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 $3 \times 10^6$ 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, $5.2 \times 10^6$, $7.7 \times 10^6$, and $7.4 \times 10^6$ ton yr$^{-1}$ respectively. The relative yields of CH$_3$Cl, CH$_3$Br and CH$_3$I 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$_2$F$_2$, CCl$_3$F, CH$_3$Cl, CH$_3$Cl$_3$, C$_2$H$_3$Cl, C$_2$Cl$_4$, CH$_3$I, CCl$_4$, and CHC$_1$_3, with concentrations summarized in Table 1. The fluorocarbons, CCl$_2$F$_2$ and CCl$_3$F, are industrial in origin, employed primarily as refrigerants and as aerosol propellants (Lovelock, 1971; Lovelock et al., 1973; Wilkniis 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$_3$Cl, and methyl iodide, CH$_3$I, 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$_3$Br (Rasmussen, 1975; Wofsy et al., 1975). Carbon tetrachloride, CCl$_4$, is used extensively as an intermediate in the manufacture of CCl$_2$F$_2$ and CCl$_3$F. 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, CHC$_1$_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 CHC$_1$_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 CHC$_1$_3, some updated estimates for the magnitude of the surface source required in order to account for the measurements of CH$_3$Cl and CH$_3$I given in Table 1.

Chloroform will be removed from the atmosphere primarily by reaction with OH, and similar remarks apply to CH$_3$Cl. 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$_3$I, determined mainly by photodissociation, was computed using cross sections measured by Porter and Gooder (1936). The lifetimes given in Table 2 represent lower 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$_3$Cl, CH$_3$I and CHC$_1$_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$_3$Cl and CH$_3$I given here may be compared with the source of 7.7 ± 7 tons yr$^{-1}$ derived earlier for CH$_3$Br (Wofsy et al., 1975).

Table 2 includes two estimates for the global production of CHC$_1$_3. The 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 CHC$_1$_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 CHC$_1$_3 in 1972, 1 x $10^5$ tons. The discrepancy is particularly serious if we recall that most CHC$_1$_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 CHC$_1$_3 of 1 x $10^5$ 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 CHC$_1$_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 CHC$_1$_3 and other haloforms produced during the chlorination of municipal water supplies (Rrock, 1974; Bellar et al., 1974).
Table 2
Lifetimes and Sources of Halocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mixing ratio (v/v)</th>
<th>Major sink</th>
<th>Rate constant (a)</th>
<th>Lifetime (s)</th>
<th>Source (if globally distributed) (10^6 metric ton/yr)</th>
<th>Source (if spatially restricted, see text) (10^6 metric ton/yr)</th>
<th>Global industrial source (10^6 metric ton/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl3</td>
<td>20</td>
<td>CHCl3 + OH</td>
<td>( k = 1.0 \times 10^{12} ) ( \text{cm}^3 \text{s}^{-1} ) ( \text{mol}^{-1} )</td>
<td>1.0 \times 10^7</td>
<td>0.99</td>
<td>0.23</td>
<td>see text</td>
</tr>
<tr>
<td>CHCl2</td>
<td>500</td>
<td>CHCl2 + OH</td>
<td>( k = 1.69 \times 10^{12} ) ( \text{cm}^3 \text{s}^{-1} ) ( \text{mol}^{-1} )</td>
<td>2.8 \times 10^7</td>
<td>5.2</td>
<td>5.2</td>
<td>.68 (f)</td>
</tr>
<tr>
<td>CHClI</td>
<td>12</td>
<td>CHClI + hv</td>
<td>( J = 6.0 \times 10^6 ) ( \text{cm}^3 \text{s}^{-1} ) ( \text{mol}^{-1} )</td>
<td>1.7 \times 10^5</td>
<td>.74</td>
<td>.74</td>
<td>1.0 (g)</td>
</tr>
<tr>
<td>C2HCl3</td>
<td>15</td>
<td>C2HCl3 + OH</td>
<td>( k = 3 \times 10^{12} ) ( \text{cm}^3 \text{s}^{-1} ) ( \text{mol}^{-1} )</td>
<td>3.7 \times 10^6</td>
<td>31</td>
<td>31</td>
<td>1.0 (f)</td>
</tr>
<tr>
<td>C2Cl4</td>
<td>28</td>
<td>C2Cl4 + OH</td>
<td>( k = 1.3 \times 10^{12} ) ( \text{cm}^3 \text{s}^{-1} ) ( \text{mol}^{-1} )</td>
<td>8.5 \times 10^5</td>
<td>31</td>
<td>31</td>
<td>.61 (f)</td>
</tr>
<tr>
<td>C2H3Cl3</td>
<td>45</td>
<td>C2H3Cl3 + OH</td>
<td>( k = 8.2 \times 10^{13} ) ( \text{cm}^3 \text{s}^{-1} ) ( \text{mol}^{-1} )</td>
<td>9.5 \times 10^6</td>
<td>.4</td>
<td>.4</td>
<td>.28 (f)</td>
</tr>
<tr>
<td>CHF2Cl</td>
<td></td>
<td></td>
<td>( k = 1.2 \times 10^{12} ) ( \text{cm}^3 \text{s}^{-1} ) ( \text{mol}^{-1} )</td>
<td>3.0 \times 10^6</td>
<td>.036</td>
<td>.036</td>
<td>.036 (f)</td>
</tr>
</tbody>
</table>

(a) Bimolecular rate constants, \( k \), and dissociation rate, \( J \), are in units \( \text{cm}^3 \text{s}^{-1} \) and \( \text{s}^{-1} \) 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).

The reaction sequence begins with

\[
\text{Cl}_2 + \text{HCO}_3^- \rightarrow \text{HOCI} + \text{Cl}^- + \text{CO}_2 \quad (1)
\]

followed by

\[
\text{HOCI} \rightarrow \text{H}^+ + \text{OCl}^- \quad (2)
\]

in which \( \text{Cl}_2 \) is hydrolyzed to \( \text{HOCI} \) and \( \text{OCl}^- \). It proceeds through a series of complicated reactions involving dissolved organic material. These reactions may be written symbolically in the form

\[
\text{CH}_3\text{COR} + 3\text{HOCI} \rightarrow \text{CCl}_3\text{COR} + 3\text{H}_2\text{O} \quad (3)
\]

followed by

\[
\text{CCl}_3\text{COR} + \text{H}_2\text{O} \rightarrow \text{CHCl}_3 + \text{RCOOH} \quad (4)
\]

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 \( \text{CHCl}_3, \text{CHCl}_2\text{Br}, \text{CHClBr}_2, \text{CHBr}_3, \) 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 \( \text{CHCl}_3 \) 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 \( \text{CHCl}_3 \) of magnitude \( 3 \times 10^6 \) tons year\(^{-1} \) and could account for the concentration of the gas given in Table 1.

Decomposition of perchloroethylene, \( \text{Cl}_2\text{C} = \text{CCl}_2 \), could provide an additional source for atmospheric \( \text{CHCl}_3 \). Perchloroethylene is widely used as a solvent, with annual rates for release in excess of \( 10^6 \) tons (U.S. Tariff Commission). Howard and Evenson (1975) found that halogenated ethylenes react with \( \text{OH} \) at rates faster than \( 10^{12} \) \( \text{cm}^3\text{s}^{-1}\text{mol}^{-1} \) to form the OH addition compound. The addition reaction should be faster than photolysis.

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

<table>
<thead>
<tr>
<th>Major Uses</th>
<th>Quantity (10^6 metric tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvents</td>
<td>2.68</td>
</tr>
<tr>
<td>Plastics and synthetics</td>
<td>2.19</td>
</tr>
<tr>
<td>Paper products(^1)</td>
<td>1.78</td>
</tr>
<tr>
<td>Automobile fluids(^2)</td>
<td>.96</td>
</tr>
<tr>
<td>Water and sanitation</td>
<td>.59</td>
</tr>
<tr>
<td>Agriculture</td>
<td>.49</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>1.18</td>
</tr>
<tr>
<td>TOTAL</td>
<td>9.88</td>
</tr>
</tbody>
</table>

\(^1\) According to B. Slating of American Paper Institute, N.Y., this chlorine is used for bleaching paper pulp.
\(^2\) Mainly used to produce automobile anti-freeze (ethylene glycol) and anti-knock compounds (ethylene chloride).
peting reactions with ozone. The fate of the radical CC\textsubscript{12}-CC\textsubscript{12} 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, HC\textsubscript{12}C\textsubscript{2}CC\textsubscript{12}OH, should be a major product. Photolysis of dichloroacetyl chloride

\begin{align*}
\text{hv} + \text{HC}1\text{2}C\text{2}C\text{cC}1\text{2} \rightarrow \text{CO} + \text{CHC}1\text{3}
\end{align*}

should take place at wavelengths as long as 3600\AA{} (cf. Capey et al., 1968) and could provide a significant source of atmospheric CHC\textsubscript{12}. A quantitative estimate for this source would however require a careful analysis of competing loss processes for HC\textsubscript{12}C\textsubscript{2}CC\textsubscript{12}. The source strength estimates in Table 2 are consistent with industrial origin for C\textsubscript{2}Cl\textsubscript{4}, C\textsubscript{2}HCl\textsubscript{2}, and CH\textsubscript{3}CC\textsubscript{3} in the atmosphere.

It is of interest to examine possible natural sources of halogenated compounds. The oceans contain 2 x 10\textsuperscript{2}, 7 x 10\textsuperscript{7} and 3-7 x 10\textsuperscript{8} parts by volume of methyl chloride, bromide 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\textsuperscript{2} - 3 x 10\textsuperscript{3} 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 x 10\textsuperscript{8} ton yr\textsuperscript{-1} and combining their data with the results of Table 2 we find production rates by weight for CH\textsubscript{3}Cl, CH\textsubscript{3}Br and CH\textsubscript{3}I in the ratio 1:0.015:0.14, within the present limits of uncertainty, consistent with the large preponderance of algal. There are no known natural sources for chloroform, although we may note that CH\textsubscript{2}Br\textsubscript{2} is a major constituent in the essential oil of the red alga Asparagopsis taxiformis, which includes in addition, detectable amounts of CH\textsubscript{2}Cl\textsubscript{2}, CH\textsubscript{2}Br\textsubscript{2}, CH\textsubscript{2}I\textsubscript{2}, and CH\textsubscript{3}I (Burreson et al., 1975). The abundance of CH\textsubscript{2}C\textsubscript{12} 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 methyl chloride and methyl bromide are 0.8% and 0.5% respectively and the present day reduction due to C\textsubscript{2}Cl\textsubscript{4} and C\textsubscript{2}HCl\textsubscript{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

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References


Dahlberg, J.A., 1969: The non-sensitized photo-oxidation of trichloroethy-

In the present estimate we note that CH\textsubscript{3}I has a lifetime short compared with the time required for vertical mixing. Consequently we assume that CH\textsubscript{3}I 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 (Miya...