Reports

Trichlorofluoromethane in the Troposphere, Distribution and Increase, 1971 to 1974

Abstract. *Trichlorofluoromethane (CCl_3F) measurements in the troposphere over the Atlantic in 1971 and over the Pacific in 1972 and 1974 were compared. A rapid increase of CCl_3F in the troposphere is evident. The observed increase of CCl_3F between 1971 and 1974 is proportional to the increase of industrially produced amounts of CCl_3F in the same time period.*

Chlorofluoromethanes (for example, (CCl_3F and CCl_2F_2) are exclusively man-made compounds. In the last 20 years they have been introduced into the global atmosphere mainly through their use as aerosol propellants (in spray cans). Recent theoretical studies (*1*) suggest a possible future reduction of the earth's ozone shield through reaction products formed in the photolysis of chlorofluoromethane molecules in the stratosphere. The projected effects on the ozone layer are based on the assumptions that the industrially produced chlorofluoromethanes will initially accumulate in the troposphere (because of their inertness to conceivable destruction mechanisms in this atmospheric region) and then slowly migrate to the stratosphere. We have examined the question of a chlorofluoromethane buildup in the troposphere by comparing measurements of trichlorofluoromethane (CCl_3F) made in 1971, 1972, and 1974.

Our measurements were made by gas chromatography with the use of an electron capture detector that allows absolute determinations of CCl_3F (*2*). Figure 1 shows the results of our 1974 measurements between 84°N and 20°S latitude. Aircraft sampling was performed in January 1974 between Washington, D.C. (39°N), and Norway (70°N), and at 84°N between Greenland and Spitsbergen (84°N) (*3*). We obtained CCl_3F data in the Pacific region between 20°N and 20°S aboard the U.S.N.S. *Hayes* on a cruise between Ecuador, Hawaii, Tahiti, and Panama in March and April of 1974. On an Arctic cruise of the *Hayes* in the Greenland and Norwegian seas in the North Atlantic, we determined CCl_3F between 80°N and 46°N in September 1974. In July 1974, we made measurements at ground level in the Washington, D.C., area (39°N) under varying meteorological conditions.

We observed generally higher concentrations of CCl_3F in the Northern Hemisphere than in the Southern Hemisphere. This supports the theoretically predicted global distribution of man-made atmospheric constituents that are mainly released in the temperate latitudes of the Northern Hemisphere (*4*). The variability of atmospheric CCl_3F in the Northern Hemisphere is considerable, because the United States, Canada, and Europe are the main sources in the world for this volatile compound. The atmospheric transport of CCl_3F from these source areas and the resulting CCl_3F concentrations are strongly dependent on prevailing meteorological conditions and air mass movements. For instance, an average of 380 parts per trillion (ppt; 1 part in 10^{12} by volume) of CCl_3F was observed in Washington, D.C., under air pollution conditions on 9 July 1974. Two days later an advancing cold front from Canada swept the polluted air out over the Atlantic and reduced the CCl_3F concentrations to about 160 ppt (average) in Washington on 12 July 1974. Similar buildup of CCl_3F in urban source areas was observed in Los Angeles by Simmonds *et al.* (*5*). The great variability in different air masses is illustrated in our Arctic winter and summer data. In the winter (the average for CCl_3F was 120 ppt at approximately 82°N), the big storms associated with the Icelandic low can cause rapid transport of European air to northerly latitudes between Greenland and Spitsbergen (*3*). In the summer, however, the prevalence of well-mixed, clean polar air for long periods in the same region is reflected in the lower summer average for CCl_3F of about 80 ppt at 80°N. Large variations in the CCl_3F content of different air masses were also observed by Lovelock over the North Atlantic in 1973 (*6*). Therefore, any assessment of CCl_3F concentration

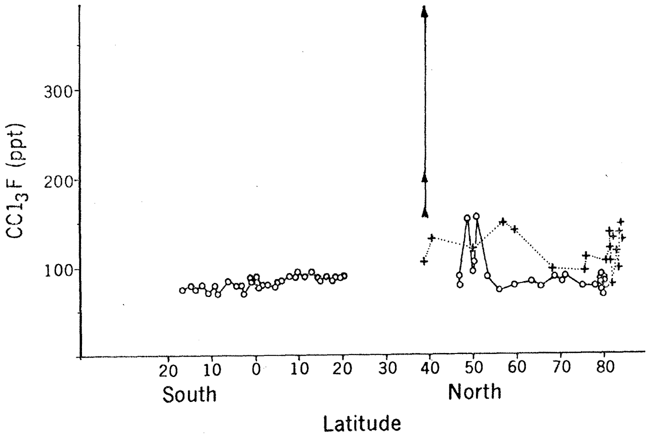

Fig. 1. Trichlorofluoromethane (CCl_3F) measurements in the troposphere in 1974 by the Naval Research Laboratory. ○, Shipboard: 20°S to 20°N, March and April 1974 between Ecuador, Hawaii, Tahiti, and Panama; 46°N to 80°N, September 1974, during a cruise from Norway to 80°N (between Greenland and Spitsbergen), then via a straight track south, just west of Ireland and to Bordeaux, France. +, Aircraft sampling, 39°N to 84°N, flight from Washington, D.C., to Norway via Iceland. From Norway, three flights to about 84°N between Greenland and Spitsbergen, January 1974. ▲, On land: 39°N, Washington, D.C. Sampling at ground level around the metropolitan area on 9, 11, and 12 July 1974 (averages of 380, 200, and 160 ppt, respectively).

trends in the troposphere should be based on average concentrations obtained over long transects from north to south (*7, 8*) or, preferably, on data obtained in remote ocean areas in the Southern Hemisphere where no great short-term variations of CCl_3F have been observed (Fig. 1) (*7, 8*).

An assessment of tropospheric CCl_3F changes should take possible environmental sinks and sources into account. A likely sink for CCl_3F is the ocean, and Lovelock (*7*) reports its presence in surface waters of the Atlantic in 1971 and its rapid decrease with depth. Our own determinations in the central equatorial Pacific in 1974 show that CCl_3F is confined to the upper 200 m —the well-mixed surface waters—with no CCl_3F detectable below that depth (*9*). These measurements and theoretical considerations (*10*) indicate that at this point only a small fraction of the tropospheric CCl_3F has migrated into the oceans.

Stoiber *et al.* (*11*) reported the occurrence of chlorofluoromethanes in volcanic emanations without assessing volcanism as a potential source. We had the opportunity to take samples of the air within 500 m of erupting Kilauea volcano in Hawaii on 18 March 1974. In hot gas samples taken from the cracks of a lava flow the CCl_3F content was 86 and 91 ppt. One day later, we sampled at the Mauna Loa observatory on the dormant volcano next to Kilauea whose eruption had subsided. Three samples taken at the observatory showed that the CCl_3F content of clean marine air was 75, 81, and 86 ppt, concentrations not significantly different from those collected during the eruption. These data imply that volcanoes most likely are not major sources or sinks of CCl_3F. To our knowledge, no other information regarding tropospheric sinks and sources or transport of CCl_3F to the stratosphere is now available.

In order to assess any increase of CCl_3F in the troposphere, we have plotted, in Fig. 2, the third-degree polynomials best fit to measurements obtained in the three surveys: Lovelock's 1971 data between 60°N and 60°S in the Atlantic (*7*), our Pacific data of 1972 between 20°N and 78°S (*8*), and our 1974 Pacific data (Fig. 1) between 20°N and 20°S. In our 1972 and 1974 surveys, several hundred measurements were made aboard ship over periods of 2 months. The data of the three surveys were obtained with the use of the electron capture detector as an absolute way of CCl_3F determination. Refinements in equipment and procedures have improved the achievable precision (aboard ship) from ± 15 percent and ± 20 percent in the 1971 and 1972 surveys to ± 8 percent in the 1974 survey (Fig. 1). Thus, there is no reason to suspect the relative CCl_3F increases shown in Fig. 2 within the limits of error discussed. The absolute values of the CCl_3F measurements may be subject to future revision within a range of ± 15 percent because the functioning of the electron capture detector as an absolute device has some uncertainty associated with it (*2*). Up to now no extensive intercalibration with a certified standard of any sort between the different CCl_3F measuring groups has been performed.

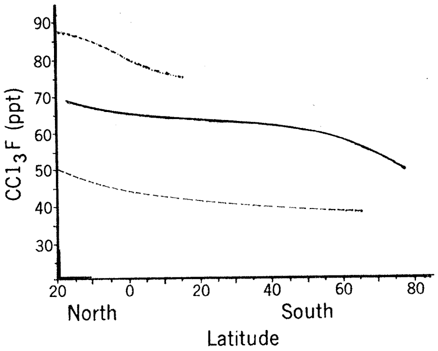

Fig. 2. Third-degree polynomial best fit to trichlorofluoromethane (CCl_3F) measurements in 1971, 1972, and 1974. Plotted are values from 20°N to most southerly latitudes only. - - - -, Lovelock (*7*) November 1971, Atlantic. ———, Naval Research Laboratory (*8*) November and December 1972, Pacific. . . . ., Naval Research Laboratory (Fig. 1) March and April 1974, Pacific.

On the basis of the mean aerial values for CCl_3F in the 1971, 1972, and 1974 data, which are 50, 61, and 80 ppt, respectively, we calculate an increase in the atmospheric level of 22 percent from November 1971 to November 1972, of 31 percent from November and December 1972 to March and April 1974, and of 60 percent between November 1971 and March and April 1974. The use of the mean CCl_3F values for this purpose is somewhat arbitrary, because the surveys start and end at different northerly and southerly latitudes. Data from remote ocean areas in the Southern Hemisphere provide a less arbitrary, more reliable basis to assess tropospheric CCl_3F trends, as discussed earlier. We have selected data from 10°S because they are available in the 1971, 1972, and 1974 surveys and especially because well-mixed, very clean marine air was encountered in each case. At 10°S, 147°W in 1972 very low levels of atmospheric carbon monoxide, radon, and continental aerosol particulates were the criteria for clean air (*8, 12*). In 1974 these measurements were repeated at 10°S, 152°W, and the results indicated clean air conditions nearly identical to those in 1972. Low CO concentrations in the atmosphere measured by Seiler (*13*) at 10°S, 31°W simultaneously with CCl_3F (*7*) confirm the presence of clean marine air during that period. The average clean air concentrations of CCl_3F at 10°S in the three surveys are 43, 53, and 72 ppt, respectively. Calculated CCl_3F increases based on these values are 23 percent (1971 to 1972), 36 percent (1972 to 1974), and 67 percent (1971 to 1974). These increases agree well with those obtained by using the mean aerial concentrations. This agreement between the two different approaches may be fortuitous. We conclude that CCl_3F has been increasing in the troposphere at a rather rapid rate in the period from 1971 to 1974.

Comparison of these observed increases with worldwide production estimates is instructive, although the uncertainties associated with those estimates may be as much as ± 25 percent (*14*). Between 1950 and (including) 1971, the total world production was estimated to be 1.49×10^6 metric tons (*14*). During 1972 and 1973, this figure increased to 1.76×10^6 and 2.02×10^6 metric tons, respectively (*14*). If the amount produced in 1974 is similar to that produced in 1972 and 1973, then the overall increase since 1971 would be about 54 percent (based on an estimated total of 2.30×10^6 metric tons in 1974). This is approximately the same magnitude as the measured increase in atmospheric concentration during the same period. We conclude, therefore, that industrially manufactured CCl_3F is quickly released to the atmosphere. The evidence provides no indication that significant sinks exist within the troposphere for the destruction or disappearance of CCl_3F.

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15. We thank D. W. Peterson, scientist in charge at the Hawaiian Volcano Observatory, for taking us to Kilauea during the eruption. We also thank the crews of the NRL aircraft for invaluable support. Gene Bugg assisted in sampling and analysis.

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Deep Seismic Reflection Results from the Gulf of Mexico: Part I

Abstract. *Deep sounding seismic reflection data show undeformed reflectors at depths down to 11 kilometers beneath the continental rise and abyssal plain and 7 kilometers in basins of the lower slope. Weak reflectors are visible beneath the salt of the Sigsbee Scarp and within salt ridges separating the lower slope basins.*

We report here results of a deep sounding common-depth-point (CDP) seismic reflection survey across a portion of the lower slope, Sigsbee Scarp, continental rise, and abyssal plain in the northern Gulf of Mexico. This powerful tool for the investigation of deep geologic structure has heretofore been used almost exclusively by the petroleum industry. It promises much to the marine geologist and geophysicist.

The CDP method was adopted by the petroleum industry in the early 1960's because this technique made it possible to attenuate multiple reflections and random noise. With the CDP technique it is possible to achieve an increased signal-to-noise ratio by summing several reflectors from what are theoretically common points in a vertical plane. The shot point and receiver geometry determine the number of reflection records to be summed. Typically, the number of summed input records is 6, 12, or 24, or, in some instances, 48 or 96. In industry terminology, the number of input traces is denoted as 6-fold, 12-fold, and so on, or 600 percent coverage, 1200 percent coverage, and so on, respectively.

Digital recording of marine seismic data was introduced into the petroleum industry at about the same time as the CDP method. By 1966, 85 percent of U.S. marine seismic data were digitally recorded (*1*), which facilitated CDP processing and simultaneously provided a mechanism for the application of sophisticated noise suppression techniques.

The CDP method and ancillary digital signal enhancement techniques have proved to be powerful tools for obtaining data on deep, detailed geological structure on land and offshore. On the continental shelves, multichannel digital seismic reflection instrumentation has yielded reflections from depths of 8 to 10 km, depths which are significantly greater than the depths of penetration of single-channel analog instrumentation. The petroleum industry, however, has shown little interest in areas of deeper water. The industry also tends to consider seismic reflection data confidential. As a result only a few deep-water CDP cross sections have been published (*2, 3*).

The geologic structure of the deeper parts of the Gulf of Mexico is well suited for CDP investigation. Little is known about details of structure and stratigraphy below depths of about 2 to 3 km beneath the sea floor, the maximum penetration of single-channel seismic reflection analog instrumentation. Multiple bottom reflections obscure primary reflections deeper than 2 to 3 km subbottom on the slope and deeper than 5 to 8 km subbottom in the abyssal plain. Seismic refraction investigations (*4*) have provided information on the gross framework of the region but no detailed structural information. Salt underlies some areas of the Gulf such as the lower slope off Texas and Louisiana (*5*). Single-channel reflection data have provided little information about the nature of salt deformation and possible subsalt reflectors because of the poor quality of deeper reflectors.

Our investigation consisted of two CDP lines resembling in plan an inverted "V" (Fig. 1). The survey was conducted on board the University of Texas Marine Science Institute R.V. *Ida Green*, and the data were processed at the University of Texas Medical Branch, Galveston.

Penetration was excellent. The deepest observed reflector was located near the southern end of line SS-2. It was received 6.5 seconds after the bottom reflection. A relatively strong deep reflector was recorded 4.5 to 5.0 seconds after the bottom reflector beneath all of the abyssal plain–continental rise portions of both lines. Sediment-filled basins separated by salt ridges (*5, 6*) underlie the lower slope. The usefulness of the CDP method is evident in this region. Multiple reflections which interfere with primary reflections deeper than about 2 seconds subbottom are strongly attenuated, permitting resolution of the primary reflections at depths of 4 to 5 seconds in some cases (Fig.

Table 1. Layer velocities, layer thicknesses, depths beneath the sea floor, and expected reflection arrival times calculated from seismic refraction data (*7*) for the northern Gulf of Mexico.

Layer velocity (km/sec)	Calculated reflection time (sec subbottom)	Layer thickness (km)	Depth (km subbottom)
1.9	0.0	0.5	0.0
2.2	0.53	2.0	0.5
3.2	2.34	2.5	2.5
3.8	3.91	2.0	5.0
4.8	4.96	4.0	7.0
6.6	6.63	5.0	11.0