Abstract. We estimate the total concentration \([CIX]\) versus altitude of \(\text{Cl}-\)containing molecules, principally \(\text{HCl}, \text{Cl}\), and \(\text{ClO}\). The predicted present stratospheric concentrations appear to be due to photolysis near 30 km of man-made \(\text{CF}_2\text{Cl}_2\) and \(\text{CF}_3\text{Cl}_3\), and \(\text{Cl}_2\) from a ground-level source, man-made or natural. Based on preliminary measurements of \(\text{CH}_2\text{O}\) at ground we estimate its contribution to stratospheric \(\text{ClX}\) through the major known loss mechanism for \(\text{CH}_2\text{O}\), abstraction by \(\text{OH}\). Ground-level sources of \(\text{HCl}\) and \(\text{Cl}_2\) are large but tropospheric processes preclude significant impact on the stratosphere. Our computed profiles are consistent with first \(\text{HCl}\) concentrations measured by Lazrus et al. [1974, 1975] in the 15-27 km region.

Molina and Rowland [1974a; 1975] have proposed that the increasing use of man-made chlorofluoromethanes may represent a serious threat to atmospheric \(\text{O}_3\). Subsequent studies by Cicerone et al. [1974], Crutzen [1974], and Wofsy et al. [1975] have not refuted this proposal; instead they have offered additional documentation and quantitative estimates of the size and timetable of the effect on \(\text{O}_3\). The potential seriousness of this problem might require this increase to cease before definitive proof of \(\text{O}_3\) depletion can be obtained. Therefore, we focus attention on some key intermediate species for which measurements are needed. In particular, we estimate the concentration of \(\text{ClX} (\text{Cl} + \text{HCl} + \text{ClO})\) now in the stratosphere due to several sources. We show that ground-level \(\text{ClX}\) or \(\text{Cl}_2\) sources (natural or anthropogenic) do not contribute appreciably to the stratosphere. With certain plausible assumptions we estimate the present stratospheric \(\text{ClX}\) profile, to be used as a baseline against which to assess future measurements. Thus, future stratospheric increases of \(\text{ClX}\) can be estimated with known rates of injection by photodissociation of chlorofluoromethanes or other chlorocarbons or by explosive volcanoes. Reliable measurements of \(\text{ClX}\) are obviously necessary and preferred over theoretical estimates but available data is sketchy and scarce.

Ground-level sources of \(\text{HCl}\) and \(\text{Cl}_2\) include the conversion of sea-salt aerosol chlorides to \(\text{HCl}\), volcanic and fumarolic emissions, diffusion through the earth's crust, and industrial processes. These have been discussed by many authors including Eriksson [1960], Valsah [1967], Duce [1969], Chesselet et al. [1972], Stolarski and Cicerone [1974], Ryan and Mukherjee [1974], and Wofsy and McElroy [1974]. The latter two references also concluded that \(\text{HCl}\) is by far the dominant \(\text{Cl}-\)containing form (barring organic compounds) in the troposphere, that is, \([\text{HCl}] = [\text{ClIX}]\), where \([\ ]\) denotes concentration \((\text{cm}^{-3})\). Ground-level and low altitude measurements by Junge [1957], Duce et al. [1965], Duce [1969] and Chesselet et al. [1972] cluster around an \(\text{HCl}\) volume mixing ratio \(f(\text{HCl}) = 10^{-9}\) but these may be upper limits because each apparatus may have permitted particle-to-gas conversion in its inlet system [Stedman et al., 1975]. We note that Farmer et al. [1974] reported from ground-level spectral observations that \(f(\text{HCl}) < 3 \times 10^{-10}\) averaged over the lowest scale volume. Measurements of \(\text{HCl}\) at all tropospheric altitudes are not available but Ryan and Mukherjee [1974] and Stedman et al. [1975] show that the tropospheric \(\text{HCl}\) profile should be proportional to the \(\text{H}_2\text{O}\) vapor profile. The \(\text{H}_2\text{O}\) vapor mixing ratio, \(f(\text{H}_2\text{O})\), at 10 km is \(10^{-3}\) to \(10^{-2}\) times its ground-level value of \(10^{-2}\) [U.S. Standard Atmosphere Supplements, 1966]. It decreases further between 10 km and a nominal tropopause height, 15 km. Thus, \(f(\text{HCl})\) at 10 km is no more than \(10^{-11}\) even if \(f(\text{HCl})\) at ground is as high as \(10^{-9}\). Just as we have an \(\text{H}_2\text{O}-\)dry stratosphere (observations show \(f(\text{H}_2\text{O}) = 3 \text{ ppm}\); Mastenbrook [1974]) we would also expect a "\(\text{ClX}-\)dry" stratosphere \((f(\text{ClX}) < 10^{-14})\) if the only sources of \(\text{ClX}\) were at ground.

Ryan and Mukherjee's conclusion that tropospheric \(\text{HCl}\) is controlled by \(\text{H}_2\text{O}\) is based on their analysis of microscopic or molecular processes involving the thermodynamics of \(\text{HCl}(\text{H}_2\text{O})_n\) polymers. Stedman et al. [1975] have reached the same conclusion for several highly soluble gases through an argument that does not invoke the existence of such polymers. They assumed that \(\text{HCl}\) gas and water vapor diffuse onto water droplets at rates proportional to their respective concentrations. From thermodynamic data they showed that the \(\text{HCl}\) vapor pressure around rain droplets is considerably less than ambient tropospheric \(\text{HCl}\) partial pressure, when the rain droplets form by condensation of all available \(\text{H}_2\text{O}\) and \(\text{HCl}\) in a given volume. Their model predicts a globally averaged \(\text{Cl}^-\)molarity of rainfall that is consistent with Duce's [1969] observation that rain droplets are considerably undersaturated in \(\text{HCl}\). The theory is not so clear...
for ice crystals, but from snow and ice composition data Stedman et al. argue that one can expect \( f(\text{HCl}) \) to decrease rapidly with altitude in the troposphere, just like \( f(\text{H}_2\text{O}) \).

The conclusion is that ground-level sources of HCl and CCl\(_4\) are inconsequential for the stratosphere despite the large size (perhaps \( 10^{14} \) g/year or \( 10^{28} \text{cm}^{-2} \text{sec}^{-1} \)) of the HCl source due to sea-salt conversion [Duce, 1969; Chesselet et al., 1972; Ryan and Mukherjee, 1974]. Clearly if ground-level sources of HCl are the only large tropospheric lifetime of gaseous HCl must be relatively short. Wofsy [1974] and Wofsy and Molloy [1974] have estimated this lifetime to be 1-9 days. Chesselet et al. [1972] have inferred that HCl in overland air may have a lifetime < 1 day. H\(_2\)O control of HCl would give HCl the same lifetime (1 week) as H\(_2\)O through the rapid and dynamic processes of H\(_2\)O evaporation, condensation, freezing, sublimation and transport [Stedman et al., 1975].

There is, of course, the possibility of other tropospheric sources of ClX, such as the release of Cl atoms from chlorocarbons, man-made or natural. Molina and Rowland [1974a, 1975] and Cicerone et al. [1974] and papers they cite show that CFC\(_2\) and CFC\(_3\) probably do not release much Cl in the troposphere. CCl\(_4\) produced at ground-level is also not likely to decompose in the troposphere. Chlorocarbons with C-H bonds should be more susceptible to attack by tropospheric OH. Lovelock [1974] has detected the presence of CH\(_2\)Cl\(_3\), CH\(_3\)C\(_2\)Cl, and CH\(_3\)Cl = CCl\(_2\), albeit in small amounts, in the atmosphere. Other such compounds, e.g., CH\(_2\)Cl\(_2\), may be present in larger amounts [R. Rasmussen, 1974, private communication], but unless they can provide tropospheric sources of HCl large enough to overcome the H\(_2\)O control of HCl (the required source strength would vary with altitude; near ground \( 10^{13} \) g/year might suffice) we expect a tropospheric ClX profile like that sketched in Figure 1, discussed later.

To estimate the present and future concentration profiles in the stratosphere we have considered the photolysis of CF\(_2\)Cl\(_2\), CFC\(_3\), and CCl\(_4\) and the reaction of atmospheric OH with CH\(_3\)Cl produced at ground. Direct stratospheric injection of Cl\(_2\) and HCl by explosive volcanoes and the projected Space Shuttle may also be important at specific times and places but estimates of temporal and global averages of injection rates [Stolarski and Cicerone, 1974; Ryan and Mukherjee, 1974; Cadle, 1975] yield relatively small masses compared to the man-made chlorofluoromethane sources.

We calculated the altitude profiles of ClX concentrations due to CF\(_2\)Cl\(_2\), CFC\(_3\), and CCl\(_4\) and CH\(_3\)Cl in the following manner: for CF\(_2\)Cl\(_2\) and CFC\(_3\) there appears little doubt that no natural sources exist. In addition, the anthropogenic release rates at ground-level are reasonably well-known [see e.g., Rowland and Molina, 1975 McCarthy, 1974]. For the time-dependent calculation of ClX concentrations we used the vertical profile of eddy-diffusion coefficient, \( K \), deduced by Hunten [Hunten, 1975 and unpublished manuscript, 1974]. For photolysis rates of CF\(_2\)Cl\(_2\) and CFC\(_3\) we used data from Rowland and Molina [1975], and procedures summarized by Cicerone et al. [1974]. For the CCl\(_4\) calculations we assumed a steady state profile and photolysis as the only sink [with photodissociation cross sections of Molina and Rowland, 1974b]. The identities and strengths of CCl\(_4\) sources are not completely clear. The steady state assumption on CCl\(_4\) is partially justified by arguments and data presented by Molina and Rowland [1974b]. If natural sources dominate one would expect steady state, but measured ClX mixing ratios show an apparent increase from about \( 7 \times 10^{-11} \) in 1972 [Lovelock et al., 1973; Wilkniss et al., 1973] to about \( 1.8 \times 10^{-10} \) in 1974 [Lovelock, 1974; Wilkniss et al., 1975]. It may not be safe to interpret these numbers as a uniform global increase, but if so, they probably imply a large anthropogenic (non U.S.) input since 1972. CCl\(_4\) released from the U.S. alone has been reasonably steady for about 20 years and M. J. Molina [private communication, 1974] has shown that the U.S. output of the last 15 years can account for about 50% of the presently measured CCl\(_4\) content of the atmosphere. This is in contrary to Lovelock's [1974] interpretation of CCl\(_4\) release statistics. Natural sources of CCl\(_4\) are suggested by certain features of the measured concentrations [Lovelock, 1974].

Our calculations yield the ClX mixing ratio profiles of Figure 1. We show separately the contributions from CF\(_2\)Cl\(_2\) and CFC\(_3\) together and from CCl\(_4\). A suggested tropospheric profile (consistent with H\(_2\)O control) due to ground-level sources of Cl-containing inorganic compounds is also indicated. We also show the HCl data points of Lazrus et al. [1974, 1975]. Two upper limits on HCl near 15 km by Farmer et al. [1974] are not shown because he has re-interpreted the data; he now estimates \( f(\text{HCl}) \) to be about \( 10^{-9} \) above 16 km, based on the total content in the zenith direction [Farmer, 1975]. A striking feature of our
In Figure 2 we display our computed vertical profile of CH$_3$Cl, along with its contribution of stratospheric CHCl$_3$ and the total CIX mixing ratio computed from CH$_3$Cl, CF$_2$Cl$_2$, CFC$_1$$_3$ and CC$_1$N$_2$ sources, and the Lazrus et al. data. Our computations for CH$_3$Cl are based on an assumed steady state vertical profile of CH$_3$Cl with a mixing ratio of $4 \times 10^{-13}$ at ground level, as suggested by recent measurements [R. Rasmussen, 1974; J. E. Lovelock, 1975, private communication]. The only significant sink for CH$_3$Cl appears to be the abstraction reaction CH$_3$Cl + OH → CH$_2$Cl + H$_2$O with immediate CH$_2$Cl decomposition by uncertain chemical reactions probably involving O$_3$. The rate for this reaction was estimated as $4.8 \times 10^{-12}$ exp$(-11800/T)$ from Davis et al. [1975] room temperature rate and a (guessed) activation energy of 2.8 kcal. For an OH profile we took model results from McElroy et al. [1974]. The present simple model implies a globally averaged ground-level source of $2.6 \times 10^6$ CH$_3$Cl molecules cm$^{-2}$sec$^{-1}$. This source is about 10 times the direct industrial production rate in the U.S. in 1972. The flux of CH$_3$Cl upward through the 15 km level is about $1.7 \times 10^6$ cm$^{-2}$sec$^{-1}$ and leads to more HCl than has been measured when it is added to the sources for Figure 1. Presumably, a natural source exists for CH$_3$Cl, but its identity is unknown. Lovelock et al. [1973] and Zafiriou [1974] have discussed possible natural sources of CH$_3$I.

Substantial agreement appears between the Lazrus et al. HCl measurements and the CIX prediction in Figure 1, where the CF$_2$Cl$_2$, CF$_3$Cl$_3$ and CCl$_4$ sources are included. Without CCl$_4$, our model predicts about one-third as much CIX as observed by Lazrus et al. Similarly, calculations for CF$_2$Cl$_2$ and CF$_3$Cl$_3$ alone by Wofsy et al. [1975], found one-half as much CIX as Lazrus et al. If the Figure 1 total CIX profile is taken as a guide one would expect C10 concentrations of about $3 \times 10^6$ cm$^{-2}$ between 30 and 35 km in late 1974 according to present schemes of CIX chemistry. Figure 2 shows that the uncertain CH$_3$Cl source implied by Rasmussen's and Lovelock's measurements may have carried as many C1 atoms to the 30 km level as CF$_2$Cl$_2$, CFC$_1$$_3$ and CC$_1$N$_2$ had by 1974. It must be emphasized, however, that CF$_2$Cl$_2$ and CFC$_1$$_3$ released after the mid-1960's will soon result in more C1 atoms injected near 30 km than the (presumed) steady state CCl$_4$ and CH$_3$Cl contributions. If CF$_2$Cl$_2$ and CFC$_1$$_3$ emissions were kept constant at 1973 levels, their tropospheric mixing ratios would increase by about a factor of 10 and stratospheric CIX mixing ratios to about $1 \times 10^{-13}$ when steady state were reached, in 50 to 100 years [Crutzen, 1974; Cicerone et al., 1975; Bowland and Molina, 1975; Wofsy et al., 1975].

Acknowledgments. We thank E. E. Ferguson, A. L. Lazrus, M. J. Molina, R. S. Narcisi and F. S. Rowland for helpful discussion, NASA for financial support through Grant NGR-23-006-616 and the Climatic Impact Assessment Program for NSF Grant DES 74-11478.
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(Received March 10, 1975
Accepted April 3, 1975)