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LONG TERM TREND OF SELECTED HALOGENATED HYDROCARBONS

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ABSTRACT

The so–called "Library of Background Air" at the Oregon Graduate Institute was used to determine the trend in volume mixing ratios of selected halogenated hydrocarbons in the time period 1977–1989. This library consists of background air samples most of them taken at Cape Meares (Oregon). For storage stainless steel containers are used. Tests have shown the gases under consideration to be stable in these containers.

Analyses using a GC/MS–system were performed for the CFCs 11, 12, 12B1 (HALON 1211, $CBrClF_2$), 22, 113, 114 and CH_3Cl, CH_3Br, CH_3CCl_3, CCl_4. The advantage of this unique investigation: Different aged air samples are analysed at the same time with the same instrument. No calibrations or intercalibrations are needed. All data are presented in normalized mixing ratios versus time. We discuss the results, derive rate constants and we present a formula to describe the nonlinear increases.

1. INTRODUCTION

Halocarbons containing chlorine and bromine have been found to deplete ozone in the stratosphere. In addition they are important greenhouse gases [Climate change, 1990; WMO, 1990]. Since there is no significant tropospheric removal mechanism for the fully halogenated hydrocarbons, they are almost inert gases in the troposphere, where they accumulate. Transported into the stratosphere by various mechanism, they decompose by UV photolysis and by reacting with $O(^1D)$, liberating chlorine and bromine. The overall lifetime of these CFC's is large, whereas the lifetime of partly halogenated hydrocarbons such as $CHClF_2$ (CFC-22) methyl chloride (CH_3Cl), methylbromide (CH_3Br) and methylchloroform (CH_3CCl_3) is relatively small and they are mostly removed in the troposphere. Nevertheless, the global release of CH_3Cl and CH_3CCl_3 is so large, that despite tropospheric removal, their contribution to the stratospheric chlorine budget is significant [Borchers et al., 1983, 1989; Fabian et al., 1981; Fabian 1986].

One of the important partly halogenated halocarbons of anthropogenic origin, CFC–22 ($CHClF_2$) is being seriously considered to be a replacement substance for CFC–11 and CFC–12. But it should be pointed out that its lifetime is ~ 10–20 years, and is not low enough to prevent it from reaching to the stratosphere and augmenting its chlorine budget.

2. MEASUREMENTS

The growth rate of the tropospheric concentration of some of the important halogenated hydrocarbons, namely CFC–11, CFC–12, CFC–22, CFC–113, CFC–114, CFC-12B1, CH_3Cl CH_3Br, CH_3CCl_3 and CCl_4 has been obtained by analysing air samples from the "Library of Background Air" at the Oregon Graduate Institute. The GC-MS-system equipped with a DB-1 capillary column has been used to analyse the air samples collected periodically during a time span of 13 years (1977–1989). All the analyses have been performed under exactly identical conditions. Considering these halogenated hydrocarbons to be stable under the storage in the stainless steel containers during the aforesaid time-frame – a plausible assumption – the data generated have been used to obtain the annual percentage growth rate by using a simple exponential formula.

RESULTS AND DISCUSSIONS

The volume mixing ratios of all these gases normalized to the value of 1989, have been plotted and are shown in Figs. 1-10. Considering the growth to be exponential and using the following expression

$$VMR_{rel} = A_o e^{B(t-1976)}$$

[where A and B are constants and t denotes the year]

the relative growth rates have been calculated. These growth rates are tabulated in Table 1 and are also shown by the solid lines in all the figures [Figs. 1–10].

The atmospheric concentrations of CH_3Cl and CH_3Br have been found stable (long term behavior) indicating that they do not have any significant anthropogenic source

(Figs. 9 and 10). The current percentage increase evaluated for the other source gases at Cape Meares are also compared with the global growth rates of these species [Climate Change 1990, WMO, 1990].

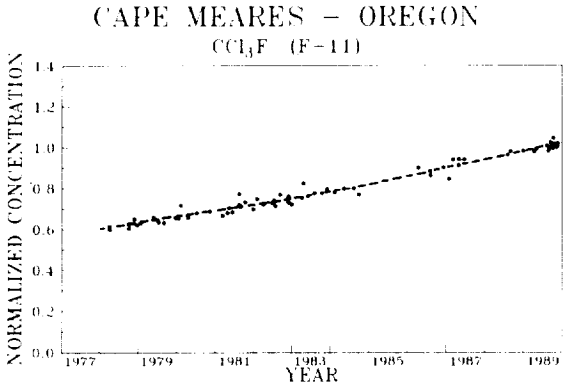

Fig. 1 Volume mixing ratios for CFC-11

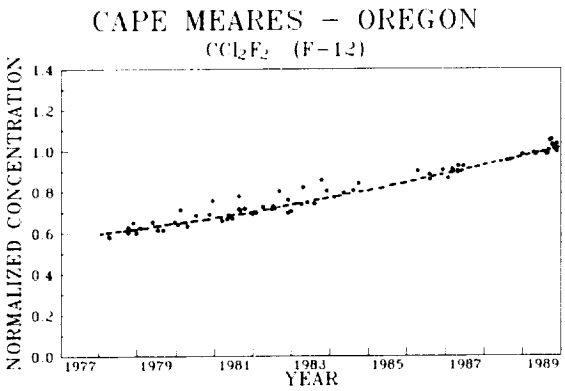

Fig. 2 Volume mixing ratios for CFC-12

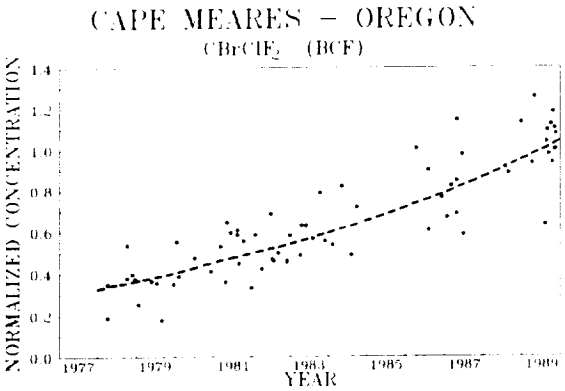

Fig. 3 Volume mixing ratios for CFC-12B1

Table 1. Growth rates obtained for different CFCs

Substance	A_o	B[year^{-1}]	Growth Rate [%/year] Present Data	WMO 1990
CFC-11	0.584	0.04360	4.50	4
CFC-12	0.561	0.04730	4.80	4
CFC-12B1	0.306	0.09560	10.00	12
CFC-22	0.424	0.06930	7.20	8 *
CFC-113	0.133	0.10700	11.30	10
CFC-114	0.591	0.04080	4.20	( )
CH_3CCl_3	0.629	0.04030	4.10	4
CCl_4	0.896	0.00944	0.95	1.5
CH_3Cl	–	–	–	–
CH_3Br	–	–	–	–

* Rasmussen, 1992 unpublished data

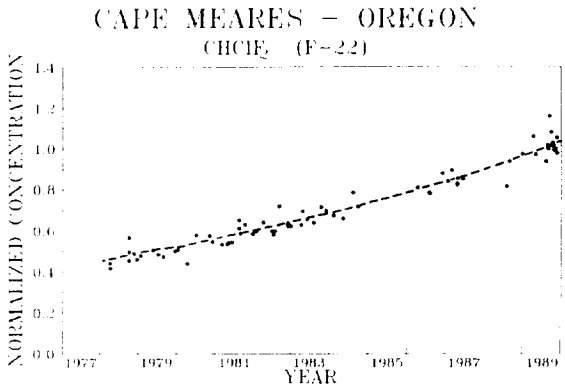

Fig. 4 Volume mixing ratios for CFC-22

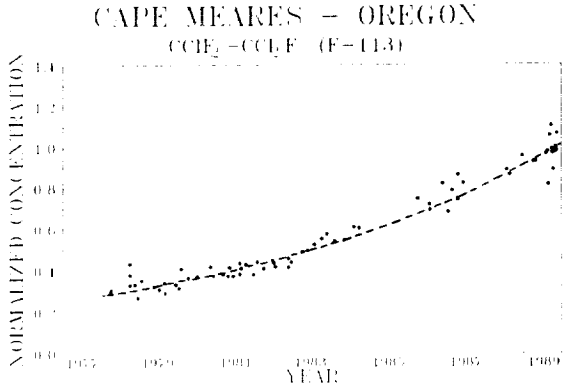

Fig. 5 Volume mixing ratios for CFC-113

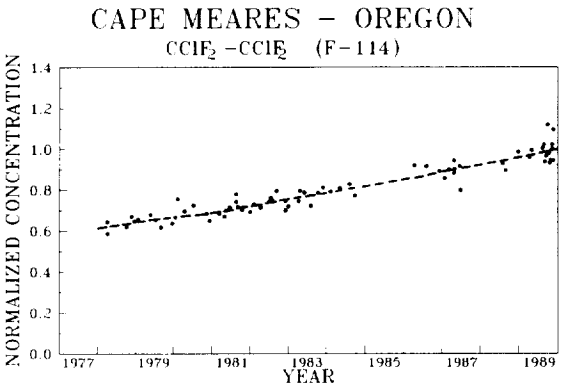

Fig. 6 Volume mixing ratios for CFC-114

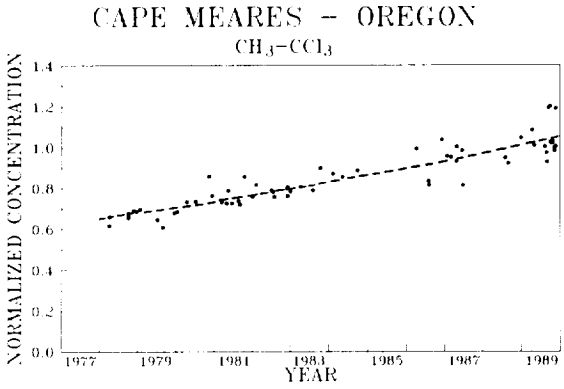

Fig. 7 Volume mixing ratios for CH_3CCl_3

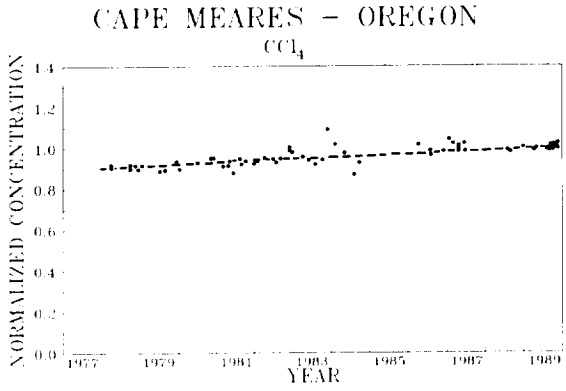

Fig. 8 Volume mixing ratios for CCl_4

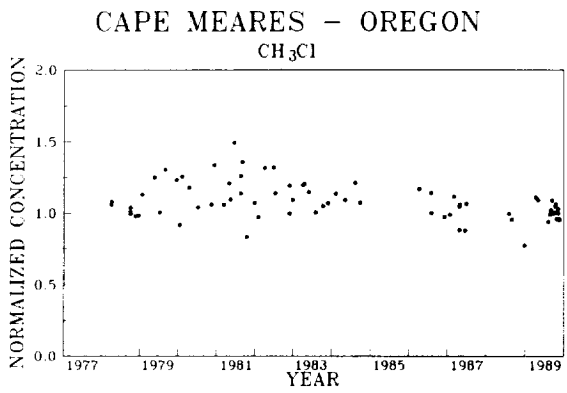

Fig. 9 Volume mixing ratios for CH_3Cl

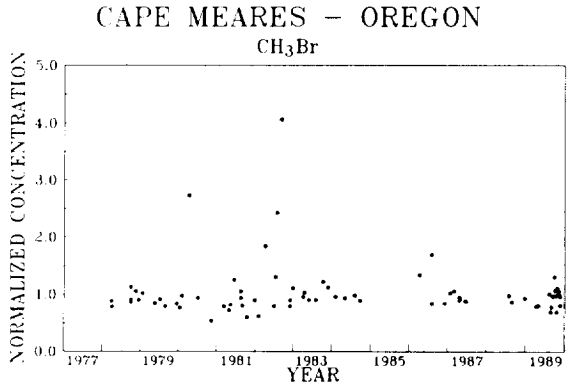

Fig. 10 Volume mixing ratios for CH_3Br

This method is projected as a superior one for calculating the annual percentage increase volume mixing ratio of these trace gases on the following counts:

1. All the analyses could be carried out under identical conditions and more or less simultaneously.
2. The growth rates were evaluated without making an absolute calibration which can rather be tricky and at times uncertain.

It may be added that the percentage increase in the concentration of all these gases in the atmosphere of Cape Meares is more or less similar to their global growth rates. The variations in some cases may be natural because these measurements pertain to a particular region.

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