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Atmospheric Trace Gases in Antarctica

Abstract. *Trace gases have been measured, by electron-capture gas chromatography and gas chromatography–mass spectrometry techniques, at the South Pole (SP) in Antarctica and in the U.S. Pacific Northwest (PNW) (~ 45°N) during January of each year from 1975 to 1980. These measurements show that the concentrations of* CCl_3F, CCl_2F_2, *and* CH_3CCl_3 *have increased exponentially at substantial rates. The concentration of* CCl_3F *increased at 12 percent per year at the SP and at 8 percent per year in the PNW;* CCl_2F_2 *increased at about 9 percent per year at both locations, and* CH_3CCl_3 *increased at 17 percent per year at the SP and 11.6 percent per year at the PNW site. There is some evidence that* CCl_4 *(~ 3 percent per year) and* N_2O *(0.1 to 0.5 percent per year) may also have increased. Concentrations of nine other trace gases of importance in atmospheric chemistry are also being measured at these two locations. Results of the measurements of* $CHClF_2$ *(F-22),* $C_2Cl_3F_3$ *(F-113),* SF_6, C_2*-hydrocarbons, and* CH_3Cl *are reported here.*

January 1980 marked the sixth year of our trace gas measurements program at the South Pole (SP). We report here the data obtained over these 5 years, estimate the average annual increases in the concentrations of CCl_3F (F-11), CCl_2F_2 (F-12), CCl_4, CH_3CCl_3, and N_2O, and report the consistency of our measurements of CCl_3F, CCl_2F_2, and CH_3CCl_3 with the emissions estimates. In January 1980 we also measured $CHClF_2$ (F-22), $C_2Cl_3F_3$ (F-113), CH_3Cl, SF_6, CH_4, CO, C_2H_2 (acetylene), C_2H_4 (ethylene), and C_2H_6 (ethane). These data are also included.

We have maintained the objective of quantifying the global trend toward increasing atmospheric concentrations of long-lived gases such as CCl_3F, CCl_2F_2, and CH_3CCl_3, which are released as a result of human activities, primarily at latitudes above 30°N, and which may adversely affect the future global environment (*1*). In order that the picture be more complete, the trends observed in the antarctic atmosphere are contrasted to those observed at (remote) Pacific Northwest (PNW) (~ 45°N) sites during the same period.

The measurements of N_2O, CCl_3F, CCl_2F_2, CCl_4, and CH_3CCl_3 made every January from 1975 to 1980 are reported in Table 1 (*2*). Concentrations for a variety of trace gases, not previously measured in Antarctica, are also shown in Table 1, including $CHClF_2$ (F-22), which is likely to gain environmental importance in the years to come (*1*). We measured these halocarbons and other trace gases, using established electron-capture gas-chromatography techniques (*3*).

The internal consistency in the absolute concentrations reported for each season has been maintained since 1976 by calibration standards. The values in Table 1 are averages over many measurements and represent our best estimates of concentrations in the antarctic troposphere during January of each year. Whenever possible, the concentrations observed in Antarctica were compared with measurements made by P. Fraser, Commonwealth Scientific and Industrial Research Organization, Cape Grim, Tasmania (~ 43°S), and measurements made elsewhere in the Southern Hemisphere. The antarctic measurements have always been consistent with these additional measurements (*2*).

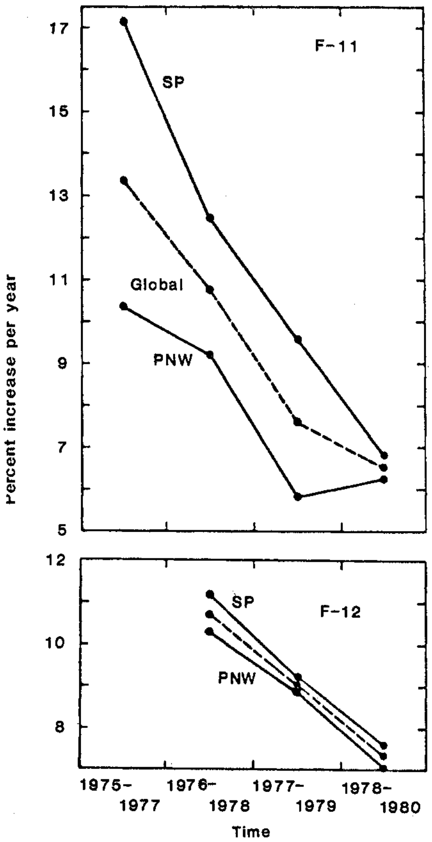

Fig. 1. Rates of growth of CCl_3F (*F-11*) and CCl_2F_2 (*F-12*) during overlapping 3-year periods from 1975 to 1980.

On the basis of the data given in Table 1, we have estimated the increases in the concentrations of CCl_3F, CCl_2F_2, CCl_4, CH_3CCl_3, and N_2O and considered the changes in the north/south (N/S) ratio. The results of these calculations are summarized in Table 2. We found that the time series data are appropriately represented by the (exponential growth) expression

$$\frac{1}{c}\frac{dc}{dt} = \beta$$

where c is the concentration and β is regarded as a constant, thus reflecting the average rates of atmospheric increase during the years when observations were made. In Table 2, we estimated β by using nonparametric statistical methods based on the Theil statistic (*4*); the estimate of the (average) value of β is denoted $\hat{\beta}$. The $\hat{\beta}$ obtained by this method is less sensitive to gross errors than the usual classical least-squares estimates. The numbers we obtained for $\hat{\beta}$ were multiplied by 100 percent to convert them to percentage increases per year. Similarly, we estimated a distribution-free approximate 90 percent confidence interval for β, using the Theil test (*4*). The results are reported in Table 2 as β_{L} (lower limit) and β_{U} (upper limit). The concentrations of CCl_3F, CCl_2F_2, and CH_3CCl_3 increased at about 10, 9, and 13 percent per year, respectively, on the average.

The data in Table 1, for 6 years, also indicate that the rate of atmospheric accumulation of CCl_3F and CCl_2F_2 (denoted β) may be slowing down. Such an observation would be consistent with, indeed required by, the leveling off in the global emissions since about 1975 (*5*). A leveling off in the emissions of these

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long-lived trace gases does not imply that the atmospheric concentrations should also stop increasing because global sources and sinks have not yet produced steady-state atmospheric concentrations. There are not enough data points to show statistically that there is a decline in the rate of accumulation of CF_3Cl and CF_2Cl_2; however, we illustrate this contention in Fig. 1, where we have plotted increases of CCl_3F and CCl_2F_2 during overlapping 3-year periods from 1975 to 1980. Figure 1 smooths over the wild fluctuations and illustrates that the rates of increase of CCl_3F and CCl_2F_2 have declined since measurements began in 1975. Thus, the $\hat{\beta}$ estimated in Table 2 are the average rates of increase from 1975 to 1980, but this rate is a composite of a faster growth in past years and a somewhat slower growth in recent times. Similar calculations for CH_3CCl_3 and CCl_4 show no such patterns. The rates of increase of CH_3CCl_3 that we do observe (Table 1) are consistent with the global emissions pattern of CH_3CCl_3 over the last 20 years (*6, 7*). These emissions patterns are not at all like the CCl_3F and CCl_2F_2 emissions patterns.

Table 1. Concentrations (in parts per trillion, by volume, unless otherwise specified) of trace gases measured at the South Pole (SP) and the Pacific Northwest (PNW); ppbv, parts per billion, by volume. The concentrations reported are for January of each year.

Gas	Site	1975	1976	1977	1978	1979	1980
CCl_3F	SP	90	113	127	145	154	166
CCl_3F	PNW	125	138	154	166	173	188
CH_3CCl_3	SP	45	57	70	85	95	102
CH_3CCl_3	PNW	87	98	107	117	135	156
CCl_4	SP	120	121	128	123	135	
CCl_4	PNW	130	133	144	154	140	153
CCl_2F_2	SP		195	216	244	260	284
CCl_2F_2	PNW		228	251	280	300	322
N_2O (ppbv)	SP			330	331	332	335
N_2O	PNW			330	332	332	335
$CHClF_2$	SP						45
$CHClF_2$	PNW						63
$C_2Cl_3F_3$	SP						11
$C_2Cl_3F_3$	PNW						17
CH_3Cl	SP						590
CH_3Cl	PNW						630
SF_6	SP						0.39
SF_6	PNW						0.57
CO (ppbv)	SP						50
CO	PNW						150
CH_4 (ppbv)	SP						1510
CH_4	PNW						1650
C_2H_2	SP						< 20
C_2H_2	PNW						600
C_2H_4	SP						50
C_2H_4	PNW						200
C_2H_6	SP						280
C_2H_6	PNW						1200

Table 2. Average rates of increase ($\hat{\beta}$) of CCl_2F_2, CCl_3F, CH_3CCl_3, CCl_4, and N_2O and the average north/south ratio ($\hat{R}$) from 1975 to 1980.

Gas	$\hat{\beta}$* (% year^{-1})	(β_L, β_U)†	$\hat{R}$‡	(R_L, R_U)	Did R change?
			South Pole		
CCl_2F_2	9	(8, 11)			
CCl_3F	12	(9, 13)			
CH_3CCl_3	17	(12, 21)			
CCl_4	3	(0.8, 6)			
N_2O	0.4	(0.3, 0.9)			
			Pacific Northwest		
CCl_2F_2	9	(7, 10)			
CCl_3F	8	(7, 9)			
CH_3CCl_3	11.6	(10, 13)			
CCl_4	3	(1, 6)			
N_2O	0.4	(0, 0.6)			
			Global		
CCl_2F_2	9	(7, 11)	1.15	(1.14, 1.17)	Yes, − 0.008 year^{-1}
CCl_3F	10	(7, 11)	1.18	(1.13, 1.30)	Yes, −0.04 ± 0.02 year^{-1}
CH_3CCl_3	13.2	(12, 14)	1.58	(1.41, 1.83)	Yes, nonlinear
CCl_4	2.5	(0.6, 4)	1.11	(1.06, 1.19)	Maybe
N_2O	0.4	(0.1, 0.5)	1.000	(0.999, 1.002)	No

*$\hat{\beta}$ is a nonparametric Theil estimate of the average yearly increase based on the model $C = C_0 \exp(\hat{\beta} t)$, where C is the concentration, t is time (0 at 1975). To reproduce the concentrations, divide $\hat{\beta}$ in Table 2 by 100 and insert into the model equation for C. †β_L and β_U are the approximate 90 percent confidence limits for the rate of increase (Theil). ‡$\hat{R}$ is the Hodges-Lehmann estimate of the (average) north/south ratio; R_L and R_U are the approximate 90 percent confidence limits.

The N/S ratio, denoted R, is equal to the concentration measured in the PNW divided by the concentration measured, at the same time, in Antarctica. We used the nonparametric Hodges-Lehmann estimator to obtain the "average" value denoted $\hat{R}$; R_L and R_U are the lower and upper values obtained by calculating the 90 percent confidence limits based on Wilcoxon's signed rank statistic (*4*). The Wilcoxon signed rank test also verifies that $R > 1$ for CCl_3F, CCl_2F_2, CCl_4, and CH_3CCl_3 ($\alpha < .03$).

The two variables β and R are based on ratios of concentrations and as such are less susceptible to errors in absolute accuracy. Since all data are referenced against the same common standards, we believe that the estimates of β and R given in Table 2 are accurate. Although the trends toward increasing concentrations are dramatically illustrated in the measurements of CCl_3F, CCl_2F_2, and CH_3CCl_3, it is also possible that CCl_4 and N_2O have been slowly increasing. For the CCl_4 time series in Antarctica, the Mann-Theil test of trend indicates that $\beta > 0$ ($\alpha = .042$). More significantly, it is also possible that N_2O concentrations may be increasing. The Antarctica data and global average show $\beta > 0$ ($\alpha = .042$, Mann-Theil test). The time span over which the N_2O data were obtained is still too short to permit one to attribute this small rate of increase to the rise in the global burden, when it may simply be an experimental artifact. Research is currently under way that should determine whether N_2O is increasing in the atmosphere.

The data in Table 1 also indicate that the N/S ratio of CCl_2F_2, CCl_3F, and CH_3CCl_3 varies from year to year (Tables 1 and 2). For CCl_3F and CCl_2F_2, R has a tendency to decrease toward some stable value lower than that found in 1975. A Mann-Theil statistical test reveals that there may be a trend toward decreasing values of R ($\alpha < .05$) (*4*). Such a trend would be expected on the basis of change in global emission patterns, namely, rapidly increasing emissions until about 1975 and approximately constant yearly emissions from then on. It is likely that we are seeing this change of emission pattern in the time series of *R* for CCl_3F and CCl_2F_2.

For CH_3CCl_3, there is no such "leveling off" in the emissions, although in the past several years the rate of increase in emissions has declined considerably. The emissions patterns over the last 16 years have shown fluctuations that may translate into fluctuations of *R* because of the delays involved in the transport of CH_3CCl_3 from high northern latitudes to the far Southern Hemisphere (*7*). Because of the common standards maintained from 1976, the high precision of the data, and the use of ratios of concentrations, it is possible that the effects of changing emissions patterns on *R* have been observed in the antarctic and PNW data (Fig. 1). Further details of the data analysis are given in (*7*).

Our antarctic program has provided an ideal location for the measurement of trace gases in the Southern Hemisphere. The site is far removed from major industrial activity, and the availability of scientific support facilities makes it unique in the Southern Hemisphere. The data obtained so far have shown remarkable internal consistency and have been used in several theoretical studies reported in the environmental literature.

R. A. RASMUSSEN
M. A. K. KHALIL
R. W. DALLUGE
Department of Environmental Science,
Oregon Graduate Center,
19600 NW Walker Road,
Beaverton 97006

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Cross-Linked Fibrinogen Dimers Demonstrate a Feature of the Molecular Packing in Fibrin Fibers

Abstract. *A stable population of fibrinogen dimers cross-linked by Factor XIIIa has been prepared and examined in the electron microscope. The trinodular fibrinogen molecules are cross-linked through their outer nodules in an end-to-end, nonoverlapping fashion. These dimers form normal banded fibers after treatment with the clotting enzyme, thrombin.*

The trinodular structure of fibrinogen (*1*) has recently been confirmed by two different electron microscopic techniques (*2*). This 340,000-dalton protein molecule has an overall length of 45 nm and consists of two identical outer nodules about 6 nm in diameter linked to a central nodule 4 to 5 nm in diameter. During blood coagulation these molecules are proteolytically activated by thrombin to form fibrin monomers, which spontaneously polymerize to form fibrin fibers. Subsequently, the molecules within these fibers may be cross-linked intermolecularly (*3*) at specific sites by a plasma transglutaminase, Factor XIIIa. Fibrinogen molecules in solution can also be cross-linked by Factor XIIIa, presumably at the same sites. The positions of these cross-link sites within the amino acid sequence of fibrinogen are known and, in models relating the sequence to the trinodular structure, one of these sites (the γ-chain cross-link site) is placed in the outer nodules. Although the fibrin polymerization scheme in Fig. 1 is generally accepted, the precise location of the intermolecular contact sites and the orientation of the molecules has not been determined. We report here the isolation and electron microscopy of fibrinogen dimers cross-linked through the γ-chain sites by Factor XIIIa. This cross-link site is located in the outer nodules, and the structural arrangement of the two cross-linked fibrinogen molecules is that indicated in Fig. 1. This is the most direct evidence for the location of an intermolecular contact site on the trinodular molecule and the molecular packing within the fibrin fiber.

Fibrinogen contains two copies each of three different polypeptide chains designated $A\alpha$, $B\beta$, and γ, with all six chains covalently linked by disulfide bonds. Although Factor XIIIa is capable of intermolecularly cross-linking two γ chains and two or more $A\alpha$ chains, sodium dodecyl sulfate-gel electrophoretic analysis shows that under our conditions only the γ chains are cross-linked. The γ-chain cross-link site consists of two closely spaced reciprocal groups, one donor and one acceptor, located near the carboxyl terminus of the chain. Since there are two γ chains in each fibrinogen molecule, incubation of a mixture of fibrinogen and Factor XIIIa can yield oligomers, as well as dimers, of fibrinogen (*4*). We found that the formation of oligomers is inhibited by including an excess of monodansyl cadaverine or glycine methyl ester in the mixture. These compounds are covalently linked by Factor XIIIa to the cross-link acceptor sites (*5*), blocking these sites and thereby inhibiting the cross-linking of fibrinogen. Whereas in the absence of inhibitor, dimers may continue to participate in the cross-linking reaction and grow to trimers and larger oligomers, in the presence of the inhibitor, the terminal cross-link acceptor sites (that is, those not participating in the formation of a dimer) may be blocked, thus making the dimer species-stable. Using this approach, we have succeeded in preparing stable dimers, which were separated from single fibrinogen molecules by gel filtration (Fig. 2).

We have studied the structure of the fibrinogen dimers by electron microscopy of negatively stained specimens prepared from the peak fraction of purified dimers. Images of representative molecules are shown in Fig. 3, a and b. The dimers are highly elongated with an average length of 89 ± 3 nm (*6*), twice that of the individual fibrinogen molecule (*2*). Such end-to-end dimers are virtually

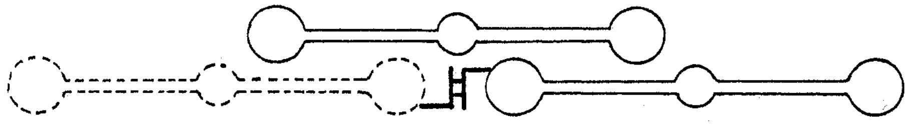

Fig. 1. In the accepted scheme for the polymerization of fibrin monomers, the first step is the lateral association of two monomers with an overlap of one half-molecule (solid lines). The next molecule adds in the position indicated by the dotted lines, forming the same type of lateral contacts and in addition a longitudinal contact. The position of the γ-chain cross-link, normally added after polymerization, is located between longitudinally oriented molecules, as indicated.