

ATMOSPHERIC HALOCARBONS: A DISCUSSION WITH EMPHASIS ON CHLOROFORM

Yuk Ling Yung, Michael B. McElroy and Steven C. Wofsy

Center for Earth and Planetary Physics
Harvard University, Cambridge, Massachusetts

Abstract. Bleaching of paper pulp represents a major industrial use of chlorine and could provide an environmentally significant source of atmospheric halocarbons. The related global production of chloroform is estimated at 3×10^5 ton yr^{-1} and there could be additional production associated with atmospheric decomposition of perchloroethylene. Estimates are given for the production of methyl chloride, methyl bromide and methyl iodide, 5.2×10^6 , 7.7×10^4 , and 7.4×10^5 ton yr^{-1} respectively. The relative yields of CH_3Cl , CH_3Br and CH_3I are consistent with the hypothesis of a marine biological source for these compounds. Concentrations of other halocarbons observed in the atmosphere appear to indicate industrial sources.

The atmosphere contains small though detectable quantities of CCl_2F_2 , CCl_3F , CH_3Cl , CH_3CCl_3 , C_2HCl_3 , C_2Cl_4 , CH_3I , CCl_4 , and CHCl_3 , with concentrations as summarized in Table 1. The fluorocarbons, CCl_2F_2 and CCl_3F , are industrial in origin, employed primarily as refrigerants and as aerosol propellants (Lovelock, 1971; Lovelock et al., 1973; Wilkness et al., 1973, 1974; Su and Goldberg, 1973; Rasmussen, 1975). Trichloroethylene perchloroethylene, and 1,1,1-trichloroethane are extensively used as solvents and dry-cleaning agents. Methyl chloride, CH_3Cl , and methyl iodide, CH_3I , appear to be produced mainly by marine biological activity (Lovelock, 1975; Rasmussen, 1975) and there is evidence for an analogous source of methyl bromide, CH_3Br (Rasmussen, 1975; Wofsy et al., 1975). Carbon tetrachloride, CCl_4 , is used extensively as an intermediate in the manufacture of CCl_2F_2 and CCl_3F . An uncertain fraction of the CCl_4 is inadvertently released to the atmosphere and, with reasonable assumptions (Molina and Rowland, 1974a), can account for the abundance listed in Table 1, although there may be additional, natural, sources (Lovelock et al., 1973). Chloroform, CHCl_3 , was used extensively as an anesthetic for almost 50 years after its discovery in 1831. In recent years it has been used mainly as an intermediate in the manufacture of penicillin, and various fluorocarbon refrigerants (Freon 22) and resins (notably Teflon).

This paper is concerned primarily with CHCl_3 . We shall attempt to define the magnitude and identify the nature of the source for this compound. There is an urgent need for a comprehensive study of atmospheric halocarbons, in light of the potentially important role which they may play in the chemistry of stratospheric ozone (Molina and Rowland, 1974, a, b; Wofsy et al., 1975). This paper describes an initial step towards this objective. It offers, in addition to the discussion of CHCl_3 , some updated estimates for the magnitude of the surface source required in order to account for the measurements of CH_3Cl and CH_3I given in Table 1.

Chloroform will be removed from the atmosphere primarily by reaction with OH, and similar remarks apply to CH_3Cl . Rate constants for the relevant reactions were measured recently at 296°K by Howard and Evenson (1975) and Davis et al. (1975). Their data, together with estimates for the relevant activation energies, were used to construct the rate constants listed in Table 2. The OH profile summarized in Figure 1 was computed in the manner described by McElroy et al., (1974). The lifetime for CH_3I , determined mainly by photolysis, was computed using cross sections measured by Porret and Goodeve (1938). The lifetimes given in Table 2 represent upper limits. The actual values could be somewhat less if there were important loss processes in addition to photolysis and reaction with OH. In like manner the sources for CH_3Cl , CH_3I and CHCl_3 given in Table 2 represent lower limits and should be adjusted upwards if additional atmospheric sinks can be identified for these species. The sources for CH_3Cl and CH_3I given here may be compared with the source of 7.7×10^4 metric tons yr^{-1} derived earlier for CH_3Br (Wofsy et al., 1975).

Table 2 includes two estimates for the global production of CHCl_3 . The

Table 1
Measurements of Halomethanes

Species	Mixing Ratio (v/v) (10^{-12})	Reference
CCl_2F_2	102 – 115	Lovelock (1974)
CCl_3F	60 – 80 80 – 90	Wilkness et al. (1973) Lovelock (1974)
CH_3Cl	400 550 ± 50	Lovelock (1975) Rasmussen (1975)
CH_3I	1.2	Lovelock (1973)
CCl_4	71 ± 7 75 ± 8 111 – 138	Lovelock et al. (1973) Wilkness et al. (1973) Lovelock (1974)
CHCl_3	19 – 27 20	Lovelock (1974) Rasmussen (1975)
C_2HCl_3	1.5 ± 1.2 (Southern Hemisphere) 15 ± 12 (Northern Hemisphere)	Lovelock (1975)
C_2Cl_4	< 1.5 (Southern Hemisphere) 28 ± 9 (Northern Hemisphere)	Lovelock (1975)
CH_3CCl_3	24 ± 3 (Southern Hemisphere) 65 ± 17 (Northern Hemisphere)	Lovelock (1975)

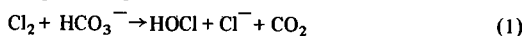
larger value would be appropriate if there were globally dispersed sources for the gas, i.e. if the abundance listed in Table 1 were representative of mean atmospheric conditions. The smaller value assumes that CHCl_3 is anthropogenic in origin and supposes that the source is restricted to populated areas of the northern hemisphere. We may note that even the smaller of the sources in Table 2 is significantly larger than the U.S. Tariff Commission's estimate for the total U.S. production of CHCl_3 in 1972, 1×10^5 tons. The discrepancy is particularly serious if we recall that most CHCl_3 produced industrially is consumed in the manufacture of other chemicals. If we adopt McCarthy's (1975) estimate for the inadvertent release rate, about 50%, we estimate a global source of atmospheric CHCl_3 of 1×10^5 tons yr^{-1} , significantly less than either of the values in Table 2. It is hard to escape the conclusion that there must be sources of atmospheric CHCl_3 in addition to those listed by the Tariff Commission. A summary of data on major industrial uses of chlorine is given in Table 3. As we may see below, the use of chlorine in the bleaching of paper pulp shows most promise as a possible source for the chloroform listed in Table 1. The mechanism suggested here, the haloform reaction, was suggested by Morris (1975) as the source of CHCl_3 and other haloforms produced during the chlorination of municipal water supplies (Rook, 1974; Bellar et al., 1974).

Table 2
Lifetimes and Sources of Halocarbons

	CHCl ₃	CH ₂ Cl	CH ₃ I	C ₂ HCl ₃	C ₂ Cl ₄	C ₂ H ₃ Cl ₃	CHF ₂ Cl
Mixing ratio (v/v) (10 ⁻¹²)	20	500	1.2	15	28	45	—
Major sink	CHCl ₃ + OH	CH ₂ Cl + OH	CH ₃ I + hν	C ₂ HCl ₃ + OH	C ₂ Cl ₄ + OH	C ₂ H ₃ Cl ₃ + OH	CHF ₂ Cl + OH
Rate constant (a)	k = 1.0 × 10 ⁻¹² e ^{-630/T} (b)	k = 1.69 × 10 ⁻¹² e ^{-1066/T} (c)	J = 6.0 × 10 ⁻⁶	k = 3 × 10 ⁻¹² (d)	k = 1.3 × 10 ⁻¹² (d)	k = 8.2 × 10 ⁻¹³ e ^{-1200/T} (e)	k = 1.2 × 10 ⁻¹² e ^{-1640/T} (i)
Lifetime (s)	1.0 × 10 ⁷	2.8 × 10 ⁷	1.7 × 10 ⁵	3.7 × 10 ⁵	8.5 × 10 ⁵	9.5 × 10 ⁷	3.0 × 10 ⁸
Source (if globally distributed) (10 ⁶ metric ton/yr)	0.99	5.2	.74	31	31	0.4	—
Source (if spatially restricted, see text) (10 ⁶ metric ton/yr)	0.23	—	—	1.0 (h)	1.0 (h)	—	—
Global industrial source (10 ⁶ metric ton/yr)	see text	—	—	.68 (f) 1.0 (g)	.61 (f) 1.1 (g)	.28 (f) .48 (g)	.036 (f)

- (a) Bimolecular rate constants, k, and dissociation rate, J, are in units cm³ s⁻¹ and s⁻¹ respectively.
 (b) Howard and Evenson (1975) (at 296°K) combined with an estimate of activation energies.
 (c) Davis et al., (1975).
 (d) Adjusted to the industrial source strength. These rates are consistent with those measured by Howard and Evenson (1975) for other haloethylenes.
 (e) Estimate by C. Howard, private communication, 1975.
 (f) McCarthy, 1975.
 (g) McConnell, 1975.
 (h) Sources restricted to populated area and planetary boundary layer (~1 km thick).
 (i) R. Atkinson, D.A. Hansen and J.N. Pitts, J. Chem. Phys. (in press, 1975).

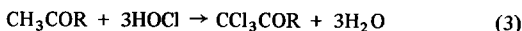
The reaction sequence begins with



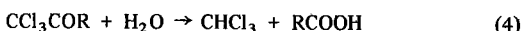
followed by



in which Cl₂ is hydrolyzed to HOCl and OCl⁻. It proceeds through a series of complicated reactions involving dissolved organic material. These reactions may be written symbolically in the form



followed by



Other reactions may lead to formation of additional halogenated species and it is interesting to note that a recent survey by the EPA (Symons, 1975) found evidence for some 35 compounds in the municipal waters of Miami, Florida. These compounds included CHCl₃, CHCl₂Br, CHClBr₂,

and CHBr₃, and there are reasons to believe that a similarly rich suite of halogenated compounds would be formed during the bleaching of paper pulp. The bleaching process, combining an abundant source of organic material with an ample supply of chlorine at high pH, would appear to provide an ideal medium for the production of the halocarbons of interest here. The yield of CHCl₃ in chlorination of water is about 1-3% by weight according to Symons' data (1975). This result represents a lower limit to the potential conversion efficiency since the production of haloforms in the treatment of municipal water supplies appears to be limited by the availability of dissolved organic material. A conversion efficiency as low as 6% in the bleaching process would supply a global source of CHCl₃ of magnitude 3 × 10⁵ tons year⁻¹ and could account for the concentration of the gas given in Table 1.

Decomposition of perchloroethylene, Cl₂C = CCl₂, could provide an additional source for atmospheric CHCl₃. Perchloroethylene is widely used as a solvent, with annual rates for release in excess of 10⁶ tons (U.S. Tariff Commission). Howard and Evenson (1975) found that halogenated ethylenes react with OH at rates faster than 10⁻¹² cm³ sec⁻¹ to form the OH addition compound. The addition reaction should be faster than photolysis

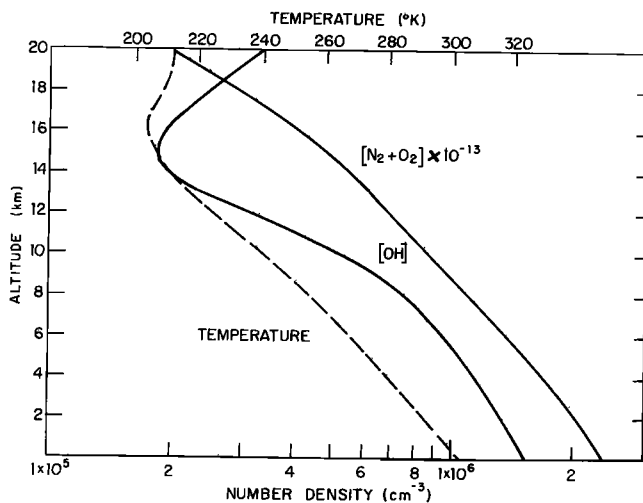


Figure 1: Model atmosphere and OH profile (see text).

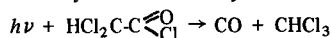
Table 3
Production and major industrial uses of chlorine for the United States in 1974 (Klingman, 1975).

Major Uses	Quantity (10 ⁶ metric tons)
Solvents	2.68
Plastics and synthetics	2.19
Paper products ¹	1.78
Automobile fluids ²	.96
Water and sanitation	.59
Agriculture	.49
Miscellaneous	1.18
TOTAL	9.88

¹According to B. Slating of American Paper Institute, N.Y. this chlorine is used for bleaching paper pulp.

²Mainly used to produce automobile anti-freeze (ethylene glycol) and anti-knock compounds (ethylene chloride).

(Tyerman, 1969) and should be more efficient also than possible competing reactions with ozone. The fate of the radical $\text{CCl}_2\text{-CCl}_2\text{OH}$ has not been studied in any detail. A number of experiments however (Dahlberg et al., 1970; Dahlberg, 1969; Mathias et al., 1974; Haszeldine and Nyman, 1959) suggest that dichloroacetyl chloride, $\text{HCl}_2\text{C-C}^{\text{O}}\text{Cl}$, should be a major product. Photolysis of dichloroacetyl chloride



should take place at wavelengths as long as 3600\AA (cf. Capey et al., 1968) and could provide a significant source of atmospheric CHCl_3 . A quantitative estimate for this source would however require a careful analysis of competing loss processes for $\text{HCl}_2\text{C-C}^{\text{O}}\text{Cl}$. The source strength estimates in Table 2 are consistent with industrial origin for C_2Cl_4 , C_2HCl_2 , and CH_3CCl_3 in the atmosphere.

It is of interest to examine possible natural sources of halogenated compounds. The oceans contain 2×10^{-2} , 7×10^{-5} and $3\text{-}7 \times 10^{-8}$ parts by weight of chlorine, bromine and iodine respectively. Seaweeds have long been known for their ability to concentrate bromine and iodine. The enrichment factors, defined with respect to the concentrations in sea water, are typically in the range 2-10 for bromine and $10^3 - 3 \times 10^4$ for iodine (Hoppe, 1969). It appears that the concentration of chlorine in sea weed is similar to that in the overall marine environment (Shaw, 1962). Wofsy et al. (1975) estimated a marine production of methyl bromide of magnitude 7.7×10^4 ton yr^{-1} and combining their data with the results of Table 2 we find production rates by weight for CH_2Cl , CH_2Br and CH_2I in the ratio 1:0.15:1.4, within the present limits of uncertainty, consistent with the halogen composition of algae.† There are no known natural sources for chloroform, although we may note that CHBr_3 is a major constituent in the essential oil of the red alga *Asparagopsis taxiformis*, which includes in addition, detectable amounts of CHClBr_2 , CHClBrI , CHBr_2I , CHBrI_2 , and CHI_3 (Burrenson et al., 1975). The abundance of CHCl_3 listed in Table 1 would supply a source of stratospheric chlorine which could account for a global reduction in ozone by as much as 0.04%. Corresponding values for the reduction in ozone due to marine biological production of methyl chloride and methyl bromide are 0.8% and 0.5% respectively and the present day reduction due to CFCl_3 and CF_2Cl_2 is 0.6%. These considerations serve to emphasize the need for a comprehensive definition of the atmospheric halogen budget. It is clear that the reservoir includes contributions from a variety of natural and anthropogenic activities ranging from certain functions of marine algae to the preparation of paper, the fumigation of agricultural soil and the large scale commercial application of aerosol sprays and refrigerants.

Acknowledgement

We are indebted particularly to J.C. Morris who shared readily with us his remarkable insights into the chemistry of chlorinated water. We thank C.L. Klingman for providing us with the contents of Table 3, and R. Rasmussen for making available his unpublished measurements. The work was supported in part by the Atmospheric Sciences Division of the National Science Foundation under Grant GA33990X and by the National Aeronautics and Space Administration under Grant NASA NSG 2031 to Harvard University.

References

- Bellar, T.A., J.J. Lichtenberg and R.C. Kroner, 1974: The occurrence of organohalides in finished drinking waters. *J. Am. Water Works Assn.*, 66, 703.
- Burrenson, B.J., R.E. Moore and P. Roller, 1975: Haloforms in the essential oil of the alga *Asparagopsis Taxiformis* (Rhodophyta). *Tetrahedron Lett.*, 7, 473.
- Capey, W.D., J.R. Majer and J.C. Robb, 1968: Photolysis of acetyl chloride. *J. Chem. Soc.*, (B), 1968, 447.
- Dahlberg, J.A., 1969: The non-sensitized photo-oxidation of trichloroethylene in air. *Acta Chem Scand.*, 23, 3081-3090.
- †In the present estimate we note that CH_3I has a lifetime short compared with the time required for vertical mixing. Consequently we assume that CH_3I is confined to the planetary boundary layer (~1 km thick). Our estimate for the production of methyl iodide is consistent with the remainder of the total budget for iodine (Miyake and Tsunogai, 1963) and agrees also with the recent study of flux gases across the air-sea interface (Liss and Slater, 1974). Earlier estimates (Lovelock et al., 1973; Zafiriou, 1974) appear to have seriously overestimated the source of methyl iodide.
- Dahlberg, J.A. and I.B. Kihlman, 1970: Gas chromatographic determination of chlorinated acetyl chlorides and phosgene present in air in very low concentrations. *Acta Chem. Scand.*, 24, 644-650.
- Davis, D.D., R.T. Watson, et al., 1975: private communication.
- Haszeldine, R.N. and F. Nyman, 1959: Oxidation of polyhalogeno compounds part II photolysis and photochemical oxidation of some chlorofluoromethanes. *J. Am. Chem. Soc.*, 81, 387.
- Hoppe, H.A., 1969: *Marine Algae, A survey of Res. and Utilization*. Ed. by T. Levring, H.A. Hoppe and O. Schmid. Cram, DeGruyter & Co.
- Howard, C.J. and K.M. Evenson, 1975: private communication.
- Klingman, C.L., 1975: *Mineral Facts and Problems*, Bureau of Mines, U.S. Dept. of the Interior. To be published.
- Liss, P.S. and P.G. Slater, 1974: Flux of gases across the air-sea interface. *Nature*, 247, 181.
- Lovelock, J.E., 1971: Atmospheric fluorine compounds as indicators of air movement. *Nature*, 230, 379.
- Lovelock, J.E., R.J. Maggs, and R.J. Wade, 1973: Halogenated hydrocarbons in and over the Atlantic. *Nature*, 241, 194.
- Lovelock, J.E., 1974: Atmospheric halocarbons and stratospheric ozone. *Nature*, 252, 292.
- Lovelock, J.E., 1975: private communication.
- McCarthy, R.L., 1975: private communication.
- MacMillan, R.T., 1970: "Chlorine", *Mineral Facts and Problems*, Bureau of Mines, U.S. Dept. of the Interior.
- Mathias, E., E. Sanhueza, I.C. Hisatsune and J. Heicklen, 1974: The chlorine atom sensitized oxidation and the ozonolysis of C_2Cl_4 . *Can. J. Chem.*, 52, 3852.
- McConnell, G., D.M. Ferguson, and C.R. Pearson, 1975: Chlorinated hydrocarbons and the environment. *Endeavor*, 34, 13.
- McElroy, M.B., S.C. Wofsy, J.E. Penner, and J.C. McConnell, 1974: Atmospheric ozone: possible impact of stratospheric aviation. *J. Atmos. Sci.*, 31, 287.
- Miyake, Y. and S. Tsunogai, 1963: Evaporation of iodine from the ocean. *J. Geophys. Res.*, 68, 3989.
- Molina, M.J., and F.S. Rowland, 1974: Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone. *Nature*, 249, 810.
- Molina, M.J. and F.S. Rowland, 1974: Predicted present stratospheric abundances of chlorine species from dissociation of carbon tetrachloride. *Geophys. Res. Lett.*, 1, 309.
- Morris, J.C., 1975: Formation of halogenated organics by chlorination of water supplies: a review. Draft report to Office of Research and Development, EPA (RD 683) Washington, D.C.
- Porret, D. and C.F. Goodeve, 1938: The continuous absorption spectrum of methyl iodide. *Proc. Roy. Soc. (London) A* 165, 31.
- Rasmussen, 1975: private communication.
- Rook, J.J., 1974: Formation of haloforms during chlorination of natural waters. *Water Treatment Exam.*, 23, 234.
- Shaw, T.I., 1962: "Halogens" *Physiology and Biochemistry of Algae*, Ed. R.A. Lewin. Academic Press, New York.
- Su, Chih-Wu, and E.D. Goldberg, 1973: Chlorofluorocarbons in the atmosphere. *Nature*, 245, 27.
- Symons, J.M., 1975: Suspect carcinogens in water supplies. Interim report to Congress. Water Supply Research Laboratory, National Env. Research Center. Office of Research and Development, Cincinnati, Ohio.
- Tyerman, W.J.R., 1969: Flash photolysis of haloethylenes. *Trans. Farad. Soc.*, 65, 2948.
- Wilkniss, P.E., R.A. Lamontagne, R.E. Larson, J.W. Swinnerton, C.R. Dickson and T. Thompson, 1973: Atmospheric trace gases in the southern hemisphere. *Nature*, 245, 45.
- Wofsy, S.C., M.B. McElroy and N.D. Sze, 1975: Freon consumption: implications for atmospheric ozone. *Science*, 187, 535.
- Wofsy, S.C., M.B. McElroy and Y.L. Yung, 1975: The chemistry of atmospheric bromine. *Geophys. Res. Lett.* 2, 215.
- Zafiriou, O.C., 1974: Photochemistry of halogens in the marine atmosphere. *J. Geophys. Res.*, 79, 2730.

(Received June 12, 1975;
accepted August 7, 1975.)