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ESTIMATE OF LATE 1974 STRATOSPHERIC CONCENTRATION OF GASEOUS CHLORINE COMPOUNDS (ClX)

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Abstract. We estimate the total concentration [ClX] versus altitude of Cl-containing molecules, principally HCl, Cl and ClO. The predicted present stratospheric concentrations appear to be due to photolysis near 30 km of man-made CF_2Cl_2 and $CFCl_3$, and CCl_4 from a ground-level source, man-made or natural. Based on preliminary measurements of CH_3Cl at ground we estimate its contribution to stratospheric ClX through the major known loss mechanism for CH_3Cl, abstraction by OH. Ground-level sources of HCl and Cl_2 are large but tropospheric processes preclude significant impact on the stratosphere. Our computed profiles are consistent with first 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 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 O_3. The potential seriousness of this problem might require this increase to cease before definitive proof of 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 ClX (Cl + HCl + ClO) now in the stratosphere due to several sources. We show that ground-level ClX or Cl_2 sources (natural or anthropogenic) do not contribute appreciably to the stratosphere. With certain plausible assumptions we estimate the present stratospheric ClX profile, to be used as a baseline against which to assess future measurements. Thus, future stratospheric increases of ClX can be estimated with known rates of injection by photodissociation of chlorofluoromethanes or other chlorocarbons or by explosive volcanoes. Reliable measurements of ClX are obviously necessary and preferred over theoretical estimates but available data is sketchy and scarce.

Ground-level sources of HCl and Cl_2 include the conversion of sea-salt aerosol chlorides to HCl, volcanic and fumarolic emissions, diffusion through the earth's crust, and industrial processes. These have been discussed by many authors including Eriksson [1960], Valach [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 HCl is by far the dominant Cl-containing form (barring organic compounds) in the troposphere, that is, [HCl] = [ClX], where [ ] denotes concentration (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 HCl volume mixing ratio $f(HCl) = 10^{-9}$ 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 $f(HCl) < 3 \times 10^{-10}$ averaged over the lowest scale volume.

Measurements of HCl at all tropospheric altitudes are not available but Ryan and Mukherjee [1974] and Stedman et al. [1975] show that the tropospheric HCl profile should be proportional to the H_2O vapor profile. The H_2O vapor mixing ratio, $f(H_2O)$, 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(HCl) at 10 km is no more than 10^{-11} even if f(HCl) at ground is as high as 10^{-9}. Just as we have an H_2O-dry stratosphere (observations show $f(H_2O) \approx 3$ ppm; Mastenbrook [1974] we would also expect a "ClX-dry" stratosphere ($f(ClX) < 10^{-11}$) if the only sources of ClX were at ground.

Ryan and Mukherjee's conclusion that tropospheric HCl is controlled by H_2O is based on their analysis of microscopic or molecular processes involving the thermodynamics of $HCl(H_2O)_n$ 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 HCl gas and water vapor diffuse onto water droplets at rates proportional to their respective concentrations. From thermodynamic data they showed that the HCl vapor pressure around rain droplets is considerably less than ambient tropospheric HCl partial pressure, when the rain droplets form by condensation of all available H_2O and HCl in a given volume. Their model predicts a globally averaged Cl^- molarity of rainfall that is consistent with Duce's [1969] observation that rain droplets are considerably undersaturated in 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(HCl) to decrease rapidly with altitude in the troposphere, just like f(H_2O).

The conclusion is that ground-level sources of HCl and Cl_2 are inconsequential for the stratosphere despite the large size (perhaps 10^{14} g/year or 10^{10} cm^{-2}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 this large the tropospheric lifetime of gaseous HCl must be relatively short. Wofsy [1974] and Wofsy and McElroy [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_2O control of HCl would give HCl the same lifetime (~1 week) as H_2O, through the rapid and dynamic processes of H_2O 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 CF_2Cl_2 and $CFCl_3$ 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 $CHCl_3$, CH_3CCl_3, and $CHCl=CCl_2$, albeit in small amounts, in the atmosphere. Other such compounds, e.g., CH_3Cl, 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_2O control of HCl (the required source strength would vary with altitude; near ground 10^{15} 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_2Cl_2, $CFCl_3$ and CCl_4 and the reaction of atmospheric OH with CH_3Cl 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_2Cl_2, $CFCl_3$, CCl_4 and CH_3Cl in the following manner: for CF_2Cl_2 and $CFCl_3$ 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_2Cl_2 and $CFCl_3$ 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 CCl_4 mixing ratios show an apparent increase from about 7 x 10^{-11} in 1972 [Lovelock et al., 1973; Wilkniss et al. 1973] to about 1.2 x 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 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_2Cl_2 and $CFCl_3$ together and from CCl_4. A suggested tropospheric profile (consistent with H_2O 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(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

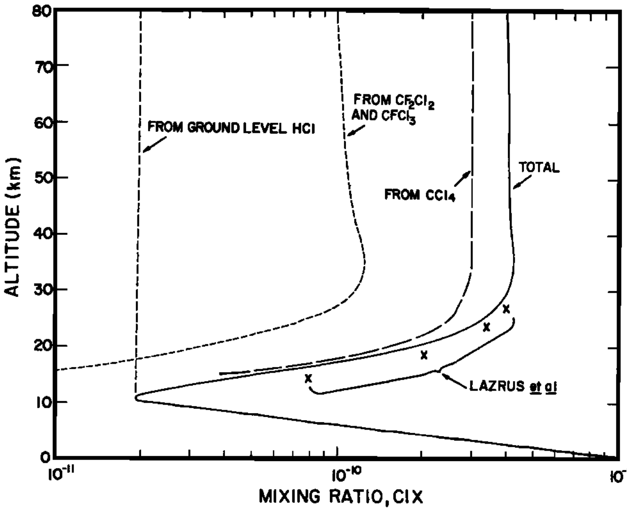

Figure 1. Computed ClX (HCl + ClO + Cl) mixing ratios versus altitude for late 1974. The ClX contribution from CF_2Cl_2 and $CFCl_3$ photolysis was calculated from the known history of anthropogenic emissions, that from CCl_4 as described in the text. Recent HCl measurements are shown by X's. Nearly all ClX is HCl below 25 km. A nominal tropospheric HCl profile is also shown, reflecting H_2O control.

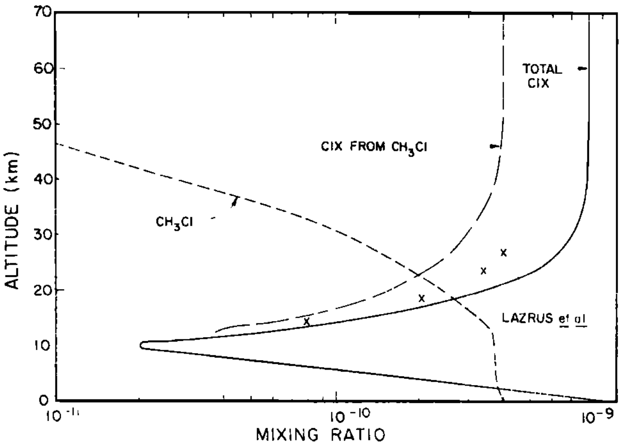

Figure 2. Computed ClX (HCl + ClO + Cl) mixing ratios versus altitude, due to a ground-level source of CH_3Cl, and the computed CH_3Cl profile for late 1974. The total ClX mixing ratio due to CF_2Cl_2, $CFCl_3$, CCl_4 and CH_3Cl is also shown, as are recent HCl measurements (X's) by Lazrus et al. [1974; 1975].

computed profiles is the positive upward gradient in ClX mixing ratio between 15 and 25 or 30 km. Such a profile shape is expected from a source of ClX in the middle stratosphere where CF_2Cl_2, $CFCl_3$ and CCl_4 photolyze [Molina and Rowland, 1974a,b; Cicerone et al., 1974; Crutzen, 1974; Wofsy et al., 1975]. This profile shape is shown clearly by the Lazrus et al. HCl values, and it indicates why HCl measurements near 15 km are difficult [Farmer et al., 1974]. It should be mentioned that ClX is almost all HCl below 20 km, according to present models [see e.g., Wofsy and McElroy, 1974; Crutzen, 1974; Molina and Rowland, 1974b]. The ClX due to CCl_4 is from 3 Cl atoms removed from each CCl_4 molecule, and a ground-level CCl_4 mixing ratio fixed at 10^{-10}. We infer that the ground flux of CCl_4 is about $6 \times 10^5 cm^{-2} sec^{-1}$ over the globe. Almost all of these molecule enter the stratosphere.

A Cl concentration of $10^5 cm^{-3}$ at 75 km was inferred from Cl^- measurements by a rocket-borne mass spectrometer between 71 and 77 km [Arnold and Krankowsky, 1971]. This mesospheric Cl concentration is consistent with our profiles in Figures 1 and 2 but it is also possible that meteoric sources contribute to the mesosphere. Further, the inference of Cl concentrations from Cl^- measurements is risky: the Cl^- might have been from contaminants, charge-exchange and recombination rate constants are poorly known, NO_3^- should not exchange charge with Cl as they assumed, and a reaction they neglected, $H + Cl^- \rightarrow HCl + e$, has a constant of $1 \times 10^{-9} cm^3 sec^{-1}$ [Ferguson, 1975, private communication]. Finally, it should be noted that the Lazrus et al. data were gathered with chemically impregnated filter paper. Efficiency of collection of gaseous HCl may be less than 100%, further calibration may demand that these HCl values be increased [Lazrus, 1975, private communication]. Possible particle-to-gas conversion could cause opposing errors.

In Figure 2 we display our computed vertical profile of CH_3Cl, along with its contribution of stratospheric ClX and the total ClX to be expected from CH_3Cl and the CF_2Cl_2, $CFCl_3$ and CCl_4 sources, and the Lazrus et al. data. Our computations for CH_3Cl are based on an assumed steady state vertical profile of CH_3Cl with a mixing ratio of 4×10^{-10} at ground level, as suggested by recent measurements [R. Rasmussen, 1974; J. E. Lovelock, 1975, private communication]. The only significant sink for CH_3Cl appears to be the abstraction reaction $CH_3Cl + OH \rightarrow CH_2Cl + H_2O$ with immediate CH_2Cl decomposition by uncertain chemical reactions probably involving O_2. The rate for this reaction was estimated as $4.8 \times 10^{-12} \exp(-1400/T)$ 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 2.6×10^8 CH_3Cl molecules $cm^{-2} sec^{-1}$. This source is about 10 x the direct industrial production rate in the U.S. in 1972. The flux of CH_3Cl 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_3Cl, but its identity is unknown. Lovelock et al. [1973] and Zafiriou [1974] have discussed possible natural sources of CH_3I.

Substantial agreement appears between the Lazrus et al. HCl measurements and the ClX prediction in Figure 1, where the CF_2Cl_2, $CFCl_3$ and CCl_4 sources are included. Without CCl_4, our model predicts about one-third as much ClX as observed by Lazrus et al. Similarly, calculations for CF_2Cl_2 and $CFCl_3$ alone, by Wofsy et al. [1975], found one-half as much ClX as Lazrus et al. If the Figure 1 total ClX profile is taken as a guide one would expect ClO concentrations of about $3 \times 10^7 cm^{-3}$ between 30 and 35 km in late 1974 according to present schemes of ClX chemistry. Figure 2 shows that the uncertain CH_3Cl source implied by Rasmussen's and Lovelock's measurements may have carried as many Cl atoms to the 30 km level as CF_2Cl_2, $CFCl_3$ and CCl_4 had by 1974. It must be emphasized, however, that CF_2Cl_2 and $CFCl_3$ released after the mid-1960's will soon result in more Cl atoms injected near 30 km than the (presumed) steady state CCl_4 and CH_3Cl contributions. If CF_2Cl_2 and $CFCl_3$ emissions were kept constant at 1973 levels, their tropospheric mixing ratios would increase by about a factor of 10 and stratospheric ClX mixing ratios to about 4×10^{-9} when steady state were reached, in 50 to 100 years [Crutzen, 1974; Cicerone et al., 1975; Rowland and Molina, 1975; Wofsy et al., 1975].

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