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19. The electron probe microanalysis measurements reported here were made during a sabbatical stay of M.O.A. at the Department of Chemistry, University of Antwerp (Universitaire Instelling Antwerpen); thanks are due to F. Adams for making this visit possible. We acknowledge the help of R. Nullens with the operation of the SEM and of P. Van Espen with the analysis of the data. This research was supported by the National Science Foundation (grant ATM-8407137), the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek, and the Belgian Ministry of Science Policy (grant 84-89/69).

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Atmospheric Trace Gases: Trends and Distributions Over the Last Decade

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Concentrations of the halocarbons CCl_3F (F-11), CCl_2F_2 (F-12), CCl_4, and CH_3CCl_3, methane (CH_4), and nitrous oxide (N_2O) over the decade between 1975 and 1985 are reported, based on measurements taken every January at the South Pole and in the Pacific Northwest. The concentrations of F-11, F-12, and CH_3CCl_3 in both hemispheres are now more than twice their concentrations 10 years ago. However, the annual rates of increase of F-11, F-12, and CH_3CCl_3 are now considerably slower than earlier in the decade, reflecting in part the effects of a ban on their nonessential uses. Continued increases in these trace gas concentrations may warm the earth and deplete the stratospheric ozone layer, which may cause widespread climatic changes and affect global habitability.

IN RECENT YEARS CONCERN HAS BEEN growing that the buildup of man-made trace gases in the atmosphere may warm the earth by contributing to the natural greenhouse effect and cause widespread climatic changes (*1*). Some man-made trace gases may deplete the O_3 layer in the stratosphere and therefore increase the amount of biologically active ultraviolet radiation that reaches the earth's surface (*1, 2*). Although it is recognized that the buildup of CO_2 is likely to increase the earth's temperature during the next century, it is also possible that continued increases of CH_4, CCl_3F (F-11), CCl_2F_2 (F-12), and N_2O may together be as effective as CO_2 in warming the earth (*3*). F-11, F-12, and N_2O may also be most effective in depleting stratospheric O_3 (*2*). Other trace gases such as CH_3CCl_3 and CCl_4 may contribute to both these phenomena but in lesser amounts (*1–3*). While singly their effects may be small, continued increases in the concentrations of these six trace gases have the potential for changing the global environment.

These trace gases are expected to play a prominent role in changing the earth's environment because they have reached relatively high concentrations in the atmosphere and persist for long times. Moreover, the increases in CO_2, CH_4, and N_2O are closely related to the production of food and energy, whereas the other gases mentioned above are used in modern industrial processes (*1, 4, 5*). Therefore, it is likely that, for a long time to come, the concentrations of these trace gases will continue to increase with increasing population. Here we report data that are useful for evaluating the future environmental consequences of the increased concentrations of six trace gases believed to have the greatest potential for contributing to global environmental changes. These data, which span the last decade, represent, as far as we know, the longest internally consistent record of atmospheric trace gas concentrations (*6*).

Table 1 shows the global concentrations (*C*) of F-11, CCl_4, CH_3CCl_3, F-12, CH_4, and N_2O for the last 10 years. These measurements were taken every January at the South Pole (SP) and in the Pacific North-

Table 1. Concentrations of atmospheric trace gases over the period from 1975 to 1985 based on measurements taken each January at the South Pole (SP) and in the Pacific Northwest (PNW). The global rates of increase are given at the bottom with 90% confidence limits. The concentrations are in parts per trillion by volume for the four chlorocarbons and in parts per billion by volume for N_2O and CH_4.

Year	CCl_4		CH_3CCl_3		CCl_3F (F-11)		CCl_2F_2 (F-12)		N_2O		CH_4	
	PNW	SP	PNW	SP	PNW	SP	PNW	SP	PNW	SP	PNW	SP
1975	104	96	70	36	120	86	200	165	297	297	1525	1400
1976	106	97	78	46	133	109	217	185	299	298	1555	1425
1977	115	102	86	56	148	122	239	205	300.3	300.3	1573	1442
1978	123	98	94	68	159	139	266	232	302.1	301.2	1596	1463
1979	116	110	112	74	167	148	283	255	302.0	301.8	1619	1483
1980	121	110	126	80	179	159	307	270	303.4	303.8	1639	1500
1981	122	113	127	90	185	170	315	288	304.3	305.0	1656	1516
1982	121	114	133	97	193	179	330	304	306.8	305.4	1671	1539
1983	126	117	144	100	205	188	350	319	306.7	306.5	1663	1549
1984	130	118	150	105	213	195	366	336	306.2	306.5	1689	1567
1985	130	116	158	109	223	205	384	354	307.3	307.5	1711	1570
Annual increase, $C \pm \delta C$	2.4 ± 0.3		8.2 ± 0.6		10.6 ± 0.8		18.5 ± 0.9		1.04 ± 0.14		17.5 ± 1.3	

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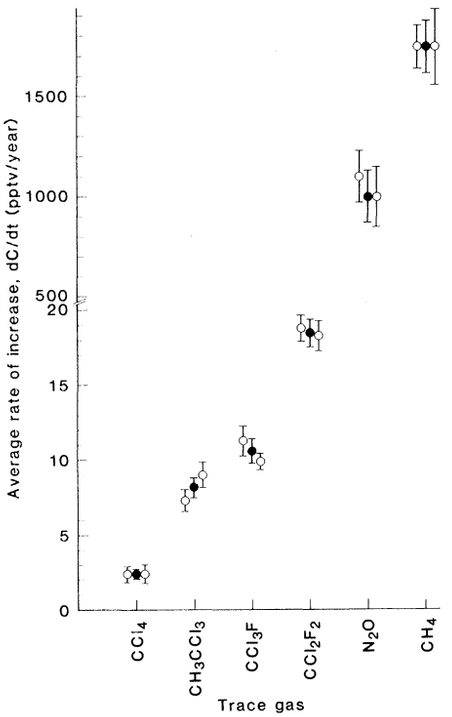

Fig. 1. Average rates of increase of trace gases dC/dt in the atmosphere in parts per trillion by volume per year based on the model $C = A + Bt$, where A and B are determined by least-squares methods. The middle dark circles in each set are the estimates of the globally averaged rate of increase, the open circles to the right show the rates of increase in the Pacific Northwest, and the circles on the left are for the South Pole. Vertical bars indicate the 90% confidence limits of the average rates of increase.

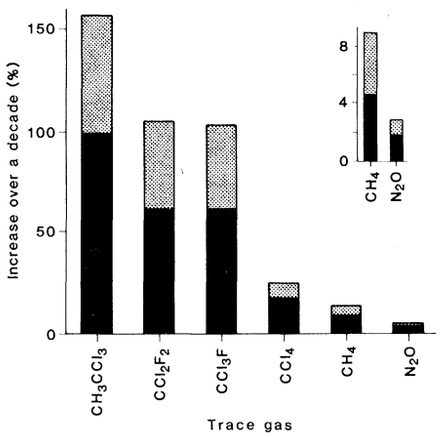

Fig. 2. The increase in trace gas concentrations over a decade (1975 to 1985): blackened portions, 1975 to 1980; stippled portions, 1980 to 1985; CCl_3F (F-11), CCl_2F_2 (F-12), and CH_3CCl_3 have more than doubled during this time (doubling = 100 on the graph). The concentrations of all gases increased more during the first half of the decade than during the second half (*11*).

west (PNW) (45°N), and some of these data were reported earlier (*7*). However, a new calibration has led to a revision of the absolute concentrations (*5, 8*). Since the atmospheric lifetimes of these trace gases are long, the averages of the measurements taken at high latitudes of the Northern Hemisphere and Southern Hemisphere are accurate representations of the average global concentrations.

All these trace gases have been increasing in both hemispheres at substantial rates ($dC/dt > 0$). The average rates of increase and the 90% confidence limits are shown in Fig. 1 (*9*). The rates of increase were about the same in both hemispheres (*10*).

A closer examination of the data shows that all these gases increased significantly more rapidly earlier in the decade (1975 to 1985) than more recently. Figure 2 depicts the total increases of the trace gases over the last decade and the slowdown of the accumulation during the last 5 years (*11*). Since 1975, the annual production and releases of F-11 and F-12 have not changed substantially, due in part to a ban on their nonessential uses in spray cans; before this time, their production had been rising rapidly. Similarly the production and uses of CCl_4 and CH_3CCl_3 have not continued to increase as in earlier years (*5, 7*). Therefore, it is expected that the rates at which these gases are accumulating in the atmosphere will slow down. During the last great El Niño of 1982–83, the CH_4 concentration decreased considerably; as a result, the total increase during the last half of the decade was somewhat less than during the first half (*12*). Predictions of future concentrations will require much more detailed knowledge of the sources and methods of removal of these trace gases and cannot be based on a simple extrapolation of the currently observed trends.

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10. The measured rates of increase at the South Pole and in the Pacific Northwest were compared by a t test; except for CH_3CCl_3, no significant differences were found. For CH_3CCl_3 the differences between the rates of increase in the two hemispheres were small and are probably inconsequential.
11. Figure 2 was generated as follows: We derived a global average (C_g) by taking the average of concentrations at the South Pole and in the Pacific Northwest. The decade of 1975 to 1985 was divided into two halves, 1975 to 1980 and 1980 to 1985. Using linear least-squares methods, with $C = A + Bt$, we calculated A_I, B_I (the coefficients for 1975 to 1980), and A_{II}, B_{II} (the coefficients for 1980 to 1985). The total increase during the first 5 years, shown as the blackened portion of the bars in Fig. 2, is $5B_I/A_I$ or the total increase relative to the initial concentration. The stippled portion of each bar is given by $5B_{II}/A_I$. The whole bar represents the increase in the trace gas concentration over the decade 1975 to 1985 relative to the level in 1975. The concentrations calculated by the linear least-squares method for the base year (1975) and described above as A_I are: 100 pptv for CCl_4, 52 pptv for CH_3CCl_3, 106.7 pptv for F-11, 185.5 pptv for F-12, 1466 ppbv for CH_4, and 297.3 ppbv for N_2O. For the statistical tests, the span of the measurements was divided into two disjoint periods of time (P_1 = 1975 to 1979 and P_2 = 1981 to 1985). The measurements from the South Pole and the Pacific Northwest were averaged to obtain an estimate of the global concentrations of trace gases. We calculated the rates of increase during these periods, using the model: $C = A + Bt$. The slopes obtained during the two periods were compared by a t test. The results show that F-11, F-12, CCl_4, CH_3CCl_3, CH_4, and N_2O increased significantly more rapidly ($\alpha = 0.05$) during the first period than during the second period. The rates of increase were as follows: for CCl_4, 3.5 pptv/year during P_1 and 1.8 pptv/year during P_2 with the difference, denoted by $\delta B = 1.8 \pm 1.2$; for CH_3CCl_3, 9.9 pptv/year during P_1 and 6.3 pptv/year during P_2 with $\delta B = 3.7 \pm 0.8$; for F-11, 13.7 pptv/year during P_1 and 9.1 pptv/year during P_2 with $\delta B = 4.6 \pm 1.8$; and for F-12, 22.1 pptv/year during P_1 and 16.9 pptv/year during P_2 with $\delta B = 5.2 \pm 1.1$; for CH_4, 21.6 ppbv/year during P_1 and 13.3 ppbv/year during P_2 with $\delta B = 8.3 \pm 3.1$; and for N_2O, 1.3 ppbv/year during P_1 and 0.6 ppbv/year during P_2 with $\delta B = 0.8 \pm 0.4$. The $\pm$ values are 90% confidence limits.
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