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Halogens in the Atmosphere

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Extant data from measurements of halogens in the atmosphere are reviewed in the following categories: gaseous chlorine compounds (inorganic and organic), particulate chloride and chloride in precipitation, gaseous bromine compounds (inorganic and organic), particulate bromide and bromide in precipitation, gaseous iodine compounds (inorganic and organic), iodine in particles and in precipitation, gaseous fluorine compounds (inorganic and organic), and fluoride in particles and precipitation. The roles that these data and other unavailable data play in defining global cycles of the halogens are discussed. Speciation of the halogen gases in the troposphere is very uncertain: the only inorganic species detected by species-specific methods are HCl and SF_6. More specific data are available on organic forms that contain halogens. Key species of gaseous halogens, either established or suspected to be important, are listed along with key processes that need investigation. Heterogeneous reactions, both gas-to-particle and particle-to-gas processes, precipitation removal, and sea-salt aerosol generation and fractionation processes need quantitative investigation to allow progress in estimating halogen sources and sinks. Where practical, as with stratospheric inorganic chlorine gases, quantitative comparisons are made between measured and predicted concentrations.

CONTENTS

A. OVERVIEW OF RESEARCH ON HALOGENS IN THE ATMOSPHERE

Questions that stimulate research on atmospheric halogens include very basic ones on nature's cycles and transformations of F, Cl, Br, and I and very practical concerns over halogen-containing compounds. The most elemental observations, for example, the presence of tropospheric gaseous halogens and the ratio of their concentrations, have not been explained quantitatively or even qualitatively in the sense that the principal sources of gaseous halogens are not certain. Similarly, the processes that enrich marine aerosol particles in iodine with respect to seawater iodine and the mechanisms that release chlorine-containing gases from marine aerosols are not understood. Thus the major pathways of nature's halogen cycles are seen only in general terms; key transformation processes and rates are not known with any accuracy. Most of the suspected key tropospheric species have never even been detected in the atmosphere, thus precluding the qualitative and quantitative testing of various hypotheses of halogen cycle behavior and evaluations of source strengths and distributions.

Several practical concerns over halogens in the atmosphere are now demanding quantitative information: stratospheric ozone layer photochemical effects of Cl and Br (direct O_3 destruction and interruption of other reaction chains), infrared effects of halocarbons, contributions of HCl to regionally acidic precipitation, atmospheric transport of persistent and often toxic pesticides (e.g., DDT, 2, 4, 5-T, dioxin), and questions on chemical intermediates in the tropospheric decomposition of chlorinated solvents (e.g., chloroethylenes). There is also interest in the use of man-made halogen compounds as potent tracers of atmospheric and hydrospheric motions.

B. THE PRESENT DATA BASE

1. *Introduction*

Our knowledge of the atmospheric chemistry and the geochemical cycles of the halogens has come from researchers with varied interests and investigative techniques. Thus the scope and depth of understanding of atmospheric halogen behavior is highly uneven amongst the individual halogens and from phenomenon to phenomenon. In sections B2–B5 I review presently available data for chlorine, fluorine, bromine, and iodine. In doing so I hope to elucidate the questions that arise from, or persist in spite of, the extant data. Because of the methods that have been used to gather data it is natural to group the data for each halogen as organic gases, inorganic gases, and particles. The fifth halogen, astatine, is not discussed. Its most stable isotope has only an 8-hour half-life, and its natural concentration in the atmosphere is probably vanishingly small.

2. *Chlorine in the Atmosphere*

a. Inorganic gases (Cl_g^i). Although it had been known for many years that chlorine is a constituent of the atmosphere both in gaseous and particulate form, modern investigations appear to have begun only after *Junge* [1956] advanced several criteria for measurements. He asserted that advances in understanding would require that the chloride content of particles and gases be measured simultaneously but separately and that the particles be separated with respect to

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TABLE 1. Summary of Available Data on Halogen-Containing Gases in the Troposphere

Halogen Form	EC-GC	Infrared Absorption	Bubblers, Charcoal Traps: Elemental Analysis, ng/m^3 STP
Cl_g^o, organic Cl	2.5 ppbv (4000 ng/m^3 STP)		3050
Cl_g^i, inorganic Cl		1–2 ppbv (by IR absorption)	1000–2000 (marine air)
Br_g^o, organic Br	10–25 pptv (36–90 ng/m^3 STP)		14–68
Br_g^i, inorganic Br	···		10–25 (marine air); 0.5–11 (continental air)
I_g^o, organic I	1–5 pptv (5.7–28 ng/m^3 STP)		3–28
I_g^i, inorganic I	···		0.4–17
F_g^o, organic F	1 ppbv (855 ng/m^3 STP)		polluted air only
F_g^i, inorganic F		0.1–0.4 ppbv (stratospheric data by IR absorption)	0.01–0.1 ppbv (stratospheric filter collections)

EC-GC represents electron capture–gas chromatography. EC-GC value of 4000 ng/m^3 for Cl_g^o is for late 1977, while the elemental analysis value, 3050 ng/m^3, is from 1976 (see text, section B2*b*). Identities and concentrations of individual organic halogen species are in Table 3. Of the inorganic gases, only HCl and SF_6 have been identified unequivocally in the troposphere. Conversion factors for monohalogenated compounds are as follows at standard temperature and pressure: for Cl, 1 ppbv = 1600 ng(Cl)/m^3; for F, 1 ppbv = 855 ng(F)/m^3; for Br, 10 pptv = 36 ng(Br)/m^3; and for I, 1 pptv = 5.6 ng(I)/m^3.

size. A further useful distinction is that between inorganic and organic gases. Until about 1971, attention was limited to the inorganic gaseous fraction of chlorine and other halogens, partly because only the inorganic species (e.g., HCl) were expected to arise in any quantity from the two conjectured sources: sea-salt spray release of HCl and volcanic and fumarolic emissions of, for example, HCl, Cl_2, and HF. Typically, the Cl-containing gases were collected by bubbling an air stream through K_2CO_3, KOH, or LiOH in aqueous solution after filtering out all particles [*Junge,* 1957; *Duce et al.,* 1965; *Chesselet et al.,* 1972], a process that was over 80% efficient for HCl. More recently, *Rahn et al.* [1976] and *Berg and Winchester* [1977] separated the inorganic and organic fractions of gaseous Cl by carbon trapping the stream after it passed through LiOH-impregnated filters. Table 1 summarizes these data; the total inorganic Cl gases Cl_g^i exhibit variability. Concentrations between 1 and 2 μg/m^3 STP are usually found in the marine atmosphere. Lower concentrations are seen over continents [*Chesselet et al.,* 1972; *Rahn et al.,* 1976], implying a marine source for Cl_g^i.

Because of the methods of collection and subsequent elemental analysis (neutron activation or colorimetric) in these studies, no species identifications were made. Indeed, the only inorganic chlorine-containing gas species identified in the troposphere is HCl [*Farmer et al.,* 1976]; IR absorption spectra allowed spectroscopic identification and column contents of 6.8×10^{15} to 1.1×10^{16} cm^{-2} of HCl to be measured. A column content of 10^{16} cm^{-2} and a 3-km scale height imply ground level HCl mixing ratios of 2.0×10^{-6} g/m^3 by mass and 1.2×10^{-9} by volume. Although this near-factor-of-2 variability of HCl seen by infrared absorption is similar to that found in the works cited above and in Table 1, Farmer et al. found no difference between inland measurements over a desert and coastal values. Thus several questions arise: is HCl the dominant inorganic Cl gas in the troposphere? If sea-salt release of HCl is its dominant source as suggested by *Robbins et al.* [1959], *Eriksson* [1960], *Duce* [1969], and others, why was no gradient seen with distance from the coast in the *Farmer et al.* [1976] data? Clearly, more species-specific measurements are needed at ground level and in the free troposphere under different meteorological conditions. Perhaps in precipitation-free and cloud-free areas the atmospheric lifetime and range of HCl are large enough to permit significant horizontal and vertical transport. On a global and seasonal average the tropospheric lifetime of HCl is probably 7 days or less [*Wofsy,* 1974; *Stedman et al.,* 1975], but this averaged figure is hardly meaningful for the interpretation of individual measurements. In the marine atmospheric boundary layer the residence time of HCl might be only 2 days [*Kritz and Rancher,* 1980].

In the stratosphere several forms of Cl_g^i have been detected: HCl by infrared absorption [*Farmer et al.,* 1976; *Williams et al.,* 1976; *Ackerman et al.,* 1976; *Eyre and Roscoe,* 1977; *Farmer et al.,* 1980]. Also, *Lazrus et al.* [1975] have detected acidic Cl^- (gaseous chlorine compounds that hydrolyze to Cl^- on a basic-impregnated filter). Generally, these IR and filter measurements show HCl mole fractions growing from less than 10^{-10} at the tropopause to $1\text{–}2 \cdot 10^{-9}$ between 30 and 40 km, approximately as predicted [*Cicerone et al.,* 1975; *Cicerone and Liu,* 1976; *Crutzen et al.,* 1978; *Wofsy,* 1978; *Logan et al.,* 1978]. Inorganic chlorine gas in the stratosphere arises from decomposition of organic chlorine compounds in the stratosphere (see section B2*b*). Additionally, and of great importance to understanding the stratospheric photochemistry, *Anderson et al.* [1977] have detected Cl atoms and ClO in the stratosphere by in situ resonance fluorescence of Cl atoms (1188-Å radiation excited by Cl_2 resonance lamps). Later, *Menzies* [1979] used an IR laser heterodyne instrument to identify and measure stratospheric (28–38 km) ClO at sunset. Menzies' peak ClO concentration, 2.5 ppbv at 38 km, and several of the *Anderson et al.* [1980] ClO profiles are higher than predicted from presently known sources of stratospheric Cl_g^i. Menzies' peak value is approximately the expected value for midday, and the present predicted diurnal variations of ClO and $ClNO_3$ state that there should be significantly less ClO at dusk, especially at 30 km and below. *Murcray et al.* [1979] have detected stratospheric $ClNO_3$ in IR absorption. The measured amounts agree well with calculated values, but only when a fast rate of formation is employed for $ClNO_3$ formation. Furthermore, the band absorption intensities used by Murcray et al. appear to be only 50% as strong as those of M. J. Molina (private communication, 1979). Thus Menzies' profile might not disagree much at peak from predictions if there is less $ClNO_3$ (and hence less diurnal variation of ClO) than predicted. Also, it should be mentioned that the bulk of the *Anderson et al.* [1977, 1980] profiles of Cl and ClO give peak values well within the range of predictions.

Because of the apparently major role that Cl_g^i species play in the photochemistry of the stratosphere [*Rowland and Molina,* 1975], more detailed information has been sought by researchers, and it should be summarized here. Also, although it is not yet clear from direct measurements that stratospheric Cl_g^i species are increasing in concentration, there is compelling evidence that they must be increasing: measured trends in tropospheric concentrations of the organic species, Cl_g^o (see section B2*b*), and theoretical predictions from known sources of stratospheric Cl_g^i. Figure 1 shows predictions of the mole fraction (or volume mixing ratio) of inorganic gaseous chlorine, Cl_g^i, in all forms for the years 1978, 1980, 1985, and 1990. Aside from explosive volcanoes the only presumably natural source of Cl_g^i in the stratosphere is from the stratospheric decomposition of CH_3Cl [*Cicerone et al.*, 1975; *Yung et al.*, 1975]. In the calculations of Figure 1 it has been assumed that CH_3Cl is present at a mole fraction of $7 \cdot 10^{-10}$ in the free troposphere (see references in section B2*b*) and that this predominantly natural compound will remain at this concentration. Similarly, although CCl_4 is thought to be primarily a man-made pollutant [*Molina and Rowland*, 1974*b*; *Singh et al.*, 1976; *Galbally*, 1976; *Altschuler*, 1976], its concentration has been assumed constant with time in the calculations (see also *Crutzen et al.* [1978] and *Logan et al.* [1978]) at a value of $1.25 \cdot 10^{-10}$. Thus although the natural Cl_g^i background of the stratosphere should be represented closely by the curve labeled 'from CH_3Cl' in Figure 1, the only contributions that are increasing with time are due to human usage of CF_2Cl_2, $CFCl_3$, and CH_3CCl_3 because the CCl_4 contribution has been assumed constant here. Relatively minor (at present) contributions to stratospheric Cl_g^i and to tropospheric Cl_g^o from other chlorocarbons (e.g., CH_2Cl_2 [*Crutzen et al.*, 1978]) and other chlorofluorocarbons have been neglected here. For a discussion of other possible but unlikely natural sources of stratospheric Cl_g^i, including volcanic inputs that are difficult to estimate, see *Cicerone* [1975]. Annual source strengths in mass per year are also presented there, as are corresponding figures for projected atmospheric injections of HCl from space shuttle rocket launches. Possible stratospheric effects of this rocket-exhaust HCl have been examined by *Whitten et al.* [1975]. Measurements to determine total Cl_g^i or even $Cl_g^i + Cl_g^o$ in the stratosphere would be very useful in determining whether our present understanding of stratospheric chlorine sources is accurate. These measurements would be especially valuable if made at altitudes above 35 km, where there is little dependence of Cl_g^i on altitude (see Figure 1) due to rapid vertical mixing. Complementary measurements to include (1) total trapping or sampling followed by elemental analysis and (2) simultaneous measurements of all the significant key Cl_g^i species would constitute a critical test of our ideas on stratospheric chlorine sources. Other than downward transport to the troposphere (probably as HCl), where rainout and washout are active sinks, there are no upper atmospheric sinks for Cl_g^i; no escape to space occurs, and there are no significant gas-phase reactions that convert inorganic Cl species to organic forms.

b. Organic gases (Cl_g^o). Two distinct types of data are available on chlorinated organic molecules in the atmosphere. One group of data has arisen from instruments designed by *Rahn et al.* [1976] and also used by *Berg and Winchester* [1977]; as discussed above, the air was flowed over activated charcoal traps. Table 1 shows representative organic Cl gas data from these investigations under the heading 'Bubblers, Charcoal Traps: Elemental Analysis.' The figure of 3050 ng/m^3 STP is from Berg and Winchester. Rahn et al. found only one-third as much. Each investigator found the organic Cl gas fraction to be less variable than the inorganic fraction.

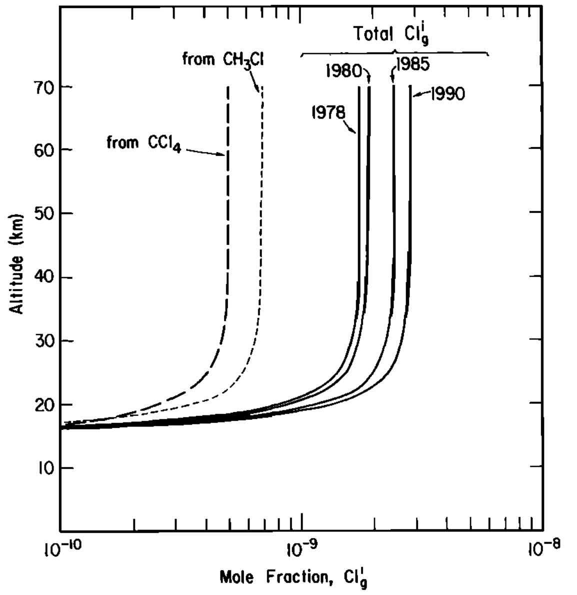


Fig. 1. Mole fraction (or volume mixing ratio) of inorganic gaseous chlorine, Cl_g^i, in the stratosphere calculated to arise from the principal organic species CF_2Cl_2, $CFCl_3$, CCl_4, CH_3Cl, and CH_3CCl_3. The contribution from CH_3Cl is presumed to be natural and constant in time, and that from CCl_4, while probably anthropogenic, is also assumed to be constant in time while growing amounts of CF_2Cl_2, $CFCl_3$, and CH_3CCl_3 are reaching the stratosphere, resulting in predicted increases in stratospheric Cl_g^i.

The second type of data on Cl_g^o is from electron capture–gas chromatography (EC-GC). Following the detection of atmospheric $CFCl_3$ by *Lovelock* [1971] and by *Su and Goldberg* [1973] and *Molina and Rowland*'s [1974*a*] report linking man-made chlorofluorocarbons with photochemical activity in the stratospheric ozone layer, a number of investigators began to detect other chlorocarbons. A summary of data through early 1978 appears in one entry of Table 1 and in Table 3 (December 1977 data of *Singh et al.* [1978]). The December 1977 total organic Cl gas found by Singh et al. was $4 \cdot 10^{-6}$ g/m^3 STP, or 2.5 ppbv. A more meaningful comparison with the organic Cl gas found by carbon sorption and elemental analysis, the March 1976 data of *Berg and Winchester* [1977] shown as $3.05 \cdot 10^{-6}$ g/m^3 STP in Table 1, can be achieved by employing March 1976 data of Singh et al., which show 2.3 ppbv total organic Cl gas, or $3.7 \cdot 10^{-6}$ g/m^3 STP. Thus the organic Cl gas measured by independent collection and analysis techniques in early 1976 agreed well; because of this and because there are no large unidentified chromatographic peaks to explain, it is likely that the Cl_g^o totals in Tables 1 and 2 are close to actual. This conclusion is quite important when one attempts to understand quantitatively the sources of stratospheric chlorine (see section B2*a*). The only qualification here is that there could be an appreciable undetected organic Cl molecule, *R*-Cl, or a series $(R\text{-Cl})_i$ of such molecules, which does not give a noticeable electron capture response. In this case, however, $(R\text{-Cl})_i$ would also have to escape the carbon sorption trapping and elemental analysis discussed above. Mention should also be made of possible decomposition products of these *R*-Cl molecules, especially of the chloroethylenes (see section C2). High molecular weight chlorinated species such as insecticides are not discussed in this report. The atmospheric detection of many of these species is reviewed by *Graedel* [1978].

For several key Cl_g^o compounds there is more information

TABLE 2. Halogen Content of Tropospheric Particles as Characterized by Mass Density per Cubic Meter of Sea Level Air, by Fractionation With Respect to Particle Size, and Gas-to-Particle Ratio for Each Halogen

	Mass/m^3 STP	Mass Versus Size	Remarks	Gas/Particle Ratio
Cl	1–10 μg, variable	large particles 1.6 < Cl/Na < 1.9; small particles show deficit: Cl/Na < 1.80	less Cl away from ocean and above boundary layer; no diurnal variations	variable: sometimes less than 1, sometimes more than 1
Br	5–10 ng	Br/Cl < in seawater	marine aerosol enriched in small particles near coast, inland; less particulate Br at night	4–10
I	1–3 ng	most I on small particles; I/Cl = 100–1000 × I/Cl in seawater	little diurnal variation	2–4
F	···	polluted air only		

available than the EC-GC data of *Singh et al.* [1979] shown in Table 3. Temporal increases in CF_2Cl_2 and $CFCl_3$ concentrations have been reported by *Singh et al.* [1979]. Measurements of CH_3Cl over a wide latitude region are found in the work of *Rasmussen et al.* [1980*a*]; systematic differences between free tropospheric concentrations that suggest an oceanic source appear there. Several workers including Watson, Lovelock, Rasmussen, and Guthrie have performed a number of unpublished investigations toward identifying natural sources of CH_3Cl and their variations. Increases in CH_3CCl_3 levels in background air have been reported by *Singh et al.* [1979], Y. Makide and F. S. Rowland (private communication, 1979), and *Khalil and Rasmussen* [1980]. Additional measurements of $CHClF_2$ are now available from *Rasmussen et al.* [1980*b*], and work is under way on CH_3Br and CH_3I.

The molecules CF_2Cl_2 and $CFCl_3$ have also been measured in the stratosphere by grab sampling and subsequent laboratory analysis by EC-GC [*Schmeltekopf et al.*, 1975; *Heidt et al.*, 1975; *Tyson et al.*, 1978; *Fabian et al.*, 1979; *Goldan et al.*, 1980]. At mid-latitudes, vertical profiles to about 40 km are available. Infrared absorption spectra at 19 km reported by *Williams et al.* [1976] taken in 1968 and 1975 showed increases in CF_2Cl_2 and $CFCl_3$ over this 7-year period. Further, the upper tropospheric data of *Goldan et al.* [1980] show temporal increases of CF_2Cl_2 and $CFCl_3$ averaging about 10.5% per year from 1976 to 1979.

c. Chlorine in particles. Chlorine as Cl^- is the major constituent of the marine aerosol. The largest of the marine aerosols, giant particles with diameters between 1 and 10 μ, are rich in Cl^-. The bulk of the Cl^- observed in marine aerosols is carried, in fact, by these giant particles. Chloride concentrations in the marine aerosol vary from 1 to 10 μg/m^3 STP, as shown in Table 2. Small particles show a definite deficit of Cl^- in comparison to the Cl/Na ratio of seawater (1.8). Values of Cl/Na larger than 1.8 are generally not found in large and giant particles except in isolated instances (see *Berg and Winchester* [1978] for a discussion and a review of the literature). Other semiquantitative findings include the facts that Cl^- in aerosols is less as distance above or away from marine areas increases, and the ratio of Cl gas to Cl^- in particles is variable, sometimes less than unity and sometimes greater. The Br/Cl and I/Cl ratios are discussed in sections B3 and B4, and particle-to-gas transformations in section C2.

The only apparent investigation too recent for Berg and Winchester to have reviewed is that of *Kritz and Rancher* [1980]. In a very stable fair weather marine atmosphere they studied the Cl^- circulation from sea to air to sea and deduced the release rate of sea-salt aerosols. From the aerosol composition, namely, that Cl^-/Na^+ was lower than that for seawater, they deduced a loss rate of Cl^- and equated it to the release rate of gaseous inorganic chlorine, Cl_g^i, presumably HCl. Thus production rates of Cl_g^i and residence times for Cl_g^i in the marine boundary layer were deduced. This quasi steady state measurement appears sound but could be performed at only one wind speed because of very stable meteorology. In a separate investigation, *Rancher and Kritz* [1980] sought diurnal variations in the Cl^- content of marine particles but found none.

d. Chloride in precipitation. Extensive sets of data exist for Cl^- in precipitation, at least for rainfall. While the data are apparently of high quality, they date mostly from pre-1960 investigations. The systematic studies of precipitation chemistry conducted in the 1950's (reviewed by *Junge* [1963] and *Eriksson* [1960]) showed Cl^- values from minima of about 0.1 mg/l for inland regions to maxima of about 10 mg/l in coastal zones and still higher locally near industrially polluted regions [*Junge*, 1963; *Likens*, 1976]. The observed patterns (highest Cl^- content near the seas, lowest Cl/Na ratios over conti-

TABLE 3. Summary of the Average December 1977 Concentrations of Measured Trace Constituents Containing Halogens

	Concentration, ppt (ppt = 10^{-12} v/v)		
Compound	Northern Hemisphere Average	Southern Hemisphere Average	Global Average
CCl_2F_2 (F12)	230 (25.5)*	210 (25.1)	220
CCl_3F (F11)	133 (13.4)	119 (11.7)	126
CCl_2FCClF_2 (F113)	19 (3.5)	18 (3.1)	18
$CClF_2CClF_2$ (F114)	12 (1.9)	10 (1.3)	11
$CHCl_2F$ (F21)	5 (2.6)	4 (1.0)	4
SF_6	0.31 (0.04)	0.27 (0.01)	0.29
CCl_4	122 (4.9)	119 (4.0)	120
CH_3CCl_3†	113	75	94
CH_3Cl	611 (83.7)	615 (103.0)	613
CH_3I	2 (1.0)	2 (1.2)	2
$CHCl_3$	14 (7.0)	≤3	8
CH_2Cl_2	44 (14.0)	20 (4.0)	32
C_2HCl_3	16 (8.0)	<3	8
C_2Cl_4	40 (12.0)	12 (3.0)	26
CH_3Br	5–20	···	5–20?
CH_2BrCH_2Br	5	···	5?

From *Singh et al.* [1978]. See also *Singh et al.* [1979] for discussion.

*Numbers in parentheses are standard deviations.

†For those species where significant variations within each hemisphere were observed, the average concentration within each hemisphere is the concentration that, when uniformly mixed in the hemisphere, represents the total burden of the species in that hemisphere.

nents) were quite repeatable, but questions of interpretation remain [see *Junge,* 1963]. Major questions involve the mechanism of gaseous Cl release from aerosol particles, the extent of wind transport of mineral particles in soil dust, and possible deviations from seawater elemental ratios in the formation of sea-salt aerosols. The latter phenomenon, elemental fractionation, is clear and dramatic for I and Br in both aerosols and precipitation, although halogen-specific mechanisms are at play. With the assumption that the Cl^- in global rainfall is almost entirely natural, one may deduce that the global precipitation rate of Cl^- is of the order of 3×10^{14} g/yr. This is the single largest sink of atmospheric chlorine gases and particles. One should realize that most of this Cl^- is very short-lived in the atmosphere. Rainout and washout of Cl^- from giant particles in sea-salt spray and of HCl evolved from the spray accounts for possibly 95-99% of the total Cl^- precipitated. It should also be noted that measurements of $^{38}Cl^-$ and $^{39}Cl^-$ in precipitation (see section C1*c*) can yield quantitative data on precipitation scavenging rates.

e. Total chlorine measurements. The discussions in sections B2*a* and B2*b* indicate that the total gaseous chlorine measured in the troposphere by independent workers (often not cognizant of the other's activities) and independent methods are in approximate agreement. Because of the importance of stratospheric chlorine and because *Anderson et al.* [1977, 1980] have occasionally measured more stratospheric ClO than was expected from known sources, there is a special need for measurements of total elemental chlorine without regard to speciation or even phase. *Berg et al.* [1980] have just reported such measurements, that is, the total number of Cl atoms per unit volume whether in organic or inorganic gases or in particles. In 12 separate collections in the lower stratosphere (altitude around 20 km), Berg et al. found very little variability. The lowest value was 2.7 ± 0.9 ppbv and the highest was 3.2 ± 0.7 ppbv, where the quoted uncertainties include all systematic analytical factors. The small variability observed over these 12 measurements argues for spatially and temporally uniform sources of stratospheric chlorine similar to those discussed in section B2*a*. Further, even though Berg et al. find 20% to 25% more chlorine in the lower stratosphere than can be explained with known sources and one- and two-dimensional tracer models, their results indicate that the much higher values (for ClO) seen on 2 of 12 flights by *Anderson et al.* [1980] were anomalous statistically if not completely.

3. *Bromine in the Atmosphere*

a. Inorganic gases (Br_g^i). There is much less data available for gaseous inorganic bromine than for inorganic gaseous chlorine. No individual Br_g^i has been identified in the atmosphere. The few available experimental studies have employed elemental analysis for Br preceded by LiOH filters [*Rahn et al.,* 1976], K_2CO_3 filters [*Duce et al.,* 1965], or activated charcoal [*Moyers and Duce,* 1972*a*] to collect samples. Evidently, the latter workers determined that Br_2 and organic Br gases would be trapped efficiently on activated charcoal, but it does not appear that the trapping efficiency for HBr was tested. *Moyers and Duce* [1972*a*] reported total gaseous bromine values between 49 and 68 ng/m^3 STP; it was widely believed that the bromine found in these studies (trapped on activated charcoal) was in inorganic form. Later work by *Rahn et al.* [1976] and by J. Rancher (described by *Kritz and Rancher* [1980]) found more organic gaseous bromine than inorganic, specifically $Br_g^o/Br_g^i \gtrsim 2$. In the data of Rahn et al. there is also a suggestion that Br_g^i is greater in the marine atmosphere than over continents. In Table 1 the range of Br_g^i concentrations (10–25 ng/m^3 STP) represents marine air; lower values are seen in continental air [*Rahn et al.,* 1976]. The only published data on stratospheric Br_g^i placed a value of 10^{-11} on the mass mixing ratio (or 13 ng/m^3 STP) in the lower stratosphere [*Lazrus et al.,* 1975]. W. Sedlacek (unpublished data, 1979) shows variability in stratospheric Br_g^i; occasionally, it has been higher than the Lazrus et al. figure. Recent collections by *Berg et al.* [1980] from the lower stratosphere (near 20-km altitude) yielded between 7 and 40 pptv for total bromine (gaseous and particulate). No latitudinal patterns emerged, but only five sample collections were reported. The available data in both the troposphere and stratosphere are thus very sparse and difficult to compare, partly because of the varying collection techniques. Similarly, it is not at all clear what species of Br_g^i were collected. Quite recently, *Rancher and Kritz* [1980] have reported a diurnal variation in Br_g^i in the marine atmosphere; almost twice as much Br_g^i was found during daylight hours as during darkness. Interpretation of these data is uncertain at present; data on Br_g^i speciation are clearly needed.

b. Organic Br gases (Br_g^o). The only Br_g^o species that have been identified in the nonurban atmosphere are CH_3Br and $C_2H_4Br_2$ [*Singh et al.,* 1978]; see Table 3, and Table 1 under the heading 'EC-GC' (chromatographic separation and electron capture detection). With nonspecific elemental analysis methods (see sections B2*b* and B3*a*), *Moyers and Duce* [1972*a*] and *Rahn et al.* [1976] have measured Br_g^o. There appears to be more Br_g^o near the oceans than inland. The range, 14–68 ng/m^3 STP, for Br_g^o includes some real variability of Br_g^o and possibly some varying efficiencies to various Br_g^o species. For example, *Moyers and Duce* [1972*a*] collected samples on activated charcoal which should trap some fraction of Br_g^o as well as Br_2 and possibly HBr according to their tests. Until more is known about the speciation of Br_g^o and Br_g^i (see section C1), it will be difficult to assess these data on total Br_g^o and Br_g^i. Singh's measured CH_3Br and $C_2H_4Br_2$ values are 10–25 pptv, or 36–90 ng Br/m^3 STP, i.e., in the range of the data on Br_g^o in Table 1. Other species are clearly possible, however, and very little work is under way to identify them. The possibility of diurnal variations in Br_g^o has not been investigated even for the marine boundary layer. The analytical methods used by *Rancher and Kritz* [1980] (actually, the methods of *Rahn et al.* [1976] exclude trapping of Br_g^o).

c. Bromide in particles. As with the gaseous bromine species there are fewer data available for particulate Br^- than for Cl^-. A recent review by *Berg and Winchester* [1978] summarizes these data, mostly work due to Duce, Moyers, Winchester, Woodcock, Rahn, and colleagues. Quantitative aspects of these data appear in Table 2. Generally, Br^- in the marine aerosol is present at 5–10 ng/m^3 STP, with most of this mass in large particles. Slightly higher values have been measured recently by *Kritz and Rancher* [1980] off the coast of West Africa. In experiments where Br^- in particles and gaseous Br were measured simultaneously [e.g., *Moyers and Duce,* 1972*a*; *Rahn et al.,* 1976], the ratios total Br gas/Br^- particulate have been between 4 and 20, in contrast to the corresponding ratio for Cl, which can be either less than or greater than unity. The recent Kritz and Rancher data found that Br_g^i/particulate Br^- was only 0.7. One surmises that if the Br_g^o had been measured simultaneously, the total Br gas to Br particulate ratio would have been greater than unity. Enrichment of Br^- in small particles, especially near coasts and inland, has been seen by several workers [e.g., *Duce et al.*, 1965; *Martens*, 1972] and attributed to combustion of gasoline containing $C_2H_4Br_2$. Also, in fresh aerosols and sea spray the Br^-/Cl^- ratio is as in seawater, but in aged aerosols the Br^-/Cl^- ratio is less than that in seawater [*Duce and Woodcock*, 1971]. During an 8-day period of a cruise off West Africa when diurnal variations were examined, *Rancher and Kritz* [1980] found about twice as much particulate bromide during night than during daylight hours in marine air.

d. Br^- in precipitation. There have been no attempts to monitor Br^- in rainfall regionally or globally to match the Cl^- data base, but several interesting isolated studies and their sequels have been performed. The Br^-/Cl^- ratios in rainfall have been found to be greater than Br^-/Cl^- in seawater or in particles in the air [*Duce et al.*, 1965]. The possibility that this is due to a loss of Cl from rainfall has been discounted by *Moyers and Duce* [1972*a*], who advanced thermodynamic equilibrium arguments that instead, Br_g^i is taken up faster by cloud and rain droplets. Clearly, one cannot hope to understand the operational mechanism without more quantitative and specific data on Br_g^i and Br_g^o. It was also seen by *Duce et al.* [1965] that the ratio of Br^-/Cl^- in rainwater increases with distance above the ocean and away from the ocean; Br^- has also been measured quantitatively in snows, at least in urban areas [*Winchester et al.*, 1967].

4. *Iodine in the Atmosphere*

a. Inorganic iodine gases (I_g^i). As with Br_g^i, no species of I_g^i has been identified in the atmosphere; instead, elemental analyses have been made. With collection techniques as described in section B2*a* for Cl_g^i, values for I_g^i between 0.4 and 20 ng/m^3 STP have been reported [*Duce et al.*, 1965; *Moyers and Duce*, 1972*b*; *Rahn et al.*, 1976; *Kritz and Rancher*, 1980]. Aside from the low value of 0.4 ng/m^3 reported by *Rahn et al.* [1976] for a remote site in the Northwest Territories of Canada and 2.5 ng/m^3 in Antarctic air [*Duce et al.*, 1973], all other data are between 5 and 20 ng/m^3. The highest value was due to *Moyers and Duce* [1972*b*] activated charcoal collections, but there is a good chance that organic I gases contributed to the 20 ng/m^3 STP, and Table 1 shows the range 0.4–17 ng/m^3 STP for I_g^i.

Until fairly recently [*Junge*, 1963] it was not clear that any gaseous I compounds existed in the atmosphere; instead it appeared then that I was present only in particles and precipitation. Early studies on iodine by Heymann, by von Fellerberg, and by Cauer (reviewed by *Junge* [1963] and by *Duce et al.* [1965]) showed very interesting facts. Measuring (presumably gas plus) aerosol iodine, they found continental regions where I in air was 100–1000 times that in clean marine air. In the mid-1930's, as the European iodine industry declined, the European I levels fell drastically. From these early studies also came the discovery of the very large enrichment of I with respect to Cl^- or Na^+ in the marine aerosol (see section B4*c*). During the cruise mentioned in section B3*c*, Rancher and Kritz found about twice as much I_g^i in daylight hours as at night in the marine atmosphere. No information is available on I_g^i species, but Rancher and Kritz could have missed species not trapped in an LiOH solution (see also section C3).

b. Organic iodine gases (I_g^o). The data shown in Table 1 for I_g^o came from very few experimental studies [*Duce et al.*, 1965; *Moyers and Duce*, 1972*b*; *Rahn et al.*, 1976]. The range 3–28 ng/m^3 STP covers the lowest I_g^o seen in Canada's Northwest Territories to maxima over Bermuda. It is possible that normal maxima are actually somewhat less; *Moyers and Duce* [1972*b*] reported 5–20 ng/m^3 STP in Hawaii for total gaseous I from activated carbon trapping that was highly efficient for I_g^i and presumably also for I_g^o.

While CH_3I is the only species of I_g^o that has been identified in the atmosphere (Table 3), relatively little effort has been expended so far. A few EC-GC measurements [*Lovelock et al.*, 1973; *Singh et al.*, 1978] have indicated that CH_3I is the dominant I_g^o species at least in the marine atmosphere. Referring to Table 3, a concentration of 2 ppt of CH_3I does not conflict with the I_g^o values mentioned above (2 ppt CH_3I = 11.4 ng(I)/m^3 at sea level). This conclusion would be premature, based as it is on very few data, but also because there are reasons to expect other interesting I_g^o species. One reason is the variety of organic I molecules found in marine organisms and the great enrichment of iodine in the organic film on surface ocean waters; I/Na is about 10^4 times that for seawater. Rupture of the surface film and subsequent ablation of I-rich surface film material (see section C3) is clearly responsible at least in part for the I enrichment of the marine aerosol. It would be surprising if a similarly magnified source of I_g^o does not exist. Measurements of CH_3I and other I_g^o species are needed before the roles of organic I as a precursor of I_g^i in air and of I_g^o dissolved in precipitation [*Dean*, 1963] can be understood.

c. Iodine in particles. Two oxidation states of I, I^- and IO_3^-, are accessible in aqueous solution as in the marine aerosol or precipitation. Aside from thermodynamic equilibrium calculations [*Moyers and Duce*, 1972*b*] there has been little distinction made between I^- and IO_3^- in particles; i.e., all analyses of I in particles have been by elemental methods. As summarized in Table 2, there is a very large enrichment of the fraction I/Cl in the marine aerosol: it is 100–1000 times I/Cl (by weight) for seawater, with the highest enrichments seen in small particles. This finding is over 50 years old, but reasons for this enrichment are still unclear. It is likely that at least two mechanisms operate, one that causes perhaps a 100-fold enrichment when large aerosols are first generated at the sea surface (probably involving I-rich organic films) and another that allows the longer-lived small particles to gather available I_g^o and I_g^i from the atmosphere (see *Moyers and Duce* [1972*b*] and *Duce et al.* [1965] for discussions). Ratios of total gaseous I to particulate I are 2–4 in the marine atmospheric boundary layer and larger elsewhere [*Rahn et al.*, 1976; *Kritz and Rancher*, 1980].

d. Iodine in precipitation. The last in-depth study of iodine in precipitation was that of *Duce et al.* [1965]. In Hawaii they collected 85 rain samples, generally from within the rain clouds. I/Cl ratios were from 500 to 1000 times I/Cl in seawater, confirming the initial observation of this dramatic iodine enrichment of Heymann in 1927. The I/Cl ratio in rain increased with distance above ground level. No global or temporally extended studies of I (as I^- or IO_3^-) in precipitation have been conducted since the 1930's.

5. *Fluorine in the Atmosphere*

a. Inorganic fluorine gases (F_g^i). There are almost no data on F_g^i in nonurban air. Tropospheric observations have been limited to man-made SF_6 (Table 3). Total gaseous F^- (probably HF because collection was by bubbling through Na_2CO_3) has been measured by *Okita et al.* [1974] in the vicinity of an aluminum refinery, where particulate and gaseous fluorine concentrations were much higher than in remote sites. Similar findings are likely to be obtained near phosphate fertilizer factories that use apatite as raw material [*Kauranen,* 1978]. In the stratosphere, HF has been detected in IR absorption by *Zander et al.* [1977], who reported a mole fraction of about 4 × 10^{-10} above 28 km. Similar observations by *Farmer and Raper* [1977] found about 1 × 10^{-10} from a measurement of the HF/HCl ratio, while *Mroz et al.* [1977] found about 10^{-10} above 30 km, decreasing to about 10^{-11} at the tropopause. *Mroz et al.* [1977] collected acidic F^- (probably HF) with basic-impregnated filters. Recently, *Farmer et al.* [1980] reported a vertical profile of HF increasing from a mole fraction of 2 × 10^{-11} at 18 km to 2 × 10^{-10} at 34 km. Because of growing inputs from CF_2Cl_2 and $CFCl_3$, stratospheric HF concentrations should be increasing. In calculations such as those described in Figure 1, I find that in 1980 there should be about 4 times as much stratospheric HF as in 1970.

b. Organic fluorine gases ($F_g{}^o$). Mostly because of interest in man-made chlorofluorocarbons and their atmospheric effects there have been a number of quantitative observations of $F_g{}^o$ in the past 5 years. The total mole fraction of all forms of $F_g{}^o$ is now about 10^{-9} as shown in Table 1, with species shown in Table 3 composing the total. A 1978 concentration of 6.5 × 10^{-11} has been taken for CF_4 [*Rasmussen et al.,* 1979], not shown in Table 3. There is a rough agreement between stratospheric HF measurements and HF values predicted from knowledge of the major fluorocarbons, $CFCl_3$ and CF_2Cl_2 [see *Sze,* 1978; *Farmer et al.,* 1980]. CF_4 appears to decompose only well above the stratosphere and does not contribute appreciably to stratospheric $F_g{}'$ [*Cicerone,* 1979]. Stratospheric CF_2Cl_2 and $CFCl_3$ have been measured by EC-GC and by IR methods (see section B2*b*). Also, IR detection of CF_4 in the stratosphere has been reported by *Goldman et al.* [1979].

c. Fluorine in precipitation and particles. While there has not been a very widespread or intense research effort to measure F^- in precipitation or in particles, there have been enough interesting findings to define key questions and phenomena fairly clearly. A recent review by *Barnard and Nordstrom* [1980] summarizes much of the available data, although a body of literature exists on fluorides in highly polluted air and is not reviewed critically by Barnard and Nordstrom or here. Pre-1970 investigations have been discussed by *Carpenter* [1969], whose own data, when combined with earlier work, suggested that natural aerosols (such as marine aerosols) were enriched in F^- and that inputs of soluble atmospheric fluorides from volcanoes, industrial processes, and soil dust were inadequate to explain observed F^- levels in precipitation. Independently, *Bewers and Hayson* [1974] concluded from mass balance calculations that terrigenous dust can account for only a few percent of the fluorine in the atmosphere. Bewers and Hayson postulated that excess F^- in rain might enter the air as a gas from the ocean or on small particles (radii less than 0.1 μ). Carpenter's data and earlier data on F^- in rain and snow were fairly consistent: 0.1 mg F^- per liter of water (100 ppb F^-) was frequently found. Values ranged from 50 ppb to several hundred parts per billion.

Following Carpenter's analysis and his suggestion that F^- is enriched in a sea surface process fractionation, *Wilkniss and Bressan* [1971] examined marine aerosols and laboratory-generated aerosols. They found that marine aerosols (diameter over 2 μ) are enriched with respect to Cl^- about 100% over the F/Cl value of seawater but that laboratory aerosols generated from seawater showed a small F^- deficit with respect to Cl^-. They concluded that collection of F^- in dust by marine aerosols was a possible explanation. Wilkniss and Bressan also reviewed earlier measurements by Kobajashi and Sugawara in which the F^-/Cl^- ratio in marine aerosols and precipitation was often 10 to 100 times that of seawater. In a later paper, *Wilkniss and Bressan* [1972] deduced that F^- is not enriched at the air-sea interface when sea-salt aerosols are generated; a slight F^- deficit with respect to Na^+ was found instead. In rain samples they found F^-/Cl^- ratios that implied a tenfold F^- enrichment with respect to Cl^- and a similar enrichment with respect to Na^+.

As has been noted by *Kauranen* [1978] and by *Barnard and Nordstrom* [1980], recent data on F^- in precipitation have shown lower F^- levels, possibly due to the examination of less polluted sampling sites. The distinction between polluted and unpolluted sites also appears in the data of *Miyake and Tsunogai* [1965], who analyzed rain on an island near Japan: F^- levels were variable, as low as 15 ppb. *Kauranen* [1978] found that in meltwater from snow, F^- was only 6 ppb in remote areas but 600 ppb near a fertilizer factory. (Industries that release fluorides and gases containing fluoride to the air include steel, aluminum, brick and ceramics, chemical or phosphate-rock fertilizer.) Kauranen suggested that his lowest values (~10 ppb) on F^- in precipitation might be more representative of global background levels than earlier large numbers (~150 ppb). Similarly, for particulate F^- in air polluted by industrial emissions, *Okita et al.* [1974] found particulate F^- concentrations that were higher than $F_g{}'$ concentrations by volume.

Most recently, the data of *Barnard and Nordstrom* [1980] from an industrial region (east coast of the United States but not near local sources) show F^- levels of 2–20 ppb, with 8 ppb being representative of two sites, one coastal and one inland. No correlation with sea-salt aerosol (as indicated by Na^+ measurements) was found. These authors also examined the fluorine cycle of the atmosphere and conclude that industrial input is nonnegligible and might even dominate.

C. KEY HALOGEN SPECIES, REACTIONS, AND TRANSFORMATIONS

1. *Key Processes and Species: Chlorine*

a. Key gas-phase chlorine species. Special importance may be attached to certain species *X* because *X* is demonstrated or expected to be significant by itself, for example, if *X* is a tracer of motions or it is toxic, carcinogenic, or radioactive, or if measurement of *X* in the atmosphere would allow a theoretical hypothesis to be tested. In Table 4 are listed a number of key Cl species along with designations as to the region and reason of interest. For CCl_4 and the (entirely man made) chlorofluorocarbons the main interest is due to the chlorine delivered to the stratosphere and the rapid increases in their industrial production since the 1960's. To be useful, measurements must be accurate (±5 or 10%) and at least this precise. Data are needed from both hemispheres, as suggested in the December 1977 data of Table 3. For CH_3Cl one seeks to identify marine locations and biological and/or physical mechanisms that cause its release from the oceans, which appear to be its natural source [*Lovelock,* 1975; *Zafiriou,* 1975; *Singh et al.,* 1978; *Rasmussen et al.,* 1980*a*]. One should not ignore, however, the 10% to 15% annual source contribution due to industry. With $C_2H_3Cl_3$ one is concerned with its potential for accelerating stratospheric impact [*Crutzen et al.,* 1978; *McConnell and Schiff,* 1978] and its usefulness as a tracer of

TABLE 4. Key Halogen Species Known or Expected To Be Significant in Atmospheric Chemistry With Regions and Reasons of Interest

Species	Atmospheric Region	Significance
CCl_4	T + S	source (A) for stratospheric Cl_g^i
$CFCl_3$	T + S	source (A) for stratospheric Cl_g^i
CF_2Cl_2	T + S	source (A) for stratospheric Cl_g^i
$CHClF_2$ (22)	T + S	source (A) for stratospheric Cl_g^i
$CHCl_2F$ (21)	T + S	source (A) for stratospheric Cl_g^i
$C_2F_3Cl_3$ (113)	T + S	source (A) for stratospheric Cl_g^i
$C_2F_4Cl_2$ (114)	T + S	source (A) for stratospheric Cl_g^i
CH_3Cl	T + S + BL	source (·90N, ·1A) for stratospheric Cl_g^i
CH_3CCl_3	T + S + BL	source (A) for stratospheric Cl_g^i; indicator of tropospheric OH
C_2Cl_4	T + BL	urban and regional pollutant
C_2HCl_3	T + BL	urban and regional pollutant
$CHCl_3$	T + S	urban and regional pollutant and minor source of stratospheric Cl_g^i
$COCl_2$	T + S	decomposition product of CCl_4, $CFCl_3$
COClF	T + S	decomposition product of CF_2Cl_2, $CFCl_3$
Σ organic Cl	T + S	precursor for T and S Cl_g^i
HCl	T + S	source-sink; see discussion on Cl_g^i in stratosphere
ClO	S	intermediate radical in Cl chain reactions
HOCl	T + S	temporary sink in Cl chain reactions
$ClONO_2$	T + S	temporary sink in Cl chain reactions
Cl	S	intermediate radical
ClOO	S	intermediate radical
OClO	S (night)	nighttime sink in Cl chains; liberated from aerosol? (photo-dissociates rapidly)
ClNO	T + S (night)	
$ClO{\cdot}O_2$	S	does ClO complex with O_2?
Σ inorganic Cl	T + S	needed for understanding Clx budget; missing species?

Regions are T, troposphere; S, stratosphere; BL, boundary layer. Sources are A, anthropogenic and N, natural.

atmospheric motions and as an indicator of hemispheric OH concentrations [*Singh*, 1977; *Lovelock*, 1977].

The carbonyl species, COF_2, $COCl_2$, and COFCl, are not of major concern in the stratosphere, where they are formed from chlorofluorocarbon decomposition, although present predictions of stratospheric F_g^i (principally HF) levels are somewhat uncertain owing to corresponding uncertainties in stratospheric photo-oxidation rates of CF_2O and COFCl. These carbonyl compounds and others are worthy of some attention in the troposphere, however. Although the exact reaction pathways and rates are unclear (see section C2), several compounds like formyl chloride, phosgene, chloroacetaldehyde, dichloroacetyl and trichloroacetyl chloride, and peroxychloroformyl nitrate are possible products of the tropospheric decomposition of common chlorinated solvents and of the dominant natural chlorocarbon, CH_3Cl. The potential importance of these possible products can be seen partially by examining the amounts of chlorine that could be involved annually. Table 5 lists production rates of several common chlorinated solvents and monomers for plastics production. Also shown is the 3×10^6 metric tons/yr CH_3Cl produced naturally [*Cicerone et al.*, 1975; *Yung et al.*, 1975; *Graedel*, 1979] and a typical 1970's yearly release of CF_2Cl_2 and $CFCl_3$ for comparison. While the relatively small amounts of CF_2Cl_2 and $CFCl_3$ are decomposed and yield decomposition products only in the stratosphere, much larger tonnages of Cl are released from, for example, perchloroethylene, C_2Cl_4, in the troposphere. If the reactions mentioned in section C2 lead to the carbonyl chlorides listed above, their behavior in the troposphere, in precipitation, and in water bodies will need to be determined.

Most of the inorganic Cl compounds listed in Table 4 are important to measure in the stratosphere to determine whether presently envisioned stratospheric photochemical reaction schemes are valid. In certain physical regimes it is necessary to measure various species simultaneously, for example, Cl, ClO, O_3, O, NO, and HCl in the high daytime stratosphere for predicted photostationary state relationships to be tested. HCl is likely to be the dominant form of tropospheric Cl_g^i [*Ryan and Mukherjee*, 1974; *Wofsy and McElroy*, 1974], although HOCl has not been ruled out, and NOCl might exist at night if evolved from marine aerosols. Total organic Cl and total inorganic Cl are listed because sources, sinks, and the overall budget of Cl_g^i will not be clearly understood until the total of the respective individual constituents when measured equals the Cl_g^o or Cl_g^i measured in a total collection–elemental analysis experiment. The present ledger for Cl is not unsatisfactory: as was noted in section B2*b*, the total Cl in the individual Cl_g^o compounds detected by electron capture–gas chromatography is only 20–25% different from (higher than) the total Cl_g^o found in total organic collection–elemental analysis studies. Because of the stratospheric impact of CF_2Cl_2, $CFCl_3$, CCl_4, CH_3Cl, and CH_3CCl_3 there is impetus to balance the Cl_g^o ledger as closely as possible. Predicted mole fractions of Cl_g^i in the high stratosphere of 1976–1978 are about 2 ppbv; see section B2*a* and Figure 1. Values as high as 8 ppbv seen at 36 km for ClO on one occasion by *Anderson et al.* [1980] are not comprehensible, given our present measured compounds and concentrations of Cl_g^o in the troposphere as shown in Tables 1 and 3.

b. Gas-phase chlorine reactions. Following the reports by *Molina and Rowland* [1974*a*] and *Rowland and Molina* [1975] the atmospheric impact of chlorocarbons and chlorofluorocarbons and the radicals Cl and ClO became clear. Key reactions

TABLE 5. U.S. Halocarbon Production, Cumulative Through 1973 and the Year in Which Production of Each Compound Reached 10^8 lb/yr

Compound	Cumulative Production, 10^9 lb	Year Production Reached 10^8 lb/yr
Carbon tetrachloride	15.2	1940
Chloroform	2.8	1962
Methyl chloride	4.3	1961
Ethyl chloride	14.3	before 1948
Ethylene dichloride	67.3	before 1943
Methylene chloride	4.7	1959
Perchloroethylene	9.1	1949
Trichloroethylene	8.8	1949
Methyl chloroform	2.9	1962
Vinyl chloride	44.7	before 1947
Fluorocarbon 12	5.3	1955
Fluorocarbon 11	3.4	1962
Phosgene	5.0	1962
Other	29	
Total	217	

1 lb = 0.453 kg. With few exceptions, production rates have grown monotonically. Corresponding approximate worldwide figures can be obtained by multiplying by 1.5 or 2 (taken from *McCarthy and Jesson* [1975]).

of stratospheric consequence have been reviewed elsewhere [e.g., *National Academy of Sciences/National Research Council*, 1976, 1979]. Quantitative uncertainties remain in the kinetics of several possible reactions between HO_2 and several $Cl_g{}'$ species, in the formation rate of $ClNO_3$ in $ClO + NO_2 + M \rightarrow ClNO_3 + M$, and in the integrated rate of OH attack on several chlorocarbons, for example, CH_3CCl_3, in the troposphere and lower stratosphere. Measurements of OH and its variations are needed, but it is also likely that improved and extended measurements of CH_3CCl_3 and CO will aid in deducing averaged OH levels.

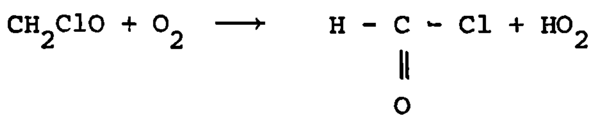
As mentioned in section C1, the tropospheric reaction paths of several chlorinated solvents such as chloroethylenes, CH_2Cl_2, C_2Cl_4, and CH_3Cl need both laboratory and field investigation. The initial reaction in the case of every compound in Table 5 except the perhaloalkanes is attack by OH, the kinetics of which are not clear for several chlorinated, double-bonded molecules. Consider these examples (suggested by P. L. Hanst):

CH_3Cl

$$CH_3Cl + OH \rightarrow CH_2Cl + H_2O$$

$$CH_2Cl + O_2 \xrightarrow{M} CH_2ClO_2$$

$$CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2$$



$$CH_2ClO + O_2 \rightarrow H-\underset{\underset{\displaystyle O}{\|}}{C}-Cl + HO_2$$

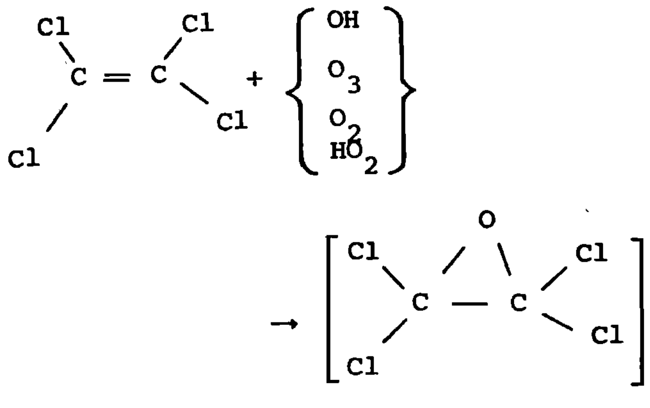
i.e., formyl chloride + HO_2

CH_2Cl_2

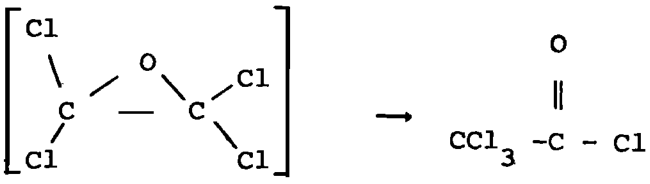
$$CH_2Cl_2 + OH \rightarrow CHCl_2 + H_2O$$

$$CHCl_2 + O_2 \rightarrow \text{formyl chloride} + ClO$$

Perchloroethylene



'hot' epoxide



trichloroacetyl chloride

Similar paths exist for decomposition of other solvents; they lead to carbonyl chlorides like phosgene (nerve gas). The kinetics of these reactions need study; the thermal, hydrolytic, and photolytic properties of the carbonyl chlorides in tropospheric (urban and nonurban) conditions need examination; and field experiments seem necessary. To the extent that NO, NO_2, O_3, and R-O_2 species are needed to drive these reactions, one need only consider polluted regions (where the chlorocarbon pollutants are also most abundant). Otherwise, the ultimate disposition of the enormous amounts of chlorine borne by the compounds of Table 5 will remain unknown. Parallel remarks apply for chlorinated molecules such as the chlorinated pesticides, defoliants, and combustion products, especially burning of plastics. Even if they are merely transported in air without atmospheric reactions, the behavior of these substances will be important in the hydrosphere and food chain.

c. Heterogeneous processes: Halogens. It is clear that much of the gaseous chlorine present in the troposphere evolves from sea spray and the Cl^- in marine aerosols (see, for example, the discussion by *Duce* [1969]) and that the dominant return path of gaseous chlorine to the continents and oceans (as well as to polluted regions) is by Cl^- in precipitation. Yet neither process is understood: the mechanism(s) that release, say, HCl from sea-salt particles or how precipitation scavenging (rainout and washout) occurs.

While specific information and ideas are needed for processes involving Cl and each respective halogen, the questions of heterogeneous transformations are presently so broad that they are discussed here for Br, F, and I as well as Cl. Figure 2 is a sketch that indicates the importance of several heterogeneous processes for a halogen X. It is well established that certain organic halides, RX, are photolyzed and/or attacked by OH and other radicals to yield inorganic halogen-containing species, $X_g{}'$, both in the troposphere and stratosphere. Also, it is apparent but not clear mechanistically that $X_g{}'$ species are released from sea-salt aerosols in the marine atmosphere. Particulate X^- (and possibly IO_3^- in the case $X = I$) interacts with water droplets, the other dissolved gases, cations and anions in the moist aerosol, and ambient gases such as NH_3, SO_2, etc. For $X = Cl$, $Cl_g{}'$ apparently is released from the aerosol as HCl or NOCl but probably not as HOCl. In any case, rapid interchange between aerosol Cl^- and $Cl_g{}'$ is well established [*Rahn et al.*, 1976; *Berg and Winchester*, 1977]. For $X = I$ it is likely that the aerosol absorbs I-containing gases from the air. For Br and I there is evidence that gases are released from aerosols by day and scavenged into aerosols by night [*Rancher and Kritz*, 1980]. The extent to which HCl release is caused by ambient SO_2 and NO_2 has been studied by *Martens et al.* [1973], and the consequences of various thermodynamic equilibria have been explored by *Moyers and Duce* [1972*a*, *b*], but few general results are established, and several important questions remain. Does the release of HCl

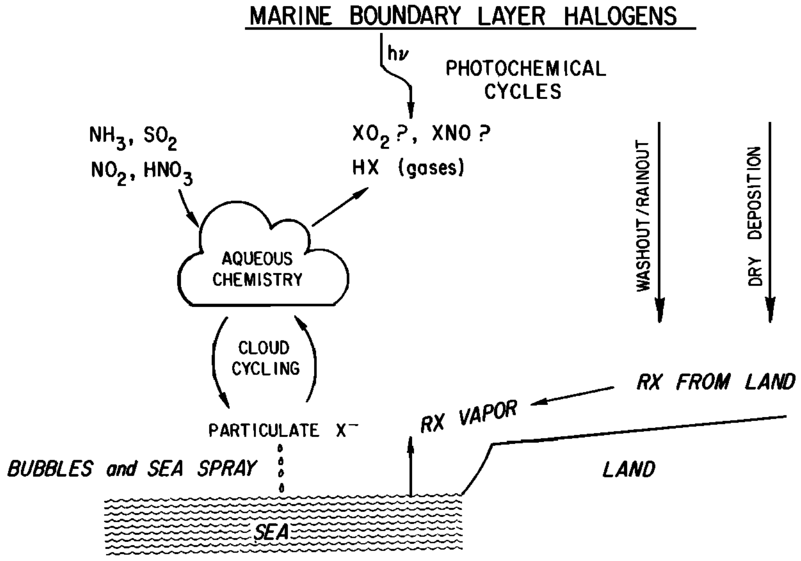


Fig. 2. Outline of the processes that release particulate and gaseous halogens (X = halogen) from the sea and of the interactions between particles, moisture, and ambient gases. Organic halogen gases, RX, are indicated to arise from both land and sea.

occur mostly in polluted regions, where SO_2 and NO_2 are at their highest concentrations? What chemistry occurs in the aqueous layer on sea spray particles? What species evaporate, and how do other atmospheric gases affect the particle-to-gas conversions? What is the subsequent photochemistry of the evaporated species? How do the major gas-to-particle conversions (if they exist) take place? What processes control the amounts of X contained in fresh aerosols, i.e., how does fractionation occur at the air-sea interface? What organohalogens are released as gases from the sea?

Precipitation and dry deposition of X^- or of gases are poorly understood. It is likely that isotopic studies can be fruitful. For example, radioactive isotopes of chlorine are produced in the earth's atmosphere continuously and uniformly by the bombardment of ^{40}Ar (1%) with incoming cosmic radiation. The two isotopes with the largest production cross sections are ^{38}Cl and ^{39}Cl, which have half-lives of 37 min and 55 min, respectively. (Another isotope, ^{36}Cl, has a half-life of 300,000 years.) The maximum in production per cubic centimeter occurs at about 30-km altitude, but smaller quantities are created essentially down to ground level.

These short-lived radioactive Cl isotopes provide tracers whose time of creation is known to have occurred within a few hours of time of measurement. Consequently, when experiment shows measurable concentrations of these isotopes in rainwater, then a short time-scale can be inferred for the precipitation scavenging of the newly formed Cl atoms (in whatever chemical forms are accessible to it within an hour or two). Calibration of the efficiency of such scavenging processes is somewhat more difficult, but the extreme constancy of production at a given millibar level (±1%) permits numerous experiments during both dry and rainy periods.

At higher levels including the stratosphere, where the interest would not be entirely in heterogeneous processes, collection of particulate or reactive halogen chemicals can be compared with the in situ production in a similar manner. Both tropospheric and stratospheric experiments were successfully carried out in the late 1960's at Batelle Northwest, with identification at very favorable signal/noise ratios of both ^{38}Cl and ^{39}Cl [*Young et al.,* 1970].

2. *Key Processes and Species: Bromine*

a. Gas-phase bromine species. Of the Br-containing gaseous species listed in Table 6 only CH_3Br and $C_2H_4Br_2$ have been identified in the atmosphere (see discussion of section

TABLE 6. Key Halogen Species Known or Expected To Be Significant in Atmospheric Chemistry With Regions and Reasons of Interest

Species	Atmospheric Region	Significance
CH_3Br	T + S	source (N, A) of Br_g^i in T and S
CH_2BrCH_2Br	T + BL	source (A, autos) of Br_g^i in T and S
$CF_xBr_yH_z$	T + S	source (A, fire retardants) of Br_g^i in T and S
Σ organic Br	T + S	budget of Br_g^o, precursor of Br_g^i
HBr	T + S	source/sink for Br chain reactions; interactions with aerosols?
$BrONO_2$	T + S	temporary sink in Br chain reactions
BrO	S	radical in Br chain reactions
Br	S	radical in Br chain reactions
HOBr	T + S	temporary sink in Br chain reactions
Σ inorganic Br	T + S	needed for understanding Br_g^i budget; missing species?
CF_4	T + S	source (A, N) of mesospheric F_g^i
SF_6	T + S	source (A) of stratospheric F_g^i
HF	T + S	dominant F_g^i species
$FONO_2$	S	possible F_g^i reservoir species?
COF_2	T + S	possible stratospheric reservoir of F_g^i; decomposition product of CF_2Cl_2
HOF	T + S	possible F_g^i reservoir species?
HI	T + S	likely I_g^i species
IO	T	likely I_g^i species
HIO	T	likely I_g^i species
I	T	likely I_g^i species
$IONO_2$ (and isomers)	T	likely I_g^i species
CH_3I	T + S	source (N), precursor of I_g^i
I_2	T (night)	source, liberated from seawater?
Σ organic I	T	precursor for T + S I_g^i
Σ inorganic I	T	needed for I budget estimates; needed to understand enrichment of I in aged marine aerosols

Regions are T, troposphere; S, stratosphere; BL, boundary layer. Sources are A, anthropogenic and N, natural.

B3*b*). CH_3Br is presumably natural, and $C_2H_4Br_2$ is probably entirely due to man's activities [*Winchester et al.,* 1967]. Measurements of these compounds, if accompanied by measurements of other selected bromohydrocarbons and of total organic gaseous bromine, would go a long way toward assessing the relative intensities of the sources of atmospheric Br compounds. The extent to which inorganic gaseous bromine, Br_g^i, is important in tropospheric processes is not at all clear. No individual Br_g^i species has been identified, and total Br_g^i can be estimated only roughly from existing data (see section B3*a*). On the basis of available kinetic and thermochemical data, HBr, HOBr, Br, BrO, and $BrNO_3$ might be the dominant species of Br_g^i. In the troposphere one expects HBr to dominate, and in the stratosphere BrO. From the stratospheric measurements of *Lazrus et al.* [1975] of gaseous acidic vapors (probably HCl and HBr) that hydrolize to Cl^- and Br^- one may conclude that the source of stratospheric Br_g^i is not seawater or volcanoes because of the measured Br/Cl ratio in the stratospheric samples. Instead, it is likely that Br_g^o species, for example, CH_3Br are at least partially responsible for delivering Br atoms to the stratosphere [see *Wofsy et al.,* 1975].

b. Gas-phase bromine reactions. Very little research has been performed on reactions of inorganic gaseous Br-containing species, Br_g^i, in the atmosphere. Of the ideas to date, the most interest has arisen from suggestions that Br_g^i species can catalytically destroy stratospheric ozone [*Crutzen,* 1974; *Watson,* 1975; *Wofsy et al.,* 1975]. Laboratory photochemical studies reviewed recently by *DeMore et al.* [1979] have confirmed that there is some potential stratospheric interest; the kinetics of reactions that couple Br_g^i species reactions to those of stratospheric Cl_g^i and nitrogen oxides still need closer attention. For example, BrO + ClO can react to form either Br + Cl + O_2 or Br + OClO; only the total reaction rate is known (at room temperature). The most thorough discussion on stratospheric bromine reactions, that of *Yung et al.* [1980], emphasizes interactions between Br_g^i species and Cl_g^i species. Generally, temperature dependences of Br_g^i reactions are unknown, as are rates and products of reactions with HO_2.

Tropospheric reactions of Br_g^o and Br_g^i have not been studied in much detail. As with other organohalogen species in the troposphere, reactions with OH are probably most important for Br_g^i [*Wofsy et al.,* 1975], although photodissociation and reactions with O_3 and HO_2 are possible. With so little interest so far in tropospheric Br_g^i speciation and no data available, one can only suggest that the species listed in Table 6 and discussed in the previous section should be sought first and their reactions studied. The data of *Rancher and Kritz* [1980] (that show more Br_g^i in the day than at night and the opposite for Br^- in particles in the marine atmosphere) imply that tropospheric Br_g^i chemistry might have an important heterogeneous component.

3. *Key Processes and Species: Iodine*

a. Gas-phase iodine species. Because very little attention has been paid to gaseous iodine forms, I_g^o or I_g^i, there is almost no information on their speciation. CH_3I has been detected in the marine atmosphere (Table 3), but there are reasons to believe that many other I_g^o compounds exist in air, for example, the relative richness of I in organic films that become airborne when bubbles break or droplets otherwise exit the ocean (see section C3*b*). No species of I_g^i has been identified in the atmosphere. Also, because HI is a weaker acid than HCl, HNO_3, and H_2SO_4, one could imagine that gaseous HI could be released from mildly acidic aerosols.

Regardless of the molecular species involved, two isotopes of iodine deserve special attention and mention. Both are fission products of uranium and emit both gamma and beta radiation: Isotope ^{131}I has an 8-day half-life and has been released into the atmosphere accidentally in nuclear power plant mishaps. It was apparently released in the March 1979 Harrisburg, Pennsylvania, incident. Isotope ^{129}I would be of greater global concern because of its 17-m.y. half-life and thus could be transported over larger distances.

b. Gas-phase iodine reactions. Despite the fact that some laboratory photochemical data are available, very little effort has gone into mapping out reaction schemes for atmospheric iodine except for that of *Zafiriou* [1974] and the recent report by *Chameides and Davis* [1980]. One phenomenon whose understanding might depend on knowing the key reactions and species is the very large enrichment of atmospheric particulates (100 to 1000 times) of I with respect to Na or Cl. While much of this enrichment is due to the organic surface-active sea surface material causing the fresh aerosol to be enriched [see *Seto and Duce,* 1972], it seems clear that the further I enrichment of aged aerosols cannot be so explained; it appears likely that gaseous iodine is taken up by marine aerosols. The species involved must be identified before the mechanism can be understood. The possibilities that gaseous I_2 is released by UV light photo-oxidation of oceanic I^- as proposed by *Miyake and Tsunogai* [1963] or by a temperature-meditated distillation process suggested by *Martens and Harriss* [1970] deserve more investigation. Miyake and Tsunogai estimated that the gaseous iodine lost from the oceans to the atmosphere annually from UV-induced release is 4×10^{11} g. Their global iodine cycle is nearly balanced by a return flux of 5×10^{11} g per year I^- in precipitation. Another possible way to supply the troposphere with I_g^i is through the release of CH_3I from oceans. From their measurements of CH_3I in surface waters and air and assumed photolysis rates, *Lovelock et al.* [1973] deduced a flux of 4×10^{13} g CH_3I per year. *Zafiriou* [1974] calculated that CH_3I would have a larger atmospheric residence and thus a smaller source than that inferred by Lovelock et al. Zafiriou estimated a minimum CH_3I release of 1-2 $\times 10^{12}$ g/yr from the oceans. Later, *Zafiriou* [1975] examined the possibility that gaseous CH_3I would react with Cl^- in sea-salt aerosols to produce I^- and subsequently lose I_g^i to air, but he concluded that insufficient I^- could be produced to compose a large source of atmospheric I_g^i, at least for his assumed concentrations of CH_3I in the droplets. Very recently, a new mechanism has been suggested for the release of iodine from ocean surface waters: reactions of atmospheric O_3 with dissolved I^- to produce I_2 [*Garland and Curtis,* 1981]. Garland and Curtis deduce a global annual source of 6×10^{10} g/yr of I_2.

Whether the primary source of oceanic iodine to the atmosphere is organic as, say, CH_3I or inorganic as, say, I_2, iodine atoms are quickly released, and the chemical reactions of I_g^i species ensue. As with Br but unlike Cl or F atoms, reaction of I with CH_4 is endothermic owing to the relatively weak H-I bond. The reaction scheme of *Chameides and Davis* [1980] suggests that chain reactions might take place with O_3 destruction in the troposphere, but various uncertainties make it difficult to estimate the chain lengths. The diurnal variations seen by *Rancher and Kritz* [1980] for I_g^i but not for particulate I^- might imply that heterogeneous reactions of iodine are not dominant.

4. *Key Processes and Species: Fluorine*

a. Gas-phase fluorine species. A number of gaseous organofluorine species, F_g^o, have been detected in the atmosphere, as discussed in section B5*b*. The impetus for most of these measurements except for the original detection by *Lovelock* [1971] has been the potential atmospheric impact of the chlorofluorocarbons listed in Table 4 under chlorine. As sources of atmospheric F_g^o (and its subsequent degradation to form inorganic F gases, F_g^i) the compounds CF_4 and, to a lesser extent, SF_6 must also be considered. The presence of CF_4 at about 10^{-10} parts by volume [*Gassman*, 1974; *Rasmussen et al.*, 1979; *Goldman et al.*, 1979] is not yet explained. The apparent long residence time of atmospheric CF_4, over 10,000 years, and its possible industrial sources have been discussed by *Cicerone* [1979]. Measurements to determine the trend in CF_4 concentrations are needed. Other F_g^o forms like COF_2 and COFCl (products of atmospheric decomposition of chlorofluorocarbons) have not yet been detected. They should be measured in the lower stratosphere and possibly in precipitation. Several forms of F_g^o, possibly including vinyl fluoride, emitted by certain African plants [*Hall*, 1972] might also be detected.

Inorganic gases, F_g^i, besides HF have not been detected in the atmosphere. Stratospheric HF (see section B5*a*) is possibly the dominant form of F_g^i [*Watson et al.*, 1978; *Stolarski and Rundel*, 1975], as is also likely the case in the troposphere, although HOF and FNO_3 might form. In the upper stratosphere and mesosphere one might find F, FO, FO_2, and F^- (possibly hydrated.).

b. Gas-phase fluorine reactions. Perhaps the only explicit studies of atmospheric reactions involving F_g^i are those of *Watson et al.* [1978] and *Stolarski and Rundel* [1975]. In the former report it is noted that laboratory kinetic and photochemical data are sparse and that once formed, HF is quite stable. Only $O(^1D)$ and vibrationally excited ($v \geq 2$) OH molecules can react with HF at subionospheric altitudes. For these reasons it appears that (1) F_g^i will not affect stratospheric O_3 concentrations at least at presently conceivable concentrations, (2) HF might be the only F_g^i species extant at presently measurable concentrations, and (3) stratospheric HF concentrations should increase with time at predictable rates owing to past and future chlorofluorocarbon release and decomposition (see section B5*a*).

Another role of atmospheric fluorocarbons must be noted, although it results from their stability rather than their reactivity. The accumulation of fluorocarbons in the air and their strong infrared absorption bands lead to possibly significant enhancements in the atmospheric trapping of outgoing planetary radiation. *Ramanathan* [1975] recognized this problem first. A similar greenhouse effect due to CF_4 has been estimated by *Wang et al.* [1980].

D. GLOBAL CYCLES OF ATMOSPHERIC HALOGENS

1. *Pathways of Chlorine Compounds*

a. Sources and sinks: Chlorine. Chlorine in gases and particles enters and leaves the atmosphere in many ways, and depending on the chemical phase and species involved, can reside in the atmosphere for very brief or very long periods of time. Thus in analyzing the global Cl cycle one must identify and account for several key subcycles, each with its own key processes and a spectrum of time constants for Cl transfer and transformations.

The largest subcycle of atmospheric Cl involves about 6 × 10^9 metric tons as particulate Cl^- that enters the air annually as the dominant constituent in sea-salt particles whose total flux is about 10^{10} tons/yr (estimated by *Blanchard* [1963]). Because the bulk of the Cl^- mass is borne by large and giant particles with radius over 1 μ, a substantial fraction of this 6 × 10^9 tons of particulate Cl^- resides in the atmosphere less than 1 or 2 days, mostly in the marine boundary layer. Smaller particles remain airborne longer, and a fraction of their Cl^- is converted to gaseous chlorine compounds, Cl_g. The fraction of sea-salt particle Cl^- that is converted to Cl_g is definitely a function of particle size and probably depends on ambient gases, humidity, temperature, etc. [*Martens et al.*, 1973], but quantitative estimates of this fraction are not easily measured or predicted. *Duce* [1969] suggests that a 10% figure is reasonable; thus 6 × 10^8 tons of Cl_g would result annually from the 6 × 10^9 tons/yr in sea-salt particles. By carefully examining Cl^-/Na^+ ratios, *Martens et al.* [1973] found that 13% of the initial Cl^- was lost from particles in clean marine air near Puerto Rico, while 54% was lost similarly in more polluted (higher SO_2, NO, and NO_2 air concentrations) San Francisco Bay area air. Relatively larger Cl^- deficits were found on small particles, and smaller deficits on large particles. Similar results were obtained by *Wilkniss and Bressan* [1972]. Smaller Cl^- losses from particles, as low as 3%, have been measured by *Chesselet et al.* [1972]; they would imply a source of Cl_g of 2 × 10^8 tons/yr. Recent measurements and analysis by *Kritz and Rancher* [1980] led to an estimate of 3 × 10^{-3} $g(Cl^-)/m^2/s$ released as sea salt under rather constant 12-knot (6 m/s) wind conditions and revealed that 6 × 10^{-4} $g(Cl^-)/m^2/day$ were lost from the particles as Cl_g under those conditions. Blanchard's estimates of 10^{10} $g(Cl^-)/yr$ for the annual sea-salt production rate was integrated over all wind conditions (from climatological data) and required assumptions for (1) particle size distributions, (2) particle fall velocities, (3) vertical gradients of particle concentrations, and (4) salinity of oceanic rains. Limited data exist for each of points 1–4, hence the fact that *Blanchard*'s [1963] estimate for sea-salt production is over 10 times larger than that of *Eriksson* [1959], mostly due to adopted values for salinity of rainfall, but also because Eriksson assumed a single, globally averaged wind speed (12 knots (6 m/s)), while Blanchard employed an empirical grid of climatological mean winds for various regions.

To examine the uptake of HCl by raindrops, *Duce* [1969] performed thermodynamic equilibrium calculations and found that more HCl remains gaseous than the equilibria permit. Thus equilibrium between gaseous and droplet-dissolved forms may not be reached. There is even less reason to expect various equilibria to apply for HCl and moist particles owing to surface films, possibly organic, on particles. *Martens et al.* [1973] determined from their measured Na/Cl ratios over particle sizes that chemical equilibrium was not attained in the particles.

The paragraphs above indicate that (1) sea-salt particles are the dominant source of atmospheric particulate Cl^-, (2) the annual input of particulate Cl^- is about 6 × 10^9 tons (uncertain enough so that even rough error bars are hard to place), and (3) between 3% and 20% of the annual Cl^- particulate input is lost from particles (presumably as HCl); i.e., this annual source of gaseous Cl compounds, Cl_g, is between 2 × 10^8 and 12 × 10^8 tons/yr, but a wider range is not unlikely. In comparison to the 9 × 10^6 tons/yr estimated to be emitted from volcanoes by *Eriksson* [1959] or the corresponding estimate of 3–7 × 10^6 tons/yr from *Ryan and Mukherjee* [1974] the sea-salt Cl^- conversion of Cl_g appears to dominate. Anthropogenic HCl release is about 3 × 10^6 tons/yr, only 1% or so of the global input but large locally or regionally. What is not at all clear is the process (or processes) that actually releases Cl_g from particulate material (preferentially from small particles). Thus although the principal source of tropospheric Cl_g is identified as sea-salt conversion, it is not understood.

Most of the particulate Cl^- is not converted to HCl; most of this Cl^- by mass is borne by large particles that reside in the (tropospheric) air less than 1 day. Sedimentation removes larger particles, while washout and rainout combine to remove smaller ones. On average, sea-salt particles might be removed two thirds by precipitation, one third by settling, 90% into oceans, and 10% to continents. These fractions actually served as the basis for *Blanchard*'s [1963] estimate of oceanic sea-salt particle production rate; i.e., he assumed that oceanic salt particle release rate equals the worldwide salt deposition rate. By contrast, *Eriksson* [1959] took precipitation and removal by dry deposition (settling) to be equally important. A further uncertainty involves the fact that both forms of removal of particles are probably size dependent, so that deposition also depends on wind speed. Thus much of our information on Cl^- in particles and Cl_g sources and sinks is interdependent. The recent study of *Kritz and Rancher* [1980] also took oceanic release and deposition rates to be equal. So even though the principal (in terms of mass) sink of atmospheric Cl_g and Cl^- in particles is identified as precipitation and sedimentation and the deposition rates are reasonably well known (see section B2*d*), the physical and chemical processes that control uptake of Cl_g by precipitation are not well understood. The excess of Br^-/Cl^- in rainfall as opposed to the Br^-/Cl^- deficit in particles indicates that gas-particle and gas-precipitation interactions vary from halogen to halogen.

Most of the discussion above derived from experiments that focused on inorganic Cl gases, Cl_g^i. As noted in sections B2*b* and C1*a*, there are many species of organic Cl (Cl_g^o) whose total concentration exceeds that of tropospheric Cl_g^i. Sources of Cl_g^o species are definitely smaller than those for Cl_g^i, but atmospheric residence times for several Cl_g^o species are measured in years rather than days. The largest Cl_g^o carrier by mass is CH_3Cl. Although its marine source is unknown (*Zafiriou* [1975] has suggested that chlorination of CH_3I in seawater is likely), the annual release of CH_3Cl is about 3×10^6 tons [*Cicerone et al.*, 1975; *Yung et al.*, 1975; *Graedel*, 1979]. As indicated in Tables 3 and 5, there is a 10% industrial component, and there are many chlorinated industrial solvents that degrade in the troposphere to produce Cl_g^i, Cl^- in precipitation, and other Cl_g^o species (see section C1*b*).

A very important fact, first recognized by *Molina and Rowland* [1974*a*], is that ground level Cl_g^o sources have stratospheric sinks. In the case of CF_2Cl_2 and $CFCl_3$, 50% to 100% is decomposed in the stratosphere by UV light in the midstratosphere, thus leading to stratospheric Cl_g^i species: Cl, ClO, and HCl. Atmospheric residence times of 50–100 years appear likely for $CFCl_3$ and CF_2Cl_2 [*Rowland and Molina*, 1975; *National Academy of Sciences/National Research Council*, 1976]. Although the stratospheric input of these molecules lags their ground level release by about 10 years, the present stratospheric Cl_g^i content is already mostly anthropogenic; see Figure 1. If CF_2Cl_2 and $CFCl_3$ emissions remain constant, they will carry 5×10^5 tons (Cl)/yr into the stratosphere. The total input of Cl_g into the stratosphere will then be $6\text{–}8 \times 10^5$ tons (Cl)/yr [*Cicerone*, 1975], including about 5 to 10% of the CH_3Cl released at ground level and smaller contributions due to CCl_4, tropospheric Cl_g^i, meteors, volcanoes, solid-fuel rockets, and particles containing Cl^-.

b. Transport processes: Chlorine. To complete the qualitative mapping out of global chlorine cycle pathways and to understand the cycle reservoirs, processes, and transfer rates quantitatively, certain features of atmospheric circulation must be considered carefully. Conversely, from atmospheric measurements of chlorine-containing species and knowledge of their atmospheric chemical behavior much can be learned about air motions.

Transport processes deliver gaseous Cl species and Cl^- in particles through the atmosphere from their sources to their sinks. In this way, air motions determine the length of time and the surrounding atmospheric conditions in which chemical reactions might occur. Specific cases of interest are the upward transport of man-made chlorofluorocarbons from ground level (mostly northern mid-latitudes) through the troposphere, upward largely at low latitudes to the photochemically active middle stratosphere, where they are decomposed by ultraviolet sunlight. In this way, Cl atoms are released in the stratosphere, and the atmospheric residence times of the chlorofluorocarbons are determined. Similarly, HCl, a product of this process, is transported downward into the troposphere for eventual removal in precipitation. Thus troposphere-stratosphere exchange processes are very important to the chlorine cycle's long-lived compounds and to the stratospheric ozone layer. With less long-lived compounds such as CH_3CCl_3, interhemispheric transport allows a great deal of the northern hemisphere's production to be consumed in the southern hemisphere. On regional scales, pollutants such as HCl and combustion products from incineration of plastics and waste chemicals are similarly dispersed. Hydrospheric transport also must be considered for chemicals such as chlorinated pesticides and insecticides.

Chlorinated and fluorinated compounds have been recognized as valuable tracers for air and water motions [*Lovelock*, 1971; *Hammer et al.*, 1978] largely because of the relative ease of measuring small concentrations and the lack of natural background levels. Global scale motions can be deduced from the measurements as can the averaged concentrations of certain reactants like tropospheric OH from CH_3CCl_3 data [*Singh*, 1977; *Lovelock*, 1977].

2. *Pathways of Bromine Compounds*

a. Sources and sinks: Bromine. A much smaller data base exists from which to estimate sources and sinks for atmospheric Br compounds and of Br^- in particles. The steady state assumption, that sea-salt particle release rates equal total deposition rates, used to estimate chlorine cycle sources (section D1*a*) is not of much utility for Br because deposition rates, for example, as in global annual precipitation, are poorly known. Indeed, there is no faintly comparable Br^- deposition data base. From the recent work of *Kritz and Rancher* [1980] one could estimate that the loss of Br_g from particle Br^- is about 0.004 times the corresponding figure for chlorine. If their measurements are extrapolated to a global average by simply assuming that the Kritz-Rancher measurements under 12-knot (6 m/s) winds near the equator can represent global averages, both for Br^- and Cl^- losses, one estimates an annual source of gaseous Br of 2.4×10^6 tons ($0.004 \times 6 \times 10^9$ tons). Clearly, the conditions that affect Cl^- loss (section D1*a*) vary over the globe, and Br^-/Cl^- fractionation does also, so this extrapolation is not solidly founded. However, there are few (if any) other means available to estimate the particle loss of Br^- source of gaseous Br, presumably Br_g^i. Under the conditions of the Kritz and Rancher study a residence time of 4.5 days was indicated for this sea-salt-evolved Br_g'. As with the Cl^- in sea-salt particles, Br^- in particles is short-lived in the atmosphere. The annual release of sea-salt Br^-, i.e., the dominant source of atmospheric particulate Br^-, may be estimated as the product of the corresponding Cl^- particulate source (section D1*a*) and the Br^-/Cl^- ratio of seawater (6×10^9 tons/yr times 0.035), given the fact that fresh marine aerosols show no Br^-/Cl^- fractionation with respect to seawater [*Duce and Woodcock,* 1971]. There is, of course, a noticeable anthropogenic component of Br^- in the smallest aerosols, especially over and near continents; see section B3*c*.

Sources and sinks of organic gaseous bromine, Br_g^o, have received no quantitative attention to date with the partial exception of CH_3Br as an agricultural fumigant. Natural sources of CH_3Br, other Br_g^o species, and the extent to which any of these can contribute to the stratospheric Br budget—all of these are open questions. Biospheric sources of Br_g^o species of atmospheric interest are also possible [*Siuda and DeBernardis,* 1973; *Faulkner,* 1977].

b. Transport processes: Bromine. Statements similar to those made in section D1*b* concerning chlorine apply for bromine except that a much less definitive picture exists for Br. For example, while the dominant source of particulate Br^- is sea salt as for Cl^-, it is not clear how much of the particulate Br^- is converted to Br_g, and the interactions between precipitation and cloud droplets appear different for Br_g and Cl_g. Thus the exact pathways through the marine boundary layer and free troposphere might differ for Br^- and Cl^- and for Br_g and Cl_g. Also, it is not yet clear whether a subcycle exists for atmospheric Br_g that involves troposphere-stratosphere exchange and atmospheric residence times of many years as is the case for Cl_g and for fluorine. Other than the observation that bromohydrocarbons often hydrolyze more readily than their chlorohydrocarbon counterparts, very little can be said about pathways of bromine compounds that wind through both the atmosphere and hydrosphere. Similarly, no use has been made of brominated tracers of air or water motions with the exception of the Br^- component in small continental aerosols as an indicator of automobile exhaust and a feasibility test with CBr_2F_2 [*Elias et al.,* 1976].

3. *Pathways of Iodine Compounds*

a. Sources and sinks: Iodine. The global cycle of iodine, mostly in and out of the seas and marine atmosphere, is ripe for exploration in that it is not yet quantitatively defined, but several clear hypotheses exist. I_2 release from the surface waters of oceans has been suggested by *Miyake and Tsunogai* [1963], *Martens and Harriss* [1970], and *Seto and Duce* [1972]. Biological methylation of seawater I^- as a source of CH_3I was proposed by *Lovelock et al.* [1973] to explain their observed concentrations of CH_3I in the marine atmosphere. By assuming rapid photolysis (and thus a short atmospheric residence time), *Lovelock et al.* [1973] estimated an annual source of 40 $\times 10^6$ tons of CH_3I. Zafiriou's calculation of the photolysis rate of CH_3I also showed a larger but still short residence time that is possibly latitude dependent owing to the overhead O_3 column. He estimated an annual sink (equal to the source) of CH_3I of only 1 or 2×10^6 tons, much closer to the 0.5×10^6 tons/yr of I deposited globally in rainfall found by *Miyake and Tsunogai* [1963]. Each of these components of the I cycle needs further exploration. The total deposition rate, wet and dry, on oceans and continents needs to be surveyed. It is likely that organic I species are important in this cycle because of the iodine richness of the organic material in the surface microlayer and the large I enrichment with respect to Cl, Br, and Na in the marine aerosol. The additional enrichment of I in aged aerosols might represent a sink for atmospheric gaseous I compounds, I_g.

Human impact on the global I cycle is probably not large when measured by mass, especially since the European iodine industry was scaled down in the 1930's, but anthropogenic ^{129}I and ^{131}I should be watched (section C3*a*).

b. Transport processes: Iodine. So little is known about the speciation of I_g and their atmospheric residence times that the importance of various scale transport processes is uncertain. Certainly, most of the annual mass cycling takes place within the marine boundary layer. The possibility of relatively long-lived I_g compounds should be investigated. If they exist, then interhemispheric and troposphere-stratosphere transport would need to be explored. Gaseous and particulate iodine levels measured in Antarctic air [*Duce et al.,* 1973], while less than in the tropics, were less diminished in relation to their low-latitude levels than were bromine and chlorine, indicating long-range transport for iodine. In any case and in any chemical form, the atmospheric hydrospheric and biospheric pathways of ^{129}I need investigation.

4. *Pathways of Fluorine Compounds*

a. Sources and sinks: Fluorine. Virtually no quantitative statements may be made about natural fluorine in the atmosphere because so few data exist. Qualitatively, there appear to be natural sources of particulate F^-, both from sea-salt aerosols and from airborne dust of continental origin. Data of Kobajashi and of Sugawara, summarized by *Wilkniss and Bressan* [1971], show F^-/Cl^- enrichments of 10 to 1000 in marine aerosols, although Wilkniss and Bressan found smaller enrichments (see also section B5*c*). Similar data and geochemical pathways of fluorine have been discussed by *Carpenter* [1969], *Barnard and Nordstrom* [1980], and *Bewers and Hayson* [1974].

It is possible that natural sources of gases containing fluorine are not significant in comparison to man's release of inorganic (F_g') and organic (F_g^o) forms. Although the industrial releases of HF and F_2 are difficult to quantify, those of SF_6 and of fluorocarbons are well known and generally can be verified to within 20%. No extant data indicate natural sources of F_g' except for volcanoes [*Cadle et al.,* 1979]. Also, there are only slight indications of F^- losses from marine or continental airborne particles [*Wilkniss and Bressan,* 1971]. Recently, *Barnard and Nordstrom* [1980] presented data and analysis to support the view that industrial F_g' and fluorides might dominate the fluorine budgets of industrialized continents. Key industries are steel, aluminum, brick, and ceramics and certain fertilizer manufacturers. For F_g^o it is possible that the biosphere emits some, from, for example, volcanoes [*Stoiber et al.,* 1971], from burning vegetation, or even from plants (a few African plants contain organofluorine compounds; see *Hall* [1972]).

b. Transport processes: Fluorine. Two features of the atmospheric transport of fluorine and its compounds distinguish F from the other halogens. One is that a significant fraction of the airborne F might originate from continents (as dust) as opposed to the oceans, and second, the extreme strength of carbon-fluorine bonds leads to longer atmospheric residence times for F_g^o species and thus to longer transport distances. Indeed, it appears that the compound CF_4 produced at ground level (presumably industrially) has its main sinks in the mesosphere and above [*Cicerone,* 1979]. Other perfluorocarbons can behave similarly. As tracers of air and water motions, these species are very attractive because of the near-zero natural background, and they have been employed profitably [*Lovelock,* 1971; *Krey et al.,* 1976] to trace both tropospheric and stratospheric motions.

5. *Interactions Between Halogens and Other Chemical Cycles*

The atmospheric chemistry of the halogens is coupled with the cycles of several other elements in essential ways, many of which processes have been identified only recently and which remain to be understood. Perhaps the broadest of these topics involves marine aerosol halides and halogen-containing gases and the associated gas-to-particle and particle-to-gas conversions. The apparent loss of Cl^- and release of HCl from the marine aerosol is believed to depend on ambient gaseous concentrations of NO_2, SO_2, NH_3, and HNO_3 as well as aerosol composition, including organic material. The apparent uptake of I^- (or IO_3^-) and of F^- by atmospheric particles and of excess Br^- by precipitation must each depend on the particular species involved, for example, I_2 or HI, HBr or HOBr, etc., but also on the uptake of other elements by the particles and precipitation. In polluted air, similar questions surround the behavior of HCl in rainfall. Liberation of iodine from seawater might depend on atmospheric O_3 levels.

Several purely gas-phase interactions that involve halogen species and reactants of other elements have been shown recently to be important. In the troposphere the reactive to moderately reactive organohalogens, for example, CH_3Cl, CH_3CCl_3, CH_3Br, and $CHCl_3$, react almost exclusively with OH radicals. In turn, tropospheric OH levels are strongly influenced by CO concentrations. To the extent that tropospheric or hemispheric CO levels change, the net flux of these organohalogens out of the troposphere or into the conjugate hemisphere will change. Also in the troposphere, any halogen atoms produced by photolysis of Cl_2, I_2, Br_2, or F_2 or by gas-phase reactions are very short-lived largely owing to reactions with O_3, CH_4, and nonmethane hydrocarbons (NMHC).

In the stratosphere the lengths of chlorine and bromine reaction chains are controlled by reactions with nitrogen oxides, hydrogen oxides, CH_4, NMHC, O_3, and oxygen atoms. In turn, the presence of Cl and Br strongly impacts stratospheric O_3 and photochemical equilibria of the NO_x species. In the high stratosphere, Cl atom reaction with CH_4 constitutes an appreciable CH_4 sink, and in the low stratosphere, Cl atom reactions with NMHC appear to be an appreciable sink for NMHC [*Chameides and Cicerone,* 1978].

The possibility exists that the impact of Br-containing species on stratospheric photochemistry is partly controlled by a synergistic interaction with Cl_x' species [*Yung et al.,* 1980].

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REFERENCES

Ackerman, M., D. Frimout, A. Girard, M. Gottignies, and C. Muller, Stratospheric HCl from infrared spectra, *Geophys. Res. Lett., 3,* 81–83, 1976.

Altschuler, A. P., Average tropospheric concentration of carbon tetrachloride based on industrial production, usage and emissions, *Environ. Sci. Technol., 10,* 596–598, 1976.

Anderson, J. G., J. J. Margitan, and D. H. Stedman, Atomic chlorine and the chlorine monoxide radical in the stratosphere, *Science, 198,* 501–503, 1977.

Anderson, J. G., H. J. Grassl, R. E. Shetter, and J. J. Margitan, Stratospheric free chlorine measured by balloon-borne in situ resonance fluorescence, *J. Geophys. Res., 85,* 2869–2887, 1980.

Barnard, W. R., and D. K. Nordstrom, Fluoride in precipitation, I, Implications for the geochemical cycling of fluorine, submitted to *Atmos. Environ.,* 1980.

Berg, W. W., and J. W. Winchester, Organic and inorganic gaseous chlorine concentrations in relation to the particle size distribution of chloride in the marine aerosol, *J. Geophys. Res., 82,* 5945–5953, 1977.

Berg, W. W., Jr., and J. W. Winchester, Aerosol chemistry of the marine atmosphere, in *Chemical Oceanography,* vol. 7, 2nd ed., edited by J. P. Riley and R. Chester, Academic, New York, 1978.

Berg, W. W., P. J. Crutzen, F. E. Grahek, and S. N. Gitlin, First measurements of total chlorine and bromine in the lower stratosphere, submitted to *Geophys. Res. Lett.,* 1980.

Bewers, J. M., and H. H. Hayson, The terrigenous dust contribution to fluoride and iodide in atmospheric precipitation, *J. Rech. Atmos., 13,* 689–697, 1974.

Blanchard, D., Electrification of the atmosphere, in *Progress in Oceanography,* vol. 1, edited by M. Sears, pp. 71–202, Pergamon, New York, 1963.

Cadle, R. D., A. L. Lazrus, B. J. Huebert, L. E. Heidt, W. I. Rose, Jr., D. C. Woods, R. L. Chuan, R. E. Stoiber, D. B. Smith, and R. A. Zielinski, Atmospheric implications of studies of Central American volcanic eruption clouds, *J. Geophys. Res., 84,* 6961–6968, 1979.

Carpenter, R., Factors controlling the marine geochemistry of fluorine, *Geochim. Cosmochim. Acta, 33,* 1153–1167, 1969.

Chameides, W. L., and R. J. Cicerone, Effects of nonmethane hydrocarbons in the atmosphere, *J. Geophys. Res., 83,* 947–952, 1978.

Chameides, W. L., and D. D. Davis, Iodine: Its possible role in tropospheric photochemistry, *J. Geophys. Res., 85,* 7383–7398, 1980.

Chesselet, R., J. Morelli, and P. Buat-Menard, Some aspects of the geochemistry of marine aerosols, in *The Changing Chemistry of the Oceans,* edited by D. Dryssen and D. Jagner, pp. 94–120, John Wiley, New York, 1972.

Cicerone, R. J., Comment on 'Volcanic emissions of halides and sulfur compounds to the troposphere and stratosphere' by R. D. Cadle, *J. Geophys. Res., 80,* 3911–3912, 1975.

Cicerone, R. J., Atmospheric carbon tetrafluoride: A nearly inert gas, *Science, 206,* 59–61, 1979.

Cicerone, R. J., and S. C. Liu, Calculations presented at International Conference on Problems Related to the Stratosphere, *Publ. 77-12,* pp. 124–125, Jet Propul. Lab., Pasadena, Calif., 1976.

Cicerone, R. J., D. H. Stedman, and R. S. Stolarski, Estimate of late 1974 stratospheric concentration of gaseous chlorine compounds (ClX), *Geophys. Res. Lett., 2,* 219–222, 1975.

Crutzen, P. J., A review of upper atmospheric photochemistry, *Can. J. Chem., 52,* 1569–1581, 1974.

Crutzen, P. J., I. S. A. Isaksen, and J. R. McAfee, The impact of the chlorocarbon industry on the ozone layer, *J. Geophys. Res., 63,* 345–363, 1978.

Dean, G. A., The iodine content of some New Zealand drinking waters with a note on the contribution from sea spray to the iodine in rain, *N. Z. J. Sci., 6,* 208–214, 1963.

DeMore, W. B., L. J. Stief, F. Kaufman, D. M. Golden, R. F. Hampson, M. J. Kurylo, J. J. Margitan, M. J. Molina, and R. T. Watson, Chemical kinetic and photochemical data for use in stratospheric modelling, *Publ. 79-27,* 124 pp., Jet Propul. Lab., Pasadena, Calif., 1979.

Duce, R. A., On the source of gaseous chlorine in the marine atmosphere, *J. Geophys. Res., 74,* 4597–4599, 1969.

Duce, R. A., and A. H. Woodcock, Difference in chemical composition of atmospheric sea salt particles produced in the surf zone and on the open sea in Hawaii, *Tellus, 23,* 427–435, 1971.

Duce, R. A., J. W. Winchester, and T. Van Nahl, Iodine, bromine and chlorine in the Hawaiian marine atmosphere, *J. Geophys. Res., 70,* 1775–1799, 1965.

Duce, R. A., W. H. Zoller, and J. L. Moyers, Particulate and gaseous halogens in the Antarctic atmosphere, *J. Geophys. Res., 78,* 7802–7811, 1973.

Elias, L., M. McCooeye, and G. Gardner, On-site measurement of atmospheric tracer gases, *Geophys. Res. Lett., 3,* 17–20, 1976.

Eriksson, E., The yearly circulation of chloride and sulfur in nature: Meteorological, geochemical and pedological implications, 1, *Tellus, 11,* 375–403, 1959.

Eriksson, E., The yearly circulation of chloride and sulfur in nature: Meteorological, geochemical and pedological implications, 2, *Tellus, 12,* 63–109, 1960.

Eyre, J. R., and H. K. Roscoe, Radiometric measurement of stratospheric HCl, *Nature, 266,* 243–244, 1977.

Fabian, P., R. Borchers, K. Weiler, U. Schmidt, A. Volz, D. Ehhalt, W. Seiler, and F. Müller, Simultaneously measured vertical profiles of H_2, CH_4, CO, N_2O, $CFCl_3$ and CF_2Cl_2 in the mid-latitude stratosphere and troposphere, *J. Geophys. Res., 84,* 3149–3154, 1979.

Farmer, C. B., and O. Raper, The HF:HCl ratio in the 14–38 km region of the stratosphere, *Geophys. Res. Lett., 4,* 527–530, 1977.

Farmer, C. B., O. F. Raper, and R. H. Norton, Spectroscopic detection and vertical distribution of HCl in the troposphere and stratosphere, *Geophys. Res. Lett., 3,* 13–16, 1976.

Farmer, C. B., O. F. Raper, B. D. Robbins, R. A. Toth, and C. Muller, Simultaneous spectroscopic measurements of stratospheric species: O_3, CH_4, CO, CO_2, N_2O, H_2O, HCl and HF at northern and southern mid-latitudes, *J. Geophys. Res., 85,* 1621–1632, 1980.

Faulkner, D. J., Interesting aspects of marine natural products chemistry, *Tetrahedron, 33,* 1421–1443, 1977.

Galbally, I. E., Man-made carbon tetrachloride in the atmosphere, *Science, 193,* 573–576, 1976.

Garland, J. A., and H. Curtis, Emission of iodine from the sea surface in the presence of ozone, *J. Geophys. Res., 86,* in press, 1981.

Gassman, M., Freon 14 in 'Krypton reinst' und in der Atmosphäre, *Naturwissenschaften, 61,* 127–128, 1974.

Goldan, P. D., W. C. Kuster, D. L. Albritton, and A. L. Schmeltekopf, Stratospheric $CFCl_3$, CF_2Cl_2 and N_2O height profile measurements at several latitudes, *J. Geophys. Res., 85,* 413–423, 1980.

Goldman, A., D. Murcray, F. Murcray, G. Cook, J. Van Allen, F. Bonomo, and R. Blatherwick, Identification of the ν_3 vibration-rotation band of CF_4 in balloon-borne infrared solar spectra, *Geophys. Res. Lett., 6,* 609–612, 1979.

Graedel, T. E., *Chemical Compounds in the Atmosphere,* 440 pp., Academic, New York, 1978.

Graedel, T. E., The kinetic photochemistry of the marine atmosphere, *J. Geophys. Res., 84,* 273–286, 1979.

Hall, R. J., The distribution of organic fluorine in some toxic tropical plants, *New Phytol., 71,* 855–871, 1972.

Hammer, P., J. Hayes, W. Jenkins, and R. Gagosian, Exploratory analyses of trichlorofluoromethane (F-11) in North Atlantic water, *Geophys. Res. Lett., 5,* 645–648, 1978.

Heidt, L. E., R. Lueb, W. Pollock, and D. M. Ehhalt, Stratospheric profiles of CCl_3F and CCl_2F_2, *Geophys. Res. Lett., 2,* 445–447, 1975.

Junge, C. E., Recent investigations in air chemistry, *Tellus, 8,* 127–139, 1956.

Junge, C. E., Chemical analysis of aerosol particles and of gas traces on the Island of Hawaii, *Tellus, 9,* 528–537, 1957.

Junge, C. E., *Air Chemistry and Radioactivity,* 382 pp., Academic, New York, 1963.

Kauranen, P., Fluoride deposition in snow in the surroundings of a mixed fertilizer factory, *Chemosphere, 6,* 537–547, 1978.

Khalil, M. A. K., and R. A. Rasmussen, Methyl chloroform (CH_3CCl_3): Accumulation in the Earth's atmosphere, submitted to *Science,* 1980.

Krey, P. W., R. J. Lagomarsino, and J. J. Frey, Stratospheric concentrations of CCl_3F in 1974, *J. Geophys. Res., 81,* 1557–1560, 1976.

Kritz, M. A., and J. Rancher, Circulation of Na, Cl and Br in the tropical marine atmosphere, *J. Geophys. Res., 85,* 1633–1639, 1980.

Lazrus, A. L., B. W. Gandrud, and R. N. Woodard, Stratospheric halogen measurements, *Geophys. Res. Lett., 2,* 439–441, 1975.

Likens, G. E., Acid precipitation, *Chem. Eng. News,* Nov. 22, 29–44, 1976.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Atmospheric chemistry: Response to human influence, *Phil. Trans. Roy. Soc. London, Ser. A, 290,* 187–234, 1978.

Lovelock, J. E., Atmospheric fluorine compounds as indicators of air movements, *Nature, 230,* 379, 1971.

Lovelock, J. E., Natural halocarbons in the air and in the sea, *Nature, 256,* 193–194, 1975.

Lovelock, J. E., Methyl chloroform in the troposphere as an indicator of OH radical abundance, *Nature, 267,* 32, 1977.

Lovelock, J. E., R. J. Maggs, and R. J. Wade, Halogenated hydrocarbons in and over the Atlantic, *Nature, 241,* 194–196, 1973.

Martens, C. S., Ion ratio variations with particle size in Puerto Rican aerosols, *J. Geophys. Res., 78,* 8867–8872, 1972.

Martens, C. S., and R. C. Harriss, Mechanisms of iodine injection from the sea surface, Precipitation Scavenging, *AEC Symp. Ser., 22,* 319–324, 1970.

Martens, C. S., J. J. Wesolowski, R. C. Harriss, and R. Kaifer, Chlorine loss from Puerto Rican and San Francisco Bay area marine aerosols, *J. Geophys. Res., 78,* 8778–8792, 1973.

McCarthy, R. L., and J. P. Jesson, Fluorocarbons as a source of stratospheric chlorine, paper presented at 169th Annual Meeting of the American Chemical Society, Philadelphia, Pa., April 9, 1975.

McConnell, J. C., and H. I. Schiff, Methyl chloroform: Impact on stratospheric ozone, *Science, 199,* 174–177, 1978.

Menzies, R. T., Remote measurement of ClO in the stratosphere, *Geophys. Res. Lett., 6,* 151–154, 1979.

Miyake, Y., and S. Tsunogai, Evaporation of iodine from the ocean, *J. Geophys. Res., 68,* 3989–3993, 1963.

Miyake, Y., and S. Tsunogai, Chemical composition of oceanic rain, *Proc. Int. Conf. Cloud Phys.,* 73–78, 1965.

Molina, M. J., and F. S. Rowland, Stratospheric sink for chlorofluoromethanes: Chlorine-atom catalysed destruction of ozone, *Nature, 249,* 810–812, 1974*a*.

Molina, M. J., and F. S. Rowland, Predicted stratospheric abundances of chlorine species from photodissociation of carbon tetrachloride, *Geophys. Res. Lett., 1,* 309–312, 1974*b*.

Moyers, J. L., and R. A. Duce, Gaseous and particulate bromine in the marine atmosphere, *J. Geophys. Res., 77,* 5330–5338, 1972*a*.

Moyers, J. L., and R. A. Duce, Gaseous and particulate iodine in the marine atmosphere, *J. Geophys. Res., 77,* 5229–5238, 1972*b*.

Mroz, E. J., A. L. Lazrus, and J. E. Bonelli, Direct measurements of stratospheric fluoride, *Geophys. Res. Lett., 4,* 149–150, 1977.

Murcray, D. G., A. Goldman, F. H. Murcray, F. J. Murcray, and W. J. Williams, Stratospheric distribution of $ClONO_2$, *Geophys. Res. Lett., 6,* 857–859, 1979.

National Academy of Sciences/National Research Council, *Halocarbons: Effects on Stratospheric Ozone,* 352 pp., Washington, D. C., 1976.

National Academy of Sciences/National Research Council, *Stratospheric Ozone Depletion by Halocarbons: Chemistry and Transport,* 238 pp., Washington, D. C., 1979.

Okita, T., K. Kaneda, T. Yanaka, and R. Sugai, Determination of gaseous and particulate chloride and fluoride in the atmosphere, *Atmos. Environ., 8,* 927–936, 1974.

Rahn, K., R. D. Borys, and R. A. Duce, Tropospheric halogen gases: Inorganic and organic components, *Science, 192,* 549–550, 1976.

Ramanathan, V., Greenhouse effect due to chlorofluorocarbons: Climatic implications, *Science, 190,* 50–52, 1975.

Rancher, J., and M. A. Kritz, Diurnal fluctuations of Br and I in the tropical marine atmosphere, *J. Geophys. Res., 85,* 5581–5587, 1980.

Rasmussen, R. A., S. A. Penkett, and N. Prosser, Measurement of carbon tetrafluoride in the atmosphere, *Nature, 277,* 549–551, 1979.

Rasmussen, R. A., L. E. Rasmussen, M. A. K. Khalil, and R. W. Dalluge, Concentration distribution of methyl chloride in the atmosphere, *J. Geophys. Res., 85,* 7350–7356, 1980*a*.

Rasmussen, R. A., M. A. K. Khalil, S. A. Penkett, and N. J. D. Prosser, $CHClF_2$(F-22) in the Earth's atmosphere, *Geophys. Res. Lett., 7,* 809–812, 1980*b*.

Robbins, R. C., R. D. Cadle, and D. L. Eckhardt, The conversion of sodium chloride to hydrogen chloride in the atmosphere, *J. Meteorol., 16,* 53–56, 1959.

Rowland, F. S., and M. J. Molina, Chlorofluoromethanes in the environment, *Rev. Geophys. Space Phys., 13,* 1–35, 1975.

Ryan, J. A., and N. R. Mukherjee, Estimate of tropospheric HCl cycle, report, 74 pp., McDonnell-Douglas Co., Huntington Bend, Calif., 1974.

Schmeltekopf, A. L., P. D. Goldan, W. R. Henderson, W. J. Harrop, T. L. Thompson, F. C. Fehsenfeld, H. I. Schiff, P. J. Crutzen, I. S. A. Isaksen, and E. E. Ferguson, Measurements of stratospheric $CFCl_3$, CF_2Cl_2 and N_2O, *Geophys. Res. Lett., 2,* 393–396, 1975.

Seto, F. Y. B., and R. A. Duce, A laboratory study of iodine enrichment on atmospheric sea-salt particles produced by bubbles, *J. Geophys. Res., 77,* 5339-5349, 1972.

Singh, H. B., Preliminary estimation of average tropospheric HO concentrations in the Northern and Southern Hemispheres, *Geophys. Res. Lett., 4,* 453–456, 1977.

Singh, H. B., D. P. Fowler, and T. O. Peyton, Atmospheric carbon tetrachloride: Another man-made pollutant, *Science, 192,* 1231-1234, 1976.

Singh, H. B., L. J. Salas, H. Shigeishi, and E. Scribner, Global distribution of selected halocarbons, hydrocarbons, SF_6 and N_2O, report, Atmos. Sci. Lab., Stanford Res. Inst., Stanford, Calif., 1978.

Singh, H. B., L. J. Salas, H. Shigeishi, and E. Scribner, Atmospheric halocarbons, hydrocarbons and sulfur hexafluoride: Global distributions, sources and sinks, *Science, 203,* 899-903, 1979.

Siuda, J. F., and J. F. DeBernardis, Naturally occurring halogenated organic compounds, *Lloydia, 36,* 107-140, 1973.

Stedman, D. H., W. L. Chameides, and R. J. Cicerone, The vertical distribution of soluble gases in the troposphere, *Geophys. Res. Lett., 2,* 333-336, 1975.

Stoiber, R., D. Leggett, T. Jenkins, R. Murrman, and W. Rose, Organic compounds in volcanic gases from Santiaguito Volcano, Guatemala, *Geol. Soc. Amer. Bull., 82,* 2299-2302, 1971.

Stolarski, R. S., and R. D. Rundel, Fluorine photochemistry in the stratosphere, *Geophys. Res. Lett., 2,* 443–444, 1975.

Su, C. W., and E. D. Goldberg, Chlorofluorocarbons in the atmosphere, *Nature, 245,* 27–28, 1973.

Sze, N. D., Stratospheric fluorine: A comparison between theory and measurements, *Geophys. Res. Lett., 5,* 781–783, 1978.

Tyson, B. J., J. F. Vedder, J. C. Arvesen, and R. B. Brewer, Stratospheric measurements of CF_2Cl_2 and N_2O, *Geophys. Res. Lett., 5,* 369-372, 1978.

Wang, W. C., J. P. Pinto, and Y. L. Yung, Climatic effects due to halogenated compounds in the earth's atmosphere, *J. Atmos. Sci., 37,* 333-338, 1980.

Watson, R. T., Chlorine, chlorine oxides and other halogen species, Monograph 1, Climatic Impact Assessment Program Final Report, *Rep. DOT-TST-75-51,* pp. 5-125 to 5-152, U.S. Dep. of Transp., Washington, D. C., 1975.

Watson, R. T., P. E. Smokler, and W. B. DeMore, An assessment of an F_2 or N_2O_4 atmospheric injection from an aborted Space Shuttle mission, *Publ. 77-81,* 41 pp., Jet Propul. Lab., Pasadena, Calif., 1978.

Whitten, R. C., W. J. Borucki, I. G. Poppoff, and R. P. Turco, Preliminary assessment of the potential impact of solid-fueled rocket engines in the stratosphere, *J. Atmos. Sci., 32,* 613–619, 1975.

Wilkniss, P. E., and D. J. Bressan, Chemical processes at the air-sea interface: The behavior of fluorine, *J. Geophys. Res., 76,* 736–741, 1971.

Wilkniss, P. E., and D. J. Bressan, Fractionation of the elements of F, Cl, Na and K at the sea-air interface, *J. Geophys. Res., 77,* 5307-5315, 1972.

Williams, W. J., J. J. Kosters, A. Goldman, and D. G. Murcray, Measurement of the stratospheric mixing ratio of HCl using infrared absorption technique, *Geophys. Res. Lett., 3,* 383-385, 1976.

Winchester, J. W., W. H. Zoller, R. A. Duce, and C. S. Benson, Lead and halogens in pollution aerosols and snow from Fairbanks, Alaska, *Atmos. Environ., 1,* 105-119, 1967.

Wofsy, S. C., Temporal and latitudinal variations of stratospheric trace gases: A critical comparison between theory and experiment, *J. Geophys. Res., 83,* 364–378, 1978.

Wofsy, S. C., and M. B. McElroy, HO_x, NO_x and ClO_x: Their role in atmospheric photochemistry, *Can J. Chem., 52,* 1582-1591, 1974.

Wofsy, S. C., M. B. McElroy, and Y. L. Yung, The chemistry of atmospheric bromine, *Geophys. Res. Lett., 2,* 215–218, 1975.

Young, J. A., C. W. Thomas, N. A. Wogman, and R. W. Perkins, Cosmogenic radionuclide production rates in the atmosphere, *J. Geophys. Res., 75,* 2385–2390, 1970.

Yung, Y. L., S. Wofsy, and M. McElroy, Atmospheric halocarbons: A discussion with emphasis on chloroform, *Geophys. Res. Lett., 2,* 397-399, 1975.

Yung, Y. L., J. P. Pinto, R. T. Watson, and S. P. Sander, Atmospheric bromine and ozone and perturbations in the lower stratosphere, *J. Atmos. Sci., 37,* 339-353, 1980.

Zafiriou, O. C., Photochemistry of halogens in the marine atmosphere, *J. Geophys. Res., 79,* 2730–2732, 1974.

Zafiriou, O. C., Reaction of methyl halides with seawater and marine aerosols, *J. Mar. Res., 33,* 75-81, 1975.

Zander, R., G. Roland, and L. Delbouille, Confirming the presence of hydrofluoric acid in the upper stratosphere, *Geophys. Res. Lett., 4,* 117-120, 1977.

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