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## Seasonal variations in the atmospheric distribution of a reactive chlorine compound, tetrachloroethene ( $\text{CCl}_2=\text{CCl}_2$ )

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**Abstract.** Tropospheric mixing ratios of  $\text{CCl}_2=\text{CCl}_2$  were measured at remote surface locations in the Pacific between 71°N and 47°S during September and December of 1989, and March and June of 1990. The observed gradient of decreasing concentrations from the northern to southern hemisphere, and very low concentrations in the southern hemisphere throughout the year, indicates a predominant input from the northern hemisphere. Our seasonal measurements in the northern hemisphere showed maximum  $\text{CCl}_2=\text{CCl}_2$  concentrations occurring in the late winter and minimum concentrations occurring in the late summer. This distinct seasonal variation is strongly coupled to the atmospheric abundance of hydroxyl radical, the only important species responsible for  $\text{CCl}_2=\text{CCl}_2$  removal. Using the estimated global  $\text{CCl}_2=\text{CCl}_2$  emissions the lifetime is calculated to be about 5.4 months which is in good agreement with the 4.0 month estimate obtained from the inverse ratio of its measured hydroxyl reaction rate constant compared with that of methylchloroform ( $\text{CH}_3\text{CCl}_3$ ).

### Introduction

The latitudinal distribution and atmospheric survival of reactive chlorinated molecules has recently attained regulatory policy significance because of concern over the effects on stratospheric ozone anticipated from the hydrochlorofluorocarbons (HCFCs) now being developed and used as substitutes for the fully-halogenated chlorofluorocarbons (CFCs) [WMO-NASA, 1990]. We have measured the atmospheric concentration of the reactive gas tetrachloroethylene,  $\text{CCl}_2=\text{CCl}_2$ , in all four seasons during 1989-1990 at remote surface locations covering the latitude range from 71°N to 47°S. Tetrachloroethene is man-made with no confirmed natural sources and is primarily used as a dry cleaning and degreasing solvent [Most, 1989]. This similarity in usage to other anthropogenic chlorocarbon compounds, especially  $\text{CH}_2\text{CCl}_3$  and  $\text{CClF}_2\text{CCl}_2\text{F}$  (CFC-113), makes its geographical emission pattern very much like those of the CFCs and CFC substitutes. The double bond in its molecular structure makes it susceptible to hydroxyl radical addition reaction, which ultimately results in its atmospheric removal [Itoh et al., 1994].

While the  $\text{CCl}_2=\text{CCl}_2$  emissions are likely to be distributed more or less uniformly throughout the year, the HO source strength is quite variable with both season and latitude, and transport between the northern and southern hemispheres also has a significant seasonal dependence. With the majority of the  $\text{CCl}_2=\text{CCl}_2$  release occurring northward of 30°N latitude and reaction with HO radicals as the only significant sink, the result-

ing distribution of this compound is a sensitive test of the interplay between atmospheric transport and chemical destruction. The year-round measurements of  $\text{CCl}_2=\text{CCl}_2$  also furnish information applicable to the atmospheric behavior of proposed short-lived HCFC and HFC substitutes [WMO 1990].

### Experimental

Air samples were collected in four periods, each approximately two weeks in length, centered in mid-September 1989, early December 1989, plus mid-March and mid-June in 1990. For each collection period, approximately 50 to 60 surface-level air samples were introduced at ambient pressure into pre-evacuated 2-liter stainless steel canisters in remote Pacific locations, covering latitudes from Barrow, Alaska (71°N) to southern New Zealand (47°S). Within 3 weeks of collection, samples were returned to the University of California Irvine laboratory for gas chromatographic (GC) analysis on separate aliquots for halocarbons [Wang, 1993] and other trace gases [Blake et al., 1994]. The halocarbon analyses in 1989-1990 were performed by cryogenically preconcentrating a 26.3 ml STP air sample aliquot at -165°C on an 1/8" stainless steel loop packed with 80/120 mesh glass beads. The loop was warmed and flushed with ultra pure nitrogen gas onto a 60m x 0.75 mm I.D. glass SPB-1 capillary column (Supelco).

Three aliquots of each air sample were analyzed, with measurements of a reference air sample of known mixing ratios bracketing each triplicate analysis. The linearity of the ECD response for various halocarbons, including  $\text{CCl}_2=\text{CCl}_2$ , has been rigorously studied. The  $\text{CCl}_2=\text{CCl}_2$  concentrations for background samples fall well within the linear working range of its calibration curve [Wang, 1993].

Mixing ratios for the halocarbons were calibrated by diluting a pure halocarbon mixture to the part per trillion by volume (pptv) level using a 4-step volumetric dilution method and a glass vacuum line. The absolute dilution error was determined from pressure and volume measurement uncertainties. The overall calibration error ( $1\sigma$ ) for  $\text{CCl}_2=\text{CCl}_2$  is estimated to be 8% at about 2 pptv and 3% at about 40 pptv. Using this dilution method, our calibration scales for CFC-12 and CFC-11 are in agreement within 2% with the absolute values in other measurement programs [NASA, 1994]. The only uncertainty not included in the error assessment is surface adsorption which for  $\text{CCl}_2=\text{CCl}_2$  is believed to be quite small on a glass surface. One torr of water vapor was added to preserve standard mixtures in the glass bulb and minimize any adsorption problems during analysis.

A second method was also employed using CFC-12 in the reference air as the basis for an indirect measurement of the dilution factor. In this method, the initial partial pressures in the mixture for CFC-12 and  $\text{CCl}_2=\text{CCl}_2$  were carefully measured. This mixture was subsequently diluted to the parts per trillion level. This method depends on the accuracy of CFC-12 in the

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reference air, the analytical precision for CFC-12 measurements and the accuracy for measuring the initial partial pressures of pure halocarbons. Both methods were used several times and they agree within 3% for  $\text{CCl}_2=\text{CCl}_2$ .

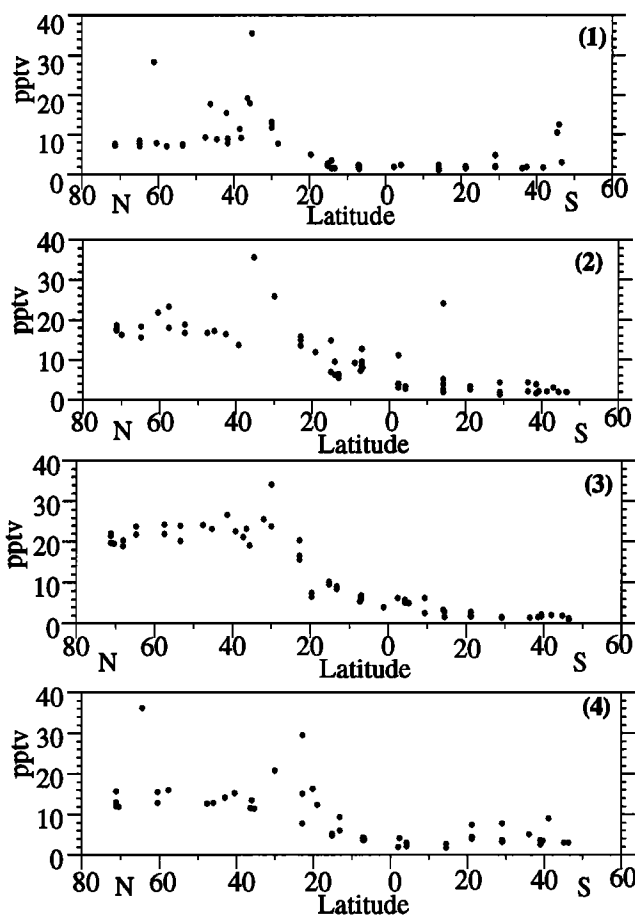
## Results and Discussion

Latitudinal distributions of  $\text{CCl}_2=\text{CCl}_2$  for the four sample periods from September 1989 to June 1990 are displayed in Figures 1-4. Almost all  $\text{CCl}_2=\text{CCl}_2$  is released to the atmosphere in heavily-populated areas, and we have regularly found  $\text{CCl}_2=\text{CCl}_2$  concentrations in the 100 to 2000 pptv range in urban air samples. The amount of  $\text{CCl}_2=\text{CCl}_2$  found in a remote location is strongly dependent on how recently the air mass being sampled has been intermixed with additional urban emissions. Thus, the measured mixing ratios of  $\text{CCl}_2=\text{CCl}_2$  are generally more variable in the northern hemisphere than in the southern hemisphere, particularly between  $20^\circ\text{N}$  and  $40^\circ\text{N}$  for which air samples collected along the California coast are more likely to have recent urban additions. Other than a few samples that show considerably higher mixing ratios than the large majority of samples, the latitudinal profiles of  $\text{CCl}_2=\text{CCl}_2$  of near "background" level for four seasons are clearly displayed. With a short-lived compound for which a significant fraction can be removed on a weekly basis, the concept of a background level is itself not very clear. We use it here as being representative of the median concentrations found in remotely collected air samples at each latitude. A very distinct gradient of decreasing concentration from north to south was observed in all four seasons, indicating northern hemispheric dominance of  $\text{CCl}_2=\text{CCl}_2$  emissions throughout the year. The mixing ratios of  $\text{CCl}_2=\text{CCl}_2$  in the northern hemisphere exhibit significant, regular seasonal variation. In the southern hemisphere, the observed concentrations of  $\text{CCl}_2=\text{CCl}_2$  represents a composite of minor southern emissions plus northern emissions modified by seasonally dependent loss and transport properties, and thus do not exhibit the direct response to HO concentration found in the north.

Large degree of disagreement exists in the literature among the reported absolute  $\text{CCl}_2=\text{CCl}_2$  mixing ratios from different research groups. For example, the mixing ratios reported in earlier literature for the northern hemisphere range from less than 10 pptv in August/September 1989 to  $56 \pm 11$  pptv in December 1981 [Cox et al., 1976; Cronn et al., 1977; Singh et al., 1977; Rasmussen and Khalil, 1982; Singh et al., 1983; Class and Ballschmiter 1986, 1987; Makide et al., 1987; Koppmann et al., 1993]. Fewer measurements have been made in the southern hemisphere where the reported mixing ratios ranges from less than 3 pptv in August/September 1989 to  $14 \pm 3$  pptv in December [Rasmussen and Khalil, 1982; Class and Ballschmiter, 1986; Koppmann et al., 1993]. Our northern hemispheric  $\text{CCl}_2=\text{CCl}_2$  measurements in March 1990 showed maximum mixing ratios around 27 pptv or less for latitudes between about  $30^\circ\text{N}$  and  $71^\circ\text{N}$  and dropped rapidly to about 6 pptv near the equator. Mixing ratios in the southern hemisphere were from 6 pptv near the equator and decreased to about 2 pptv south of the tropics (Figure 3). By contrast, after excluding several significantly elevated samples for which the concentrations of other halocarbons also suggested recent urban augmentation, the  $\text{CCl}_2=\text{CCl}_2$  measurements in the September 1989 showed minimum mixing ratios for the northern hemisphere of less than 10 pptv. The southern hemispheric mixing ratios were about 1-2 pptv, not much different from those of the March 1990 trip. Overall, our

reported mixing ratios fall in the lower end of published values, but are in good agreement with the measurements made by Koppmann et al. [1993] in August/September, 1989 and the measurements made by Rudolph et al. [1984] in spring 1983. Our data also agree with the summer and winter measurements made in Hokkaido, Japan between  $42^\circ$ -  $45^\circ\text{N}$  [Makide et al., 1987].

After removing the significantly elevated samples shown in Figures 1-4, the mixing ratios at the remote locations in the northern temperate and north polar regions generally fall into the 7 to 26 pptv range, while the southern hemispheric values are typically 1 to 5 pptv. The highest concentrations of  $\text{CCl}_2=\text{CCl}_2$  in the north temperate region, averaging more than 20 pptv, occur near the end of the northern winter. Because HO formation is dependent on water vapor and  $\text{O}(^1\text{D})$  atoms generated from the ultraviolet photolysis of ozone, the source strength of HO is increased by the longer hours and shortened atmospheric ultraviolet path lengths of summer sunlight. The higher humidities of summer also increase the collision frequency between  $\text{O}(^1\text{D})$  and water vapor, which is in competition with conversion of  $\text{O}(^1\text{D})$  to  $\text{O}(^3\text{P})$  by collision with  $\text{N}_2$  and  $\text{O}_2$ . The September  $\text{CCl}_2=\text{CCl}_2$  concentrations, the lowest northern hemispheric seasonal values, reflect the shorter average atmospheric lifetimes accompanying the elevated summer levels of HO radicals. By contrast, molecules of  $\text{CCl}_2=\text{CCl}_2$  found in the northern temperate regions in March have been exposed during the previ-



Figures 1 - 4. Latitudinal distribution of  $\text{CCl}_2=\text{CCl}_2$ : (1) during September 1989; (2) during December 1989; (3) during March 1990; and (4) during June 1990.

ous several months to the minimum HO concentrations, allowing a buildup of  $\text{CCl}_2=\text{CCl}_2$  molecules.

Because the observed concentrations represent an integration over the HO reactivity for the previous several months, the June and December concentrations of  $\text{CCl}_2=\text{CCl}_2$  in the north are intermediate between those of the other two sampling periods. The northern hemisphere contains most of the  $\text{CCl}_2=\text{CCl}_2$  sources and, its seasonal concentration dependence largely responds to the time integration of the seasonal oscillation in HO levels. As a result, the  $\text{CCl}_2=\text{CCl}_2$  mixing ratios in the northern hemisphere should show an opposite oscillation to that of the HO mixing ratios, with a shift by about one season. Koppmann et al. [1993] cited unpublished data of Rudolph et al. that showed a seasonal cycle for  $\text{CCl}_2=\text{CCl}_2$  at Alert, Canada ( $82^\circ\text{N}$ ). The highest mixing ratios were measured in early April and the lowest mixing ratios were in September with an amplitude of  $15 \pm 3$  pptv. Measurements made by Makide et al. [1987] in Hokkaido ( $42\text{--}45^\circ\text{N}$ ) showed  $\text{CCl}_2=\text{CCl}_2$  mixing ratios varied between less than 10 pptv and about 25 pptv for the summer and late winter, respectively. Our measurements showed that samples collected in Alaska at latitudes ranging from  $53.5^\circ\text{N}$  (Summers Bay, Alaska) to  $71.2^\circ\text{N}$  (Point Barrow) had quite uniform mixing ratios of  $7.6 \pm 0.5$  pptv for 9 samples for September 1989 and  $21.5 \pm 1.8$  pptv for 12 samples for March 1990. Thus, based on the work performed by these three groups, the amplitude for  $\text{CCl}_2=\text{CCl}_2$  seasonal cycle for the northern high latitudes is in very good agreement.

In contrast, the seasonal dependence in the southern hemisphere represents an amalgam of austral variation in HO levels mixed with the seasonal effects in the southward transport across the ITCZ of  $\text{CCl}_2=\text{CCl}_2$  originating in the northern hemisphere. The  $\text{CCl}_2=\text{CCl}_2$  concentrations in northern hemisphere air masses are as much as three times larger in March than in September, implying significant differences in air transported across the ITCZ into the southern hemisphere. However, the general lack of strong seasonal characteristics in southern hemispheric concentrations implies modification by variations in rate of transport and by substantial photochemical losses in tropical latitudes. Koppmann et al. [1993] cited unpublished data of Rudolph et al. and reported a seasonal variation over the Antarctic of  $2 \pm 0.14$  pptv and an seasonal amplitude of  $0.9 \pm 0.2$  pptv, with the maximum in October and minimum in May. Although our southern hemispheric measurements do not reveal any seasonality, they are in good agreement with those reported by Koppmann et al. [1993] whose September/October  $\text{CCl}_2=\text{CCl}_2$  measurements in 1989 fell between 2 and 3 pptv.

If both the  $\text{CCl}_2=\text{CCl}_2$  atmospheric burden and its emissions are known, the atmospheric lifetime of  $\text{CCl}_2=\text{CCl}_2$  can be calculated, and therefore by inference the average HO concentration can be estimated, as has been done for  $\text{CH}_3\text{CCl}_3$  [Makide and Rowland, 1981; Prinn et al., 1992]. Using  $\text{CCl}_2=\text{CCl}_2$  in some respects could be more beneficial than using  $\text{CH}_3\text{CCl}_3$ , because the interplay with HO is more sensitive for  $\text{CCl}_2=\text{CCl}_2$  than for  $\text{CH}_3\text{CCl}_3$ .

Based on the production and sale records provided by the principal producers, the global emissions of  $\text{CCl}_2=\text{CCl}_2$  during 1989-90 were estimated to be about 400 kilotons/year, with over 98% of the emissions having occurred in the northern hemisphere. Because the sales were not seasonal either into particular end uses or geographical areas, therefore the emissions were not likely to be seasonal [McCulloch and Midgley, private communication, 1994]. This estimate of 400 kilotons/year is signifi-

cantly lower than the 1984 value of 580 kilotons/year estimated by Class and Ballschmiter [1987], because the world production of  $\text{CCl}_2=\text{CCl}_2$  has been decreasing since the early 1980s [McCulloch and Midgley, private communication, 1994].

When the data shown in Figures 1 to 4 are globally integrated on an area-weighted basis to provide a measurement of the atmospheric burden of  $\text{CCl}_2=\text{CCl}_2$ , the average surface mixing ratios for September, December, March and June are 4.3, 8.2, 9.5, and 7.0 pptv, respectively. Assuming the average mixing ratios for the other months fall linearly between the measured months in the northern hemisphere but maintain a constant value of about 2.7 pptv in the southern hemisphere throughout the year, the yearly global average surface mixing ratio is  $7.3 \pm 1.0$  pptv. Vertical profiles of  $\text{CCl}_2=\text{CCl}_2$  obtained during numerous airborne missions suggest the amount of  $\text{CCl}_2=\text{CCl}_2$  above the tropopause is negligible. The profiles showed slight declining gradients from the surface to the tropopause. Datasets obtained from missions over Canada in Summer 1990 [Blake et al., 1994], the Azores in Summer 1992 [Smith et al., 1993], as well as flights in connection with NASA PEMWEST-A, -B and TRACE-A expeditions suggest that  $\text{CCl}_2=\text{CCl}_2$  surface concentrations are about 10% higher than upper free tropospheric values. Thus, the yearly surface mixing ratio of  $7.3 \pm 1.0$  pptv can be translated into a global yearly burden of  $180 \pm 25$  kilotons. Dividing this average amount by the estimated emissions of 400 kilotons/year with its associated error. We calculate an average atmospheric lifetime for  $\text{CCl}_2=\text{CCl}_2$  of about  $5.4 \pm 1.2$  months.

The lifetime of  $\text{CCl}_2=\text{CCl}_2$  in the atmosphere can also be calculated by analogy with the lifetime of  $\text{CH}_3\text{CCl}_3$ . The primary atmospheric sink for  $\text{CH}_3\text{CCl}_3$  is also by reaction with HO radical. The tropospheric lifetime of  $\text{CH}_3\text{CCl}_3$  has been recently estimated at about 5.7 years [Prinn et al., 1992]. With the ocean considered as a weak sink [Butler et al., 1991], the  $\text{CH}_3\text{CCl}_3$  lifetime from HO removal alone is about 6 years. The lifetime estimate for  $\text{CCl}_2=\text{CCl}_2$  encompasses a wide range of expected lifetimes for individual releases of  $\text{CCl}_2=\text{CCl}_2$ . The removal rate experienced following injection at  $60^\circ\text{N}$  in December is surely much slower than for an injection at  $20^\circ\text{N}$  in June. The effective lifetimes for comparable releases of  $\text{CH}_3\text{CCl}_3$  are much less variable because north-south transport within and between the northern and southern hemispheres is sufficiently rapid relative to the 5.7 year tropospheric lifetime to give most molecules a nearly globally averaged exposure over time. By comparing laboratory determined reaction rate constants of HO with  $\text{CCl}_2=\text{CCl}_2$  and  $\text{CH}_3\text{CCl}_3$  [DeMore et al., 1992] and assuming an average temperature of 280K, the average tropospheric lifetime of  $\text{CCl}_2=\text{CCl}_2$  can be estimated as 4.0 months, which is in good agreement with the 5.4 months estimated from atmospheric burden and emissions of  $\text{CCl}_2=\text{CCl}_2$ .

These observations provide two additional insights into the problem of ozone depletion by chlorine released in the stratosphere from organochlorine compounds. First, the transport of such molecules from the troposphere to the stratosphere takes place almost entirely through the tropical tropopause. Because the typical mixing ratios in the tropics in all seasons are around 5 pptv of  $\text{CCl}_2=\text{CCl}_2$  or 20 pptv of Cl, the fraction of the current 4,000 pptv of tropospheric organochlorine attributable to  $\text{CCl}_2=\text{CCl}_2$  as a source is about 0.5%. The delivery of only 20 pptv Cl to the stratosphere from yearly atmospheric emissions of about 400 kilotons contrasts strikingly with the delivery of more than 1,000 pptv Cl from  $\text{CCl}_2\text{F}_2$  (2 Cl atoms  $\times$  500 pptv mixing ratio) from the accumulation from yearly emissions over the 1970's and the 1980's of about 400 kilotons/year.

The second point is a corollary of the first. When chlorocarbon molecules have effective tropospheric sinks, they do not reach the tropical tropopause in large concentration. Furthermore, the close comparison for  $\text{CCl}_2=\text{CCl}_2$  between average lifetime calculated versus  $\text{CH}_3\text{CCl}_3$  and the observed average lifetime from actual atmospheric burden lends strong support for the use of the reaction rate constant ratio versus  $\text{CH}_3\text{CCl}_3$  procedure for molecules not yet introduced into the atmosphere. This is particularly relevant for lifetimes calculated in this manner for HCFCs, HFCs, and other hydrogen-containing molecules proposed as technological substitutes for the CFC's being replaced under the terms of the Montreal Protocol.

## Conclusion

The latitudinal distribution of the anthropogenically released chlorine species,  $\text{CCl}_2=\text{CCl}_2$ , was measured during four seasons between 1989 and 1990. The mixing ratios of  $\text{CCl}_2=\text{CCl}_2$  varied with season in the northern hemisphere with maximum values occurring in March 1990 and minimum in September 1990. The mixing ratios in the north for December 1989 and June 1990 were intermediate between those of the other two seasons. No apparent seasonal variations were observed in the southern hemisphere where mixing ratios below 5 pptv were typical. The 14 pptv amplitude in the  $\text{CCl}_2=\text{CCl}_2$  seasonal cycle in the northern hemisphere is in good agreement with results at similar latitudes reported by other groups.

Using global emission estimates the atmospheric lifetime of  $\text{CCl}_2=\text{CCl}_2$  was calculated to be about 5.4 months. This is in good agreement with the 4.0 month estimate obtained by comparison of  $\text{CCl}_2=\text{CCl}_2$  and  $\text{CH}_3\text{CCl}_3$  reaction rate constants and an assumed  $\text{CH}_3\text{CCl}_3$  atmospheric lifetime of 5.7 years. The fact that these two methods agree well suggests current global average HO concentrations obtained from the  $\text{CH}_3\text{CCl}_3$  lifetime calculations are reasonably accurate.

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