

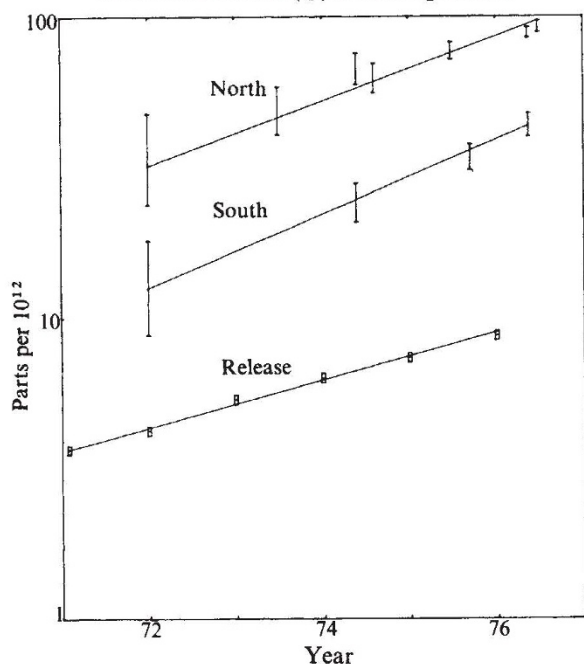
- ³ Rose, G., Widdel, H. U., Azcarraga, A. & Sanchez, J. *Planet. Space Sci.* 20, 871 (1972).
- ⁴ Bragin, Y. A., Tulinov, V. F., Smirnykh, L. N. & Yakovlev *Kosm. issledovaniya* 11, 488-489 (1973).
- ⁵ Widdel, H. U., Rose G. & Borchers, R. *Pure appl. Geophys.* 84, 154 (1971).
- ⁶ Stewart, R. W. & Hoffert, M. L. *J. Atmos. Sci.* 32, 195-210 (1975).
- ⁷ Beauchamp, J. L. & Buttrill, S. E. Jr, *J. chem. Phys.* 48, 1783 (1968).
- ⁸ Karpas, Z. & Klein, F. *Int. J. Mass Spectrom. Ion Phys.* 10, 289-306 (1975).
- ⁹ Smith, D., Adams, N. G. & Church, M. J. *Planet. Space Sci.* 24, 697-703 (1976).
- ¹⁰ Kebarle, P., Searles, S. K., Zolla, A., Scarborough, J. & Arshadi, M. J. *Am. chem. Soc.* 89, 6393 (1967).
- ¹¹ D'Ans-Lax *Taschenbuch für Chemiker und Physiker* (Springer-Verlag, Berlin, 1970).
- ¹² CIRA 1972, *COSPAR International Reference Atmosphere*, (Akademie-Verlag, Berlin, 1972).
- ¹³ Bohringer, H. & Arnold, F. *Jahresbericht 1976* (Max-Planck-Institut für Kernphysik, Heidelberg, Germany, in preparation).
- ¹⁴ Mahan, G. H. *Adv. Chem. Phys.* 23 (Wiley, New York, 1973).

Methyl chloroform in the troposphere as an indicator of OH radical abundance

METHYL chloroform (111 trichloro ethane) was introduced into general use in 1955-60 in response to the need for a general solvent which was less toxic than those then in use. Its ubiquitous presence in the northern and southern hemispheres, first reported in 1974 (ref. 1), has since been confirmed^{2,3}. The only significant sources of methyl chloroform are industrial releases from its use as a cleaning agent and solvent. A principal sink for its removal from the atmosphere seems to be the reaction with OH radicals. The rate of its release to the atmosphere is known with some accuracy, and consequently the measurements of its growth in the atmosphere could provide valuable information on the strength of the OH reaction sink, not only for methyl chloroform but also for other important atmospheric gases which undergo similar reactions. This communication reports measurements of the abundance of methyl chloroform made during 5 yr in the northern and southern tropospheres.

Methyl chloroform was analysed directly from 5-ml air samples using a gas chromatograph equipped with an electron capture detector. The method was that described for other halocarbons, including the fluorocarbons and carbon tetrachloride⁴. Figure 1 shows the concentration observed during the past 5 yr at measuring sites in rural

Fig. 1 Observed concentrations: parts per 10^{12} by volume of CH_2Cl_2 in the northern hemisphere (British Isles) and southern hemisphere (South Africa and Antarctica) during 1972-77. Cumulative releases (○) are in megatonnes.



regions of the British Isles, in the southern hemisphere in Cape Province South Africa and aboard the RV Shackleton. Northern hemisphere measurements were all made, except in 1972, during periods of unpolluted Atlantic air.

The observations in the southern hemisphere have been followed from just about the noise level in 1971, at an abundance of 1.2×10^{-11} , to the present level of 5×10^{-11} . The low initial finding suggests that there is no significant natural source of this compound. The absolute accuracy of the analytical method is not likely to be worse than 30% which is in general agreement with the experience of other analysts^{2,4}. Figure 1 also shows the annual releases of methyl chloroform to the atmosphere from industrial sources (personal communication from W. B. Neeley and J. Plonka). When applied to the observations here reported, using a simple two box model of the atmosphere, these data suggest an atmospheric residence time of between 5 and 10 yr. H. B. Singh (personal communication) reports observations also pointing to a longer residence time for methyl chloroform. Previous estimates of the residence time have varied from 1 to 2 yr (refs 3 and 5). It is unlikely that the measured rate of reaction of OH radicals with methyl chloroform⁵ is seriously in error, and the most likely source of the anomaly is in the time averaged value assumed for the OH concentration. The yearly average concentration is usually taken to be in the range $3-5 \times 10^6$ radicals per ml. This is a mean of several estimates⁷⁻⁹. One outstanding exception, however, is the estimate by Warneck¹⁰ of 7×10^5 per ml, for the yearly average. This lower value is more consistent with the observations reported here. The discrepancy in OH concentration is considerable and if it propagates to the reaction of the other atmospheric gases such as methane, CO and other hydrocarbons, could influence the interpretation of the chemistry of both the troposphere and the stratosphere. The comparatively uncomplicated industrial source and natural OH sink of this gas suggests that it may serve as a useful indication of the distribution of OH radicals.

Crutzen⁸ has discussed the consequences of the presence of this compound on the ozone layer. If current theories of ozone depletion by chlorine-containing species are confirmed by atmospheric measurements and if methyl chloroform is produced in ever increasing quantities for several decades, I agree with Crutzen that the atmospheric burden would give cause for concern.

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J. E. LOVELOCK

Bowerchalke,
Salisbury,
Wiltshire, UK

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- ¹ Lovelock, J. E. *Nature* 252, 292 (1974).
- ² Grimstrud, E. P. & Rasmussen, R. A. *Atmosph. Env.* 9, 1 (1975).
- ³ Cox, R. A., Derwent, R. G., Eggleton, A. E. & Lovelock, J. E. *Atmosph. Env.* 10, 305 (1976).
- ⁴ Lovelock, J. E., Maggs, R. J. & Wade, R. J. *Nature* 241 (1973).
- ⁵ 'Halocarbons': *Effects of Stratospheric Ozone* (National Academy of Sciences, Washington DC, 1976).
- ⁶ Watson, R. T., Machado, E. S., Conway, B., Wagner, S. & Davis, D. D. *J. phys. Chem.* (in the press).
- ⁷ Levy, H. *Adv. Photochem.* 9, 369 (1974).
- ⁸ Crutzen, P. *Tellus* 26, 47 (1974).
- ⁹ Wofsy, S. C., McConnell, J. C. & McElroy, M. B. *J. geophys. Res.* 77, 4477 (1972).
- ¹⁰ Warneck, P. *Planet. Space Sci.* 23, 1507 (1975).

Inhomogeneities in the water properties of fogs and clouds

ALTHOUGH there is good evidence that entrainment of undersaturated environmental air exercises a profound influence upon the development of the droplet spectra in clouds, the classical description of the mixing process¹ has