE data is shown in Figure 9.

We first applied this procedure early in 1982 to an evaluation of the yearly emissions of CCl_2F_2 . The C.M.A. estimates published in 1981 indicated progressive reductions in atmospheric emissions of CCl_2F_2 from a peak of 420.3 kilotons per year in 1974 to 333.7 kilotons in 1980 [12], but we were not able to confirm this from the atmospheric measurements. The slope of atmospheric concentrations versus time indicated that the peak emissions occurred in 1978 or 1979, and were still in the 400 kiloton per year

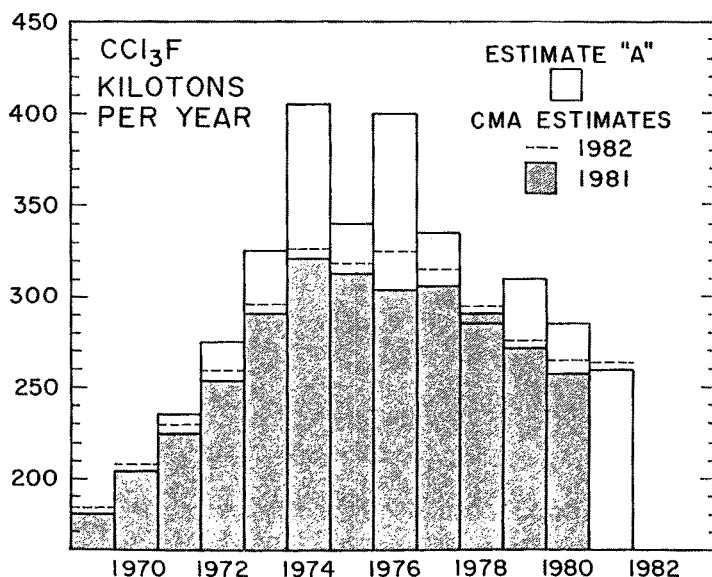


Fig. 11. Estimated yearly emissions of CCl_3F to atmosphere C.M.A. 1981 (ref. 12); C.M.A. 1982 (Ref. 13); A from Ref. 16.

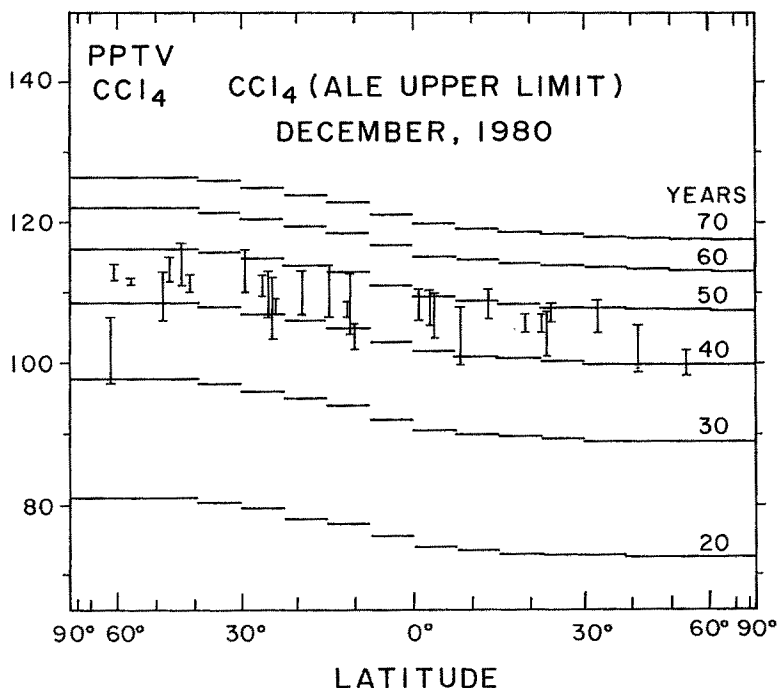
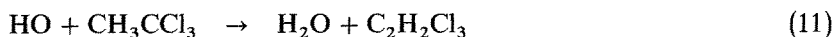


Fig. 12. Measured and calculated tropospheric concentrations for CCl_4 , December 1980.

range, comparable to the emissions in 1974. Much of this discrepancy was removed when substantially increased estimates were published in 1982 [13] and 1983 [14] by C.M.A., showing an average value of 412 kilotons per year from 1974 through 1981, and 422.8 kilotons in 1982.

We have also measured carbon tetrachloride, and have regularly found only a small gradient in concentration from northern to southern latitudes, as shown in Figure 12. We have calibrated a simple atmospheric model with latitudinal transport parameters fitted to reproduce the CCl_3F data, and then applied the same parameters to the CCl_4 data. Carbon tetrachloride has been produced and released to the atmosphere over a much longer time than the chlorofluorocarbons, and the data are fitted quite satisfactorily. The atmospheric lifetime shown in Figure 12 is 45 years, but other plausible emission estimates are consistent with other lifetimes as long as 90 years. Previous indications of concentrations of CCl_4 too large to be explained solely by industrial sources have disappeared with reevaluation of absolute calibrations.

We have measured the latitudinal distribution of CH_3CCl_3 , which shows a much steeper north/south gradient, as illustrated in Figure 13. In contrast to the observations with CCl_3F and CCl_2F_2 for which most of the emitted gas is still in the atmosphere, only about half of the released CH_3CCl_3 is still there, corresponding to an atmospheric lifetime evaluated by us as 6.9 ± 1.2 years. [15] The hydrogen atoms in CH_3CCl_3 can readily be attacked by hydroxyl radicals in the troposphere, as in (11), and this is



its dominant removal process. With the same atmospheric transport model used for CCl_3F and CCl_4 , we can generally reproduce the observed changes in concentration with latitude if the atmospheric lifetime is assumed to be 6 to 7 years, as shown in Figure 13. [16]

From such measurements of the changing concentrations of several chlorocarbon compounds, it is possible to reconstruct the probable organochlorine concentrations in the troposphere earlier in this century, and to predict the likely developments in the future. The five organic compounds carrying the most chlorine in the troposphere in 1983 are CH_3Cl , CCl_4 , CCl_3F , CCl_2F_2 and CH_3CCl_3 . Methyl chloride is observed now at about 600 pptv and was presumably there in 1900 at about the same level because its sources are believed to be largely of natural origin. At the beginning of the century, however, none of the other four chloro compounds had yet been manufactured for widespread industrial use. For that reason, the total organochlorine concentration in 1900 was probably around 600 pptv, with CH_3Cl the prime component. Then, along in the 1920s and 1930s carbon tetrachloride began to be used extensively, followed by the other three in the 1950s and 1960s. The organochlorine concentration of the troposphere probably reached 1500 pptv about 1970 when Lovelock first started measuring CCl_3F , and passed 3000 pptv in the early 1980s. The total amount of organochlorine in the troposphere approximately doubled from the early part of the

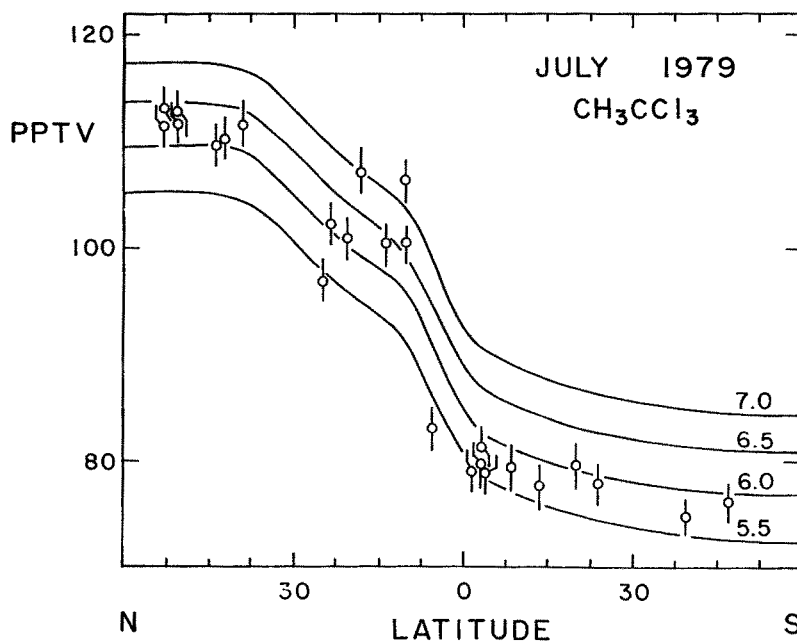


Fig. 13. Measured and calculated tropospheric concentrations for CH_3CCl_3 . Summer 1979.

century to 1970, and has doubled again during the past dozen years. We can expect the concentration of CH_3CCl_3 to level off in the next one or two decades, barring major increases in emission rates, because of its atmospheric lifetime of only 6 or 7 years. However, the lifetimes for CCl_4 , CCl_3F and CCl_2F_2 are all 60 to 100 years or more, and these will continue to accumulate rapidly as long as they continue to be released at the current yearly rates of about 100, 300 and 400 kilotons, respectively.

The atmospheric lifetime of methane can be estimated by comparison with that of methylchloroform because both are primarily removed by reaction with hydroxyl radicals, as in (11) and (12). The measured laboratory

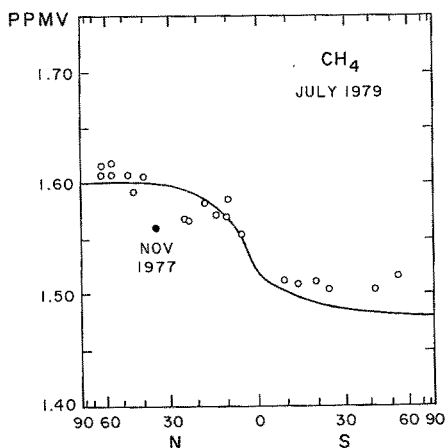


Fig. 14. Summer 1979.

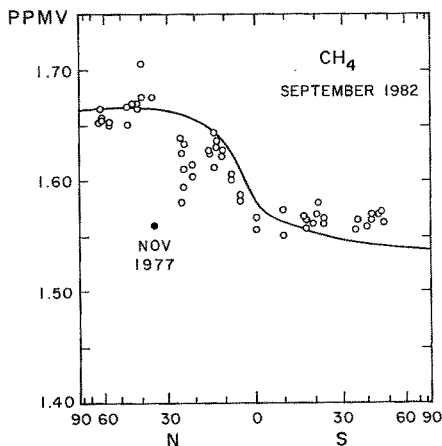


Fig. 15. September 1982.

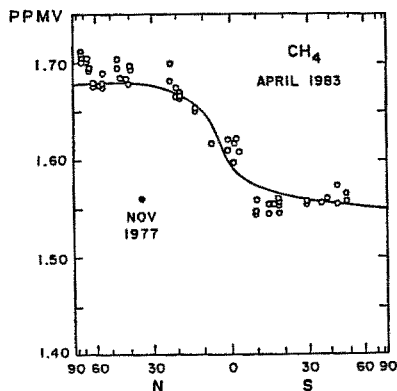


Fig. 16. April 1983.

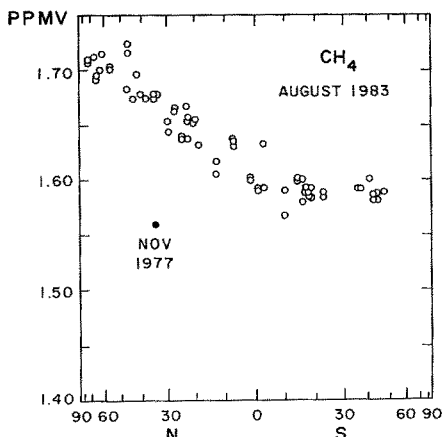


Fig. 17. August 1983.

Figs. 14 to 17. Tropospheric methane concentrations

reaction rates are in the ratio $k_{11}/k_{12} = 1.5$, which should lead to an atmospheric lifetime for CH_4 1.5 times longer than for CH_3CCl_3 – 9 or 10 years. Our initial measurements for methane concentrations were made on the canisters returned in January 1978, and we adopted as our secondary standard air collected in the California desert in November 1977. [17] In successive collection periods, we have had larger and larger numbers of samples, providing better coverage of the entire latitude range. [18] Figures 14, 15 and 16 show measurements made in July 1979, September 1982 and April 1983, and the secondary reference from November 1977. In April 1983 the concentration in the entire southern hemisphere was about 1.56 ppmv, the same value found in California more than 5 years earlier. Figure 17 shows the southern hemispheric concentrations had risen to 1.59 ppmv by August 1983, an increase there of 0.03 ppmv in only four months, but partially offset by reduced concentrations in the northern hemisphere tropics.

We can readily see that the amount of methane in the atmosphere has been going up steadily world-wide [17-21] since our measurements began in late 1977, by approximately 1.2% per year. A year or so ago the methane discussions among the atmospheric scientists focussed on the question of whether the amount of methane was increasing [22], but that now appears to be settled at least over the last six years. The question now is: Why? Basically, the major sources of methane have been generally identified and acknowledged, and are almost entirely biological in origin [23]. This gas with carbon in its most reduced state is released by biological processes occurring in the absence of oxygen. Such anaerobic conditions are found, for example, in swamps. Another important source is the rumen of domestic animals, especially of cattle. A third major identified source is the emission of methane during the growing of rice. Both cattle and rice are essentially under the direct control of man, and these methane emissions can certainly be classified at least indirectly as anthropogenic in origin.

The Food and Agriculture Organization (FAO) of the United Nations regularly compiles statistics on the number of farm animals in the world, and indicates that the numbers of Cattle and Buffalo (actually mostly cattle, although water buffalo are important in Asia) have grown from about 800 million in 1950 to about 1300 million in the 1970s. Most of this increase had already occurred by the mid-1970s, with no more than 1% further increase indicated over the time period of our actual methane measurements. The indications are that the total world-wide acreage devoted to cultivation of rice has not been increasing rapidly, but the methods of using that acreage have been changing – more multiple cropping, more time spent flooded with water, favoring anaerobic biology, and shifts to high-yield varieties of rice. The overall yield of rice has been rising rather rapidly during the past two decades, but the relationship of methane emissions to rice yields has not been established.

Very little information exists to justify detailed quantitative predictions of any changes over the past 20 years in the yearly total emissions of methane into the atmosphere. Measurements have been made on the methane emissions from cattle, and indicate yields of the order of 200 grams per day per animal. It is obvious that the methane yields from cattle are probably dependent upon the geographical location of

the animal, the quality and quantity of its feed, and perhaps other factors, but almost no information is available about the effects of these various plausible parameters on methane emission from cattle. Data have been collected from some rice fields, and certainly confirm substantial emission from them, but again very little information is available about variations with other parameters such as latitude, season, type of plant, etc. For these reasons, the proposed emission scenarios for methane have wide uncertainties in them, both as to present absolute quantities and the trend versus time in these values. We could postulate (but do not) that the source strength might have been increasing by 1.2% per year since 1977, and probably could not prove the postulate wrong. Similarly, we could postulate (but do not) that the rate of removal by reaction (12) with hydroxyl radical might be slowing down by 1.2% per year – for example, because of increased availability of other reactants for HO, such as carbon monoxide – and again could not prove the postulate wrong. The true situation is probably a combination of both. In any event, even without a firm quantitative explanation to answer the question why, we can recognize that the concentration of methane in the atmosphere is definitely increasing at a non-trivial rate, and can ask another question: What difference will it make if the methane concentration of the atmosphere is increasing?

One immediate answer is that all of the gases whose measurements I have described today – methane and four chlorocarbons – contribute to the greenhouse effect in the atmosphere [24]. One's first reaction about greenhouse contributions is apt to be that CO₂ is present at 340 parts per million by volume (ppmv), and is increasing yearly by about 1 ppmv, so that it is hard to see how the greenhouse effect from CCl₂F₂ could possibly be important on the same scale, when the total concentration of CCl₂F₂ is still only 0.0004 ppmv and increasing by about 0.00002 ppmv yearly. However, you have to remember that the greenhouse effect occurs through the absorption of infrared radiation into specific vibrational frequencies of polyatomic molecules in the atmosphere. Infrared radiation of the wavelengths which can be absorbed by CO₂ vibrations are already exposed to absorption by 340 ppmv of CO₂, and absorption by these vibrations is nearly saturated. Increasing the concentration to 341 ppmv will increase the probability of absorption a little, but it is hard to increase the total absorption very much if it is already 99.9%. On the other hand, the amounts of CCl₃F and CCl₂F₂ in the atmosphere are very much smaller and absorption in their vibrational frequencies is very far from saturation. Some of these halocarbon absorptions happen to fall into infrared 'windows' in which absorption by H₂O, CO₂ and O₃ are all very weak or non-existent, and the individual molecule can be much more effective than for CO₂. The typical added molecule of CCl₃F or CCl₂F₂ is about 10 000 times more effective in retaining infrared radiation than is the added molecule of CO₂ when the latter concentration is already 340 ppmv. The individual molecule of CH₄ is about 20 times as effective as for CO₂. When you consider the effects from increasing concentrations of CH₄ and CCl₃F and CCl₂F₂ and N₂O and tropospheric O₃, etc., the combined absorptions from increments in these gases over the past decade become approximately as important as the increment in carbon dioxide in contributions to the anticipated overall greenhouse effect.

I shall return briefly to consideration of the effects of increasing chlorine in the atmosphere. As the amount of chlorine found in the troposphere increases, the amount of chlorine in the forms of Cl and ClO in the upper stratosphere will also increase after a delay period for them to reach the 35 to 45 km altitude range. We can expect that there will be a progressive diminution of ozone in the upper stratosphere [3-7]. Indeed, there are now two scientific papers in press which have concluded that just such a diminution has been observed in the 40 km range over the past decade – a loss of about 3% at that altitude in that time period [25, 26]. The maximum efficiency in percentage removal of ozone by chlorine has always been calculated to fall around 40 km, with eventual losses approaching 50% to 60% as the organochlorine compounds approach a steady-state condition, and the atmospheric observations confirm this expectation.

Overall, we can see that the trace composition of the atmosphere has been changed appreciably in the past two decades, is continuing to be changed now, and will certainly be changing still more in the future. Some of the consequences can be predicted with some confidence, but others cannot and may only be realized after they have occurred. A large scale experiment is in progress which should be of great interest to all of us.

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