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NATURAL CHLORINE AND FLUORINE IN THE ATMOSPHERE, WATER AND PRECIPITATION

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1. GEOCHEMICAL CONSIDERATIONS

The Origins of Chlorine and Fluorine

A summary of the principal features of the geochemical cycles of chlorine and fluorine is given here and is based on National Research Council (1971) for fluorine and on Siever (1974), MacIntyre (1970) and Sillen (1967) for chlorine. Chlorine and fluorine are volatile elements that are considered to have been extensively outgassed from the interior of the earth and now are concentrated in the crust. The principal reservoir for the storage of chlorine is the oceans where it is dissolved as Cl^- ions while that for fluorine is in the lithospheric rocks mainly as the minerals fluorapatite, fluorspar, and cryolite. Soils may contain fluoride in these and several other mineral forms. The upper layers of soil tend to have somewhat lower concentrations of fluorine than the underlying layers.

Volcanoes are the vents through which recycled sediments containing fluorine and chlorine reach the earth's surface and the atmosphere. Volcanoes are important natural sources of gaseous atmospheric fluorine, primarily as HF as indicated by Symonds et al. (1988), but other gases as well as solid compounds have been variously reported in fumeroles. Because of the uncertainties in estimating volcanic emissions, it is impossible to know whether or not volcanic sources are responsible for most of the natural atmospheric contents of fluorine. Though chlorine concentrations in volcanic emissions are higher than those of fluorine, volcanoes are relatively lesser sources of atmospheric chlorine. They are, however, of some importance since the injection of HCl into the stratosphere by large explosive volcanic eruptions can have consequences for ozone chemistry.

The most important source of atmospheric chlorine is the ocean surface which, through the actions of wind, waves and bubbles, injects sea salt particles. Much of this particulate matter is redeposited in the ocean by sedimentation, diffusion and impaction. However, important amounts of chloride ions in this maritime aerosol find their way into precipitation over both continents and oceans. Furthermore, a highly uncertain amount (ranging from 2 to 20%) of the chlorine in sea salt aerosol is released as gas. Although the identity of the species released has not been definitely established, recent investigators have been inclined to the view that it is HCl. Also, as discussed below, they indicate that the interaction with acidic sulfate residing in submicrometer particles is responsible for the release. Sea salt also contains fluorine as F^-, and like Cl^-, a portion is transported over land and deposited in precipitation and in dry fallout. As in the case of chlorine, the release of gaseous fluorine, as HF or other species, from fresh sea salt aerosol could be an important process as in the case of chlorine. However there exists very little direct observational data to reveal the extent and nature of such a process.

The problem of assessing the rates and amounts of gaseous release of Cl and F from marine aerosol particles is complicated by the fact that the soluble gases (presumably HCl and HF) are readily reincorporated with unreleased sea salt components by absorption into cloud droplets and precipitation. This phenomenon makes it difficult, if not impossible, to use the results of chemical analyses of precipitation to determine the amounts of gaseous and aerosol Cl and/or F that might have been present in the atmosphere. Another complicating factor is that the admixture of soil dust with marine aerosols presents a challenge to the scientist/analyst to determine the amounts of soil mineral components which may be present in aerosol samples in order to correct for additions of the relevant elements (such as Na and F) to the marine components. The challenge here (aside from representative sampling) is to provide such precise analyses of the necesessary components that the propagated errors still permit a reasonable determination of the sea salt contributions. Size segregation of aerosol samples has proved to be very useful in this regard.

When the possibilities for anthropogenic contributions to airborne mineral fluoride and gaseous chlorine and fluorine compounds (organic as well as inorganic) are taken into account, the difficulties in deciphering the natural cycles of F and Cl are further enhanced. Analyses of aerosols and precipitation that have been affected by pollution sources have to meet at least the same challenge as those described above for separating the soil and marine components. The situation is most complex in coastal areas where all three classes of materials may blend together in varying proportions. The realization of the many difficulties and the amounts of time and effort necessary have probably discouraged scientists and their sponsors from attempting to define more accurately the global cycles of chlorine and fluorine.

From a global geochemical perspective, precipitation and river waters, especially in the tropics where rainfall dominates the river flow, derive much of their composition from sea salt. This gives rise to the notion of "cyclic salts" which are placed in the atmosphere as sea salt aerosol, blown over the land, deposited by wet and dry processes, run off to rivers, and returned to the oceans. A remarkable comparison discussed by Raiswell et al (1979) based on the work of Gibbs (1970) (see Figure 1) illustrates the similarity of relative proportions of Na, K, Mg, Ca, Cl, HCO_3 and Si in average precipitation and water from Rio Tefe (a tributary of the Amazon River) with average sea water. The river water contained relatively larger proportions of K and Si because of dissolved minerals from weathering of igneous rocks. The bicarbonate ion, HCO_3^-, is also quite different relative to the others in the various waters due to different geochemically important interactions with terrestrial sedimentary rocks, atmospheric CO_2, and marine sediments.

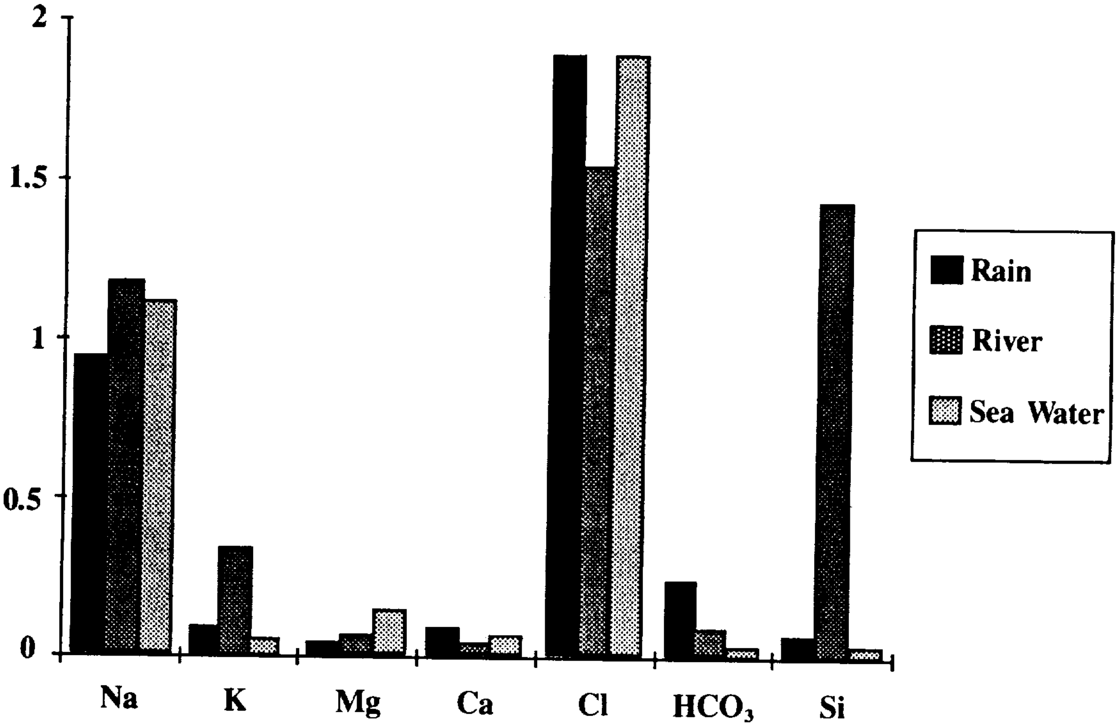


Figure 1. The Composition of Rio Tefé Water (mg/1), Rainwater in the Rio Tefé Basin (mg/1) and Sea Water ((g/1)/(10)) (from Gibbs, 1970).

The Chlorine Cycle

> *"All of the chlorine that has appeared at the surface of the earth through geologic time, ultimately derived from outgassed hydrogen chloride, has either accumulated in the oceans or has been deposited in sedimentary rocks as salt beds or briny pore waters."*
>
> *Siever, R. (1974).*

Figure 2 shows the chlorine cycle corresponding to Siever's statement. The transformation of HCl to Cl^- occurs when HCl is absorbed in cloud droplets, raindrops, and moist surfaces. These and other processes important in the atmospheric behavior of natural chlorine are schematically depicted in Figure 3.

a. The sea salt source

The largest source of atmospheric chlorine is the injection of sea-salt aerosol through the air-sea interface where wind and waves interact to produce droplets, foam and bubbles. The mass of the aerosol has essentially the same composition as the dissolved sea salt and resides in large and giant particles having radii $> 0.5\ \mu m$. These large particles originate from the mechanical injection of droplets by the various air-sea interactions. The small particle fraction, which comprises about 10% of the mass of the sea-salt aerosol, derives from the breakup of surface film by bursting bubbles. Estimation of the annual fluxes of sea-salt into and out of the atmosphere is a challenging task which has been undertaken by very few investigators. The most recent assessment is by Erickson and Duce (1988). This thorough and systematic study provides a global sea-salt flux through a plane of 15 m elevation of $(1 - 3) \times 10^{16}$ g yr^{-1}. Further it finds that about 85% of the injected sea salt that crosses returns by dry deposition while the remainder

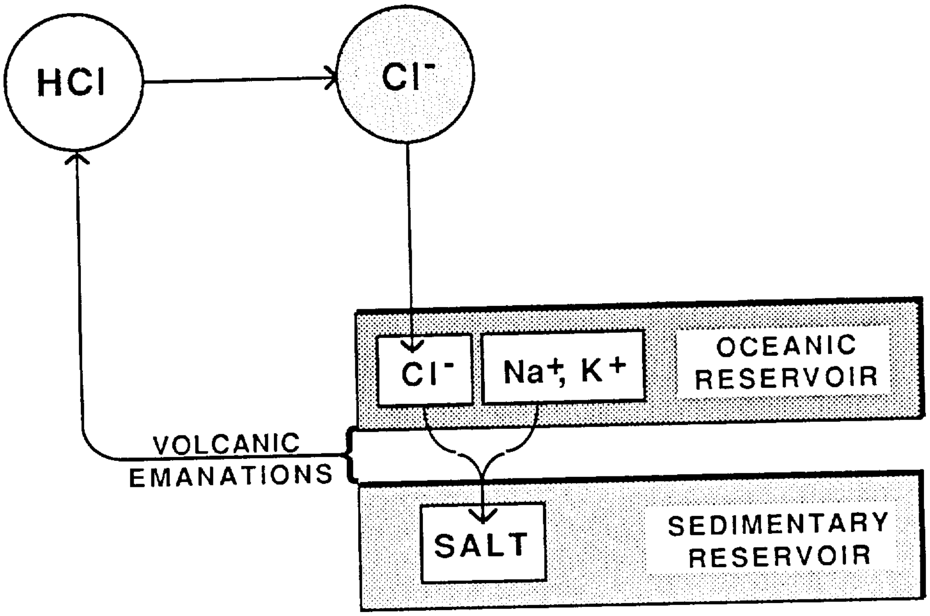
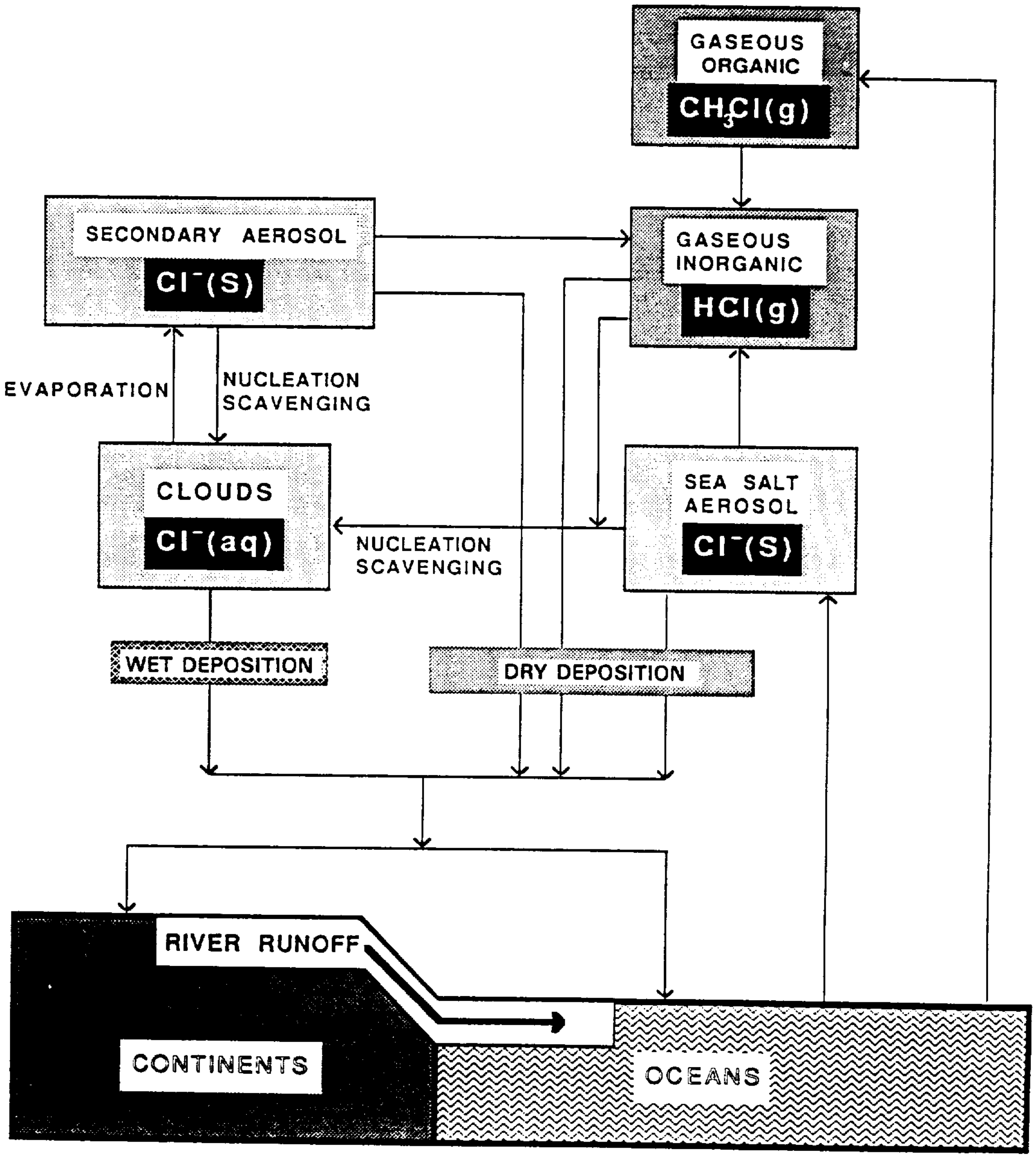


Figure 2. The Global Cycle of Chlorine.



THE GLOBAL CYCLE OF ATMOSPHERIC CHLORINE

Figure 3. The Wet and Dry Depositions onto the Respective Continental and Ocean Surfaces are not Explicitly Depicted.

is deposited in precipitation. Erickson and Duce (1988) accept the estimate made by others (cf. Eriksson, 1959) that about 10% of the sea-salt aerosol is deposited on continents. Chloride fluxes derived from these estimates using a factor of 0.55 (the fraction of Cl in the dissolved matter in sea water) as the fraction of the chlorine mass in sea salt are shown schematically in Figure 2 and listed in Table 1.

MacIntyre (1970), following Eriksson (1959), indicates that about 90% of the chloride in rivers derives from the cycling of the sea-salt aerosol to the continents and subsequent deposition and runoff from soil. This is the general view of geochemists concerned about global cycles as exemplified by Sillen (1967). In accord with this cyclic salt view, he suggested that the Cl^--contents of river water derives mainly from sea salt blown inland over the continents, deposited and then washed back. The average concentration of Cl^- in the world's rivers is about 220 μM (Livingstone, 1963). Table 1 lists the annual flux of Cl^- carried to the oceans by rivers based on Livingstone's (1963) estimates. While it appears that the river water flux is too small to balance the land deposition, it must be born in mind that the sea salt deposition falls off approximately exponentially with distance inland (as noted by Hutton, 1976 and shown quite definitively by Junge and Werby, 1958) and that water deposited on coastal plains mostly drain to the oceans in small streams rather than major rivers. Thus the amount of 260 tg yr^{-1} of river runoff is not incommensurate with the range given for land deposition in Table 1. Further comment on the balance of the cycle is given below.

b. Forests as sources

Recent studies of aerosols in Amazonia [Artaxo et al. (1988) and Talbot et al. (1988)] found that forested areas of the world can emit particulate material derived from plant components. Their results raise the possibility that there may be another independent cycling mechanism involving a considerable amount of global atmospheric chlorine and other materials, especially particulate organic carbon. The chlorine contents of the aerosol over Amazonia were of the order of 1/5 to 1/10 those of aerosols over the mid-oceans, but were equivalent to those measured in continental air over Europe. See below for further discussion.

c. The volcanic source

Symonds, Rose and Reed (1988) provide an estimate of the average annual volcanic flux of HCl to the atmosphere of 0.4 -11 Tg. They estimate that $> 90\%$ of the emissions are to the troposphere. The remainder is injected into the stratosphere in large explosive eruptions. Eventually those emissions enter the troposphere where they join with the gases there. These flux estimates reflect a considerable uncertainty, due in part to the great variability of volcanic activity in time and location and due in part to the great difficulties in sampling plumes under various conditions of eruptive activity. In view of the uncertainties, the earlier estimate made by Eriksson (1960) of 9 Tg yr^{-1} is essentially in agreement with the present estimates of Symonds et al.(1988).

Table 1. Global Atmospheric Fluxes of Chlorine

Cl - Carrier and Transfer	Fluxes of Cl (Tg/yr)	Ref
Cl(sea-salt) to atmosphere	5200 - 15000	a
Cl(sea-salt) land deposition (10% of above)	520 - 1500	a,b
Cl(aq) precipitation (global deposition)	830 - 2500	a
Cl(sea-salt) dry deposition (global)	4400 - 12000	a
Cl(river water) to oceans	260	b,c
Cl(g) sea-salt aerosol to atmosphere (3 - 20%)	160 - 3000	d
CH_3Cl ocean to atmosphere	3.5	e
Cl(g) volcanos to atmosphere	0.4 - 11	f
Cl (g) anthropogenic input to atmosphere	3	f

References: a. Erickson and Duce (1988); b.Eriksson (1959); c. Livingstone (1963); d. Cicerone (1981); e. Logan et al. (1981); f. Symonds et al. (1988)

d. The gaseous inorganic chlorine source

Among the most perplexing and uncertain aspects of the atmospheric chemistry of chlorine are (i.) the chemistry underlying the release of gaseous chlorine from sea-salt particles and (ii.) the amounts of chlorine involved. There have been several studies of limited scope in terms both of the regions of the oceans studied and the duration of the observations (Duce et al.,1965, Chesselet et al., 1972, Martens et al., 1973 and Kritz and Rancher, 1980). Martens et al.(1973) studied aerosols at coastal and inland sites in Puerto Rico using size separation techniques and found that the Cl/Na ratio decreased with decreasing size as shown in Figure 4 which is a composite of four samples. Martens et al.(1973) attributed this decrease of Cl enrichment ($EF_{Na} = [(Cl/Na)_{sample}/(Cl/Na)_{sea\ salt}] -1$) to the release of gaseous Cl from the aerosol. Upon correction for Na contributions for weathered crustal material, Martens et al.(1973) calculated Cl depletions in their samples of 7 - 25% relative to sea water. Wilkniss and Bressan (1972) found that the lower stages of cascade impactor samples of marine aerosols were more depleted in Cl than the upper stages which contained the larger particles. This reinforces the findings of Martens et al. (1973).

Duce and Hoffman (1976) systematically reviewed chemical fractionation processes at the air/sea interface including those of concern here. They point out that the observations support the idea that chlorine is released from the aerosol particles once they are in the atmosphere and not during the process of generation from the ocean surface. They also underscore the need to take into account contributions from and interactions with non-sea salt atmospheric components, even over the oceans. Cicerone (1981), in the most recent review of atmospheric halogens, summarized by noting that the amounts of chlorine released were variously found to be in the range 3 - 20%. The recent paper by Vong et al.(1988) indicates that during April and May of 1984 maritime air in the Pacific Northwest contained aerosol derived predominantly from sea-salt and that only the submicrometer fraction was, on the average, depleted in Cl relative to sea water. The overall average depletion, though unstated, would thus have amounted to something of the order of a few percent because about 90% of the mass of sea salt aerosol is in particles with $r > 1\ \mu m$. Table 2 surveys numerous investigations of the depletion of Cl from marine aerosols. Only those samples that were clearly dominated by marine aerosols are included in this compilation.

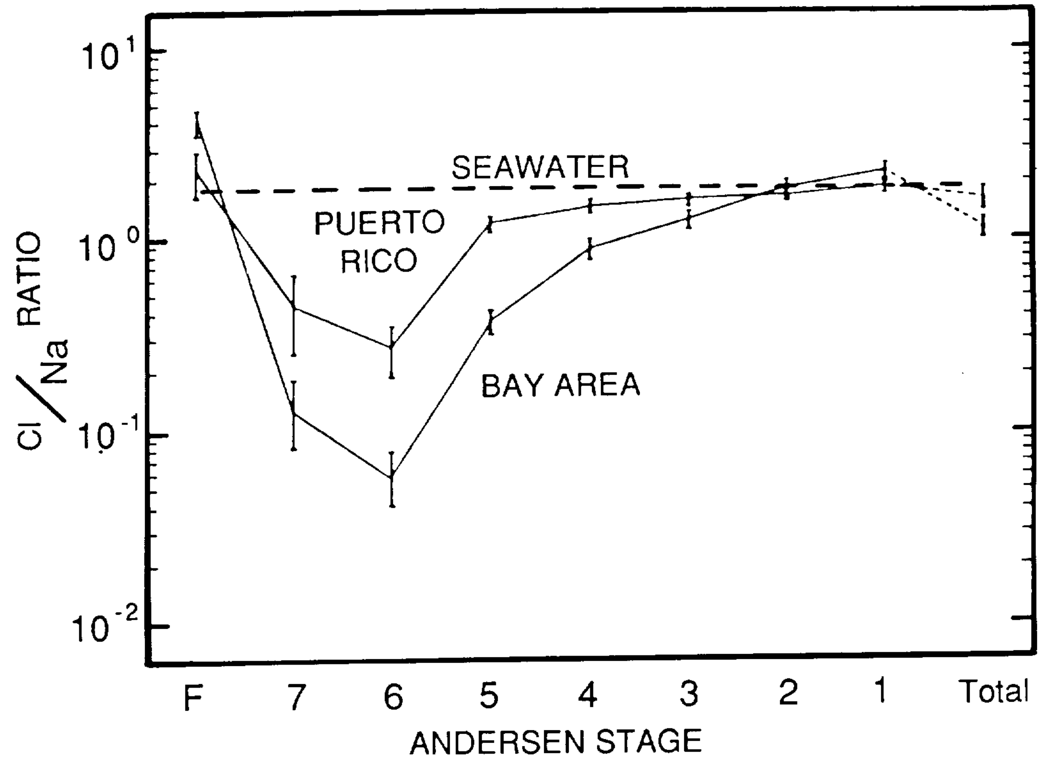


Figure 4. Average Cl/Na Ratios Versus Anderson Impactor Stage for Puerto Rican and Bay Area Marine Aerosols.

Warneck (1988), in a summary of marine aerosol constituents, uses the data of Buat-Menard et al. (1974) to suggest an average depletion of 12%. In reviewing the information of Table 2 and recalling that the submicrometer particle fraction bears most of the depletion, it is seen that, except for the results of Kritz and Rancher (1980), all results are consistent with average overall depletions of considerably less than 20%, probably less than 10%. In calculating the annual fluxes of gaseous chlorine released from sea-salt aerosol in Table 1, the uncertainties (as reflected by the ranges) in the flux of sea-salt aerosol and those in the fraction of gas released combine to give the range of a factor of 20.

Table 2. Chlorine depletions from marine aerosols.

Location	EF(range)	EF(ave)	Comment	Reference
U.S. East Coast	-0.99 to -0.31	—	Continental Na present.	Wilkniss and Bressan (1972)
Mid-Ocean	-0.39 to +0.22	-0.07		Wilkniss and Bressan (1972)
Mid-Ocean		-0.04		Chesselet et al. (1972)
Shetland Is.		-0.09		Peirson et al. (1974)
Mid-Pacific		-0.03		Wada and Kakubu (1973)
North Atlantic		-0.12		Buat-Menard et al. (1974)
Puerto Rico	-0.25 to -0.07	-0.12	Corrections for soil Na	Martens et al. (1973)
Gulf of Guinea	-0.51 to -0.11	-0.28	Maritime winds	Kritz and Rancher (1980)
Mid Pacific	-0.34 to +0.39	-0.08	20°N to 55°S	Parungo et al. (1986)
Pacific N.W.		-0.23	Particles with r> μm.	Vong et al. (1988)

Robbins et al. (1959) suggested that aerosol chloride could react according to

$$NaCl + 2NO_2 \rightarrow NaNO_3 + NOCl. \qquad (R1)$$

Thus nitrosyl chloride (NOCl) would be the form in which the chlorine is released from aerosol. Robbins et al (1969) noted that NOCl would rapidly hydrolyze in the atmosphere to form HCl. This mechanism is deemed unlikely now (cf. NRC, 1975). Eriksson (1959), and Duce et al. (1973) assumed that the gaseous inorganic chlorine is most likely to be HCl which is released via

$$H_2SO_4 + \underset{\text{(sea-salt)}}{2NaCl} \rightarrow Na_2SO_4 + 2\ HCl. \qquad (R2)$$

Hitchcock et al. (1980) found high correlations between Cl-depletion and excess (non-sea salt) SO_4^{2-} in filter samples of aerosols collected on the coast of North Carolina and interpreted their findings as strong confirmation of Eriksson's hypothesis of R2.

Clegg and Brimblecombe (1986) have shown that Henry's law considerations involving equilibrium between gaseous HCl and the aqueous ions indicate that reaction R2 or any similar reaction involving a mineral acid that is less volatile than HCl goes essentially to completion for relative humidities below 98%. In respect to the atmosphere, this means that HNO_3 can release HCl as well as H_2SO_4. Thus to explain the release of gaseous HCl to the atmosphere when the primary sea salt particles dehydrate, R2 can be rewritten as

$$H^+ + \underset{\text{(sea-salt)}}{NaCl} \rightarrow Na^+ + HCl. \qquad (R3)$$

In this equation, it must be understood that the hydrogen ion is supplied by acids of lower volatility than HCl and that for the atmosphere H_2SO_4 and HNO_3 are the most abundant species available for the task. Given the observations that the degree of chlorine depletion of sea salt aerosols is generally less than 20%, it is clear that the gaseous and aerosol forms of HCl are not in equilibrium, even over the oceans.

The mechanism represented by R3 has received considerable support from the recent work of Legrand and Delmas (1988) who examined the results of several ice core (Delmas et al. 1982, Legrand and Delmas, 1984, 1985) and air sampling programs (Duce et al., 1973 and Maenhaut et al., 1979) in Antarctica concerning chlorine. They used ion balances and calculated acidity for two circumstances as indicated below.

1. When Cl^- is in excess of Na^+ relative to bulk sea water:
   $$[H^+] = [xsSO_4^=] + [NO_3^-] + [xsCl^-].$$
2. When Cl^- is depleted relative to Na^+ :
   $[H^+] = [xsSO_4^=]_a + [NO_3^-]$, where $[xsSO_4^=]_a$ is the portion of excess sulfate that has not been neutralized by the above reaction.

This system thus assumes that when Cl^- is in excess the reaction has not proceeded to an important extent, whereas when Cl^- is depleted the reaction has proceeded toward completion leaving some unneutralized $xsSO_4^=$ behind to contribute its acidity (thus the subscript a). All quantities in brackets are chemical equivalent concentrations, which is the reason there is no factor of 2 preceding the sulfate terms. Excess sulfate is that which cannot be ascribed to sea-salt based on the assumption that all of the sodium comes from sea-salt. The original sea-salt contents are assumed to have the same relative composition as bulk sea water. The excess sulfate is considered to be the result of the conversion of gaseous SO_2 to particulate $SO_4^=$. The difference between the total excess sulfate and $xsSO_4{}^={}_a$ represents the amount by which the Cl^- is depleted.

Legrand and Delmas (1988) used the above model and the observed concentrations of Na^+, $SO_4^=$, NO_3^- and Cl^- in the ice cores to calculate the acidity which they then compared to the observed H^+. The agreement was very good for the two-hundred year period (a 16m long ice core) studied in detail. All of the major features and most of the minor variations were very closely in agreement. The model was able to account for the acidity during prolonged periods when Cl^- was both in excess and in deficit relative to Na^+. The authors could not state with certainty that the HCl (i.e., the $xsCl^-$) was derived entirely from sea-salt since volcanoes and other sources, including human activities, are known. However, they suggest that the aerosol source is the most likely one to account for the Antarctic data. A glance at Table 1 shows that even at the lower limit, the flux of gaseous Cl derived from sea salt is estimated to be much larger than the sum of all of the known other sources. This then supports Legrand's and Delmas' conclusion and permits a useful view of the global chlorine cycle.

From a global perspective, the operation of reaction R3 represents an important link between the sulfur and nitrogen cycles on the one hand and the chlorine cycle on the other because, as shown in Table 1, it may be the main source of reactive chlorine in the troposphere. Over continents where much of the excess sulfate is from pollution sources, the amounts of HCl released must be considered to be affected by human activities.

e. The organic chlorine source

The most abundant natural chlorine containing molecule in the atmosphere is methyl chloride, CH_3Cl which has its origin in the oceans. The details of its source in the oceans are not known. Zafiriou (1975) has shown that CH_3I readily exchanges its iodine atom for a chlorine atom in the laboratory at temperatures approximating that of the surface oceans. CH_3I also has been found in low concentrations in ocean water and in the air over the oceans. Lovelock et al. (1973) suggested that biomethylation of I in the oceans is the source of CH_3I. So it is possible through the exchange reaction that CH_3Cl is a secondary product of biological processes in the oceans. Despite the uncertainty of the origin of CH_3Cl it is relatively straightforward to estimate its flux into the atmosphere based on measured concentrations in surface ocean waters and tropospheric air and on its tropospheric lifetime. Other organic chlorine molecules have been found in marine organisms (cf Burreson et al., 1975) but their concentrations are so small as to be entirely negligible as sources of atmospheric chlorine. Finally it is noteworthy that CH_3Cl represents the major natural source of active chlorine in the stratosphere which in turn represents a natural regulator of stratospheric ozone concentrations.

f. The cycle and its balance

From the above discussion of chlorine sources it is clear that the oceans are the overwhelming source of atmospheric chlorine and that the bulk of atmospheric chlorine exists over the oceans in the forms of aerosol derived from sea salt and gas, probably HCl, released from the aerosol. The continents receive both forms of chlorine by transport from the marine atmosphere. About 90% of the sea-salt derived chlorine is deposited back into the oceans. Thus it is seen that most of the atmospheric chlorine cycle operates over the oceans. The 10% of chlorine transported to the continents is deposited on the surface from which it finds its way to rivers and streams and back to the oceans. Recent studies indicate that there may be significant aerosol chlorine contributions by forested areas. The possible release of gaseous chlorine from the plant derived aerosol has not been investigated. Chlorine found in continental air, particularly in industrial regions, in excess of that which can be ascribed to sea salt (relative to sodium) has generally been presumed to be of anthropogenic origin.

The amounts of chlorine injected into the atmosphere in sea salt and the amounts deposited as given in Table 1 represent a forced balance. The magnitude of the uncertainty of sea salt source strength makes it is possible that a secondary source, such as forests might make a significant contribution to natural chlorine in continental air. This is a subject for further investigation. We can judge the consistency of the cycle by using the estimates of Cl-deposition in precipitation on continents and the known total precipitation over continents to estimate the average Cl concentrations in precipitation and compare them to observed concentrations. Table 3 provides the necessary information. The precipitation data of Junge and Werby (1958) for the United States (mid 1955 - mid 1966) were selected because they are continental in extent and are less affected by pollution than subsequent surveys. The relatively close agreement between the calculated and observed quantities listed in Table 3b reflect consistency in the quantitative aspects of the cycle. That is to say that there appear to be no unknown sources or sinks of chlorine that could significantly alter the balance as represented by the rather generous ranges in Table 1. However, it is clear that there is much more insight to be gained by narrowing the ranges of uncertainty in the various components of the chlorine cycle. Obviously lacking are reliable global average values of concentrations in air and precipitation.

Table 3a. Fluxes of water and chlorine (Tg yr^{-1})

Precipitation over continents	9×10^7
Cl deposition	520 - 1500

Table 3b. Cl concentration (ppm)

	Calculated from above	Observed
Precipitation	6 - 17	0.1 - 8[a]

Reference: a. Junge and Werby (1958)

The Fluorine Cycle

Most of the fluorine in the earth's crust is in solid mineral form where it constitutes between 0.06% and 0.09% by weight of the upper layers of the lithosphere (National Research Council, 1971). Wind-borne soil dust can and does contribute to the atmospheric burden of fluorine in the form of soil minerals. The abundance of fluorine in the oceans is 1.3 ppm by weight and is controlled by equilibrium relationships among the dissolved species F^-, MgF^+, CaF^+, and NaF and the solids MgF_2 and CaF_2. The mass ratio of F/Cl in seawater is 6.7 X 10^{-5}. The marine aerosol is therefore a source of atmospheric fluorine as it is for chlorine. The question arises as to what extent, if any, gaseous fluorine is released to the atmosphere from the sea salt aerosol.

Cicerone (1981) noted in his review that there is virtually no quantitative information about natural fluorine in the atmosphere. Barnard and Nordstrom (1982) have reviewed most of the prior work, which is mainly concerned with fluoride in precipitation. The work of Symonds, Rose and Reed (1988) provides a new perspective for the role of volcanoes, albeit the flux estimates range over an order of magnitude. In contrast to the case of chlorine, volcanic activity could be the most important natural source of gaseous fluorine, most likely in the form of HF. Symonds, Rose and Reed (1988) give estimates of various emission rates for natural and anthropogenic sources of fluorine. These estimates along with information from Erickson and Duce's (1988) study of sea-salt flux are incorporated in Table 4.

Table 4. Global Atmospheric Fluxes of Fluorine

Natural	
F(sea-salt) to atmosphere:	0.4 - 1 Tg yr^{-1}
HF(g) sea salt to atmosphere:	0 - 1 Tg yr^{-1}
HF (g) volcanos to atmosphere:	0.06 - 6 Tg yr^{-1}
Soil dust to atmosphere:	<0.5 Tg yr^{-1}
Other	
HF (g) coal burning:	0.18 Tg yr^{-1}
F (g) as halocarbons:	0.27 Tg yr^{-1}

The recent work by Brimblecombe and Clegg (1988) and prior work by both authors cited therein on equilibrium (Henry's law) of acid gases in the marine atmosphere indicates that the low solubility of aqueous undissociated HF favors the gas phase and suggests rather strongly that HF should be totally depleted from the aerosol. If that is the case, the marine aerosol could be a major source of tropospheric HF(g), as can be seen from the figures in Table 4. However, as in the case of chlorine generated in the marine atmosphere, most of the cycling of fluorine, as both aerosol and gas, is confined to air over the oceans. The studies of Wilkniss and Bressan (1971, 1972) were aimed at trying to understand apparently complex fractionation behavior of F and Cl in marine aerosols. They found average F^- depletions of 62%, which now appears to be consistent with the idea of Brimblecombe and Clegg that much of the fluoride is released as HF(g).

As indicated above, soil dust contributes to the atmospheric burden of fluorine. Bewers and Haysom (1974) estimated that atmospheric dust could contribute a maximum of 1 ppb fluoride to precipitation which globally, amounts to a flux of about 0.5 Tg. yr^{-1}(This calculation uses a global annual rainfall amount of 4.8 x 10^8 Tg yr^{-1} as per Barnard and Nordstrom (1982).) This estimate is very close to an upper limit for total soil fluorine emissions that can be calculated using the annual flux of soil particles (radius < 20 μm) of 200 - 3000 Tg yr^{-1} (Ryaboshapko, 1983) in conjunction with an average surface soil F-content of 200 ppm.

Bewers and Haystrom (1974) also examined the global fluorine cycle and concluded that terrigenous dust, sea salt, volcanos and known industrial emissions could not supply enough fluorine to account for the observed concentrations of F^- in precipitation. That is, they could not balance the cycle. The minimum amount of F missing was 10 Tg yr^{-1}. The quantities used by Bewers and Haysom (1974) that differ from those in Table 4 are: maximum fluoride from sea salt (0.06 Tg yr^{-1}) and maximum volcanic emissions (1 Tg yr^{-1}). Assuming F^- derived from sea salt is unfractionated in precipitation, Bewers and Haysom (1974) calculated a cyclic salt component in precipitation of 0.062 Tg yr^{-1}. Bewers and Yeats (1975), citing a calculation using the thin film transfer model of Liss and Slater (1974), suggested that direct outgassing of HF from the ocean water to the atmosphere is sufficient to account for the entire F-contents of global precipitation. To the knowledge of this author, no computations to support this suggestion have been published. Table 4 and Table 5, which do not contain estimates of HF outgassing from the oceans, show that our present precipitation of the fluorine cycle is quite different from that of Bewers and his coworkers, primarily because of larger estimated sea salt-to-atmosphere and β volcanic fluxes. Now there is a sufficiency of fluorine sources to be able to account for the amounts observed in the hydrologic cycle. Whether or not the direct outgassing of HF from the oceans is a significant contributor remains to be seen.

As we did with the chlorine cycle, we can use flux estimates for fluorine and precipitation to provide an estimate of average F-concentration in precipitation and compare it to observed values. This is done in Table 5. Here we need however, to estimate wet and dry deposition on a global basis. The assumptions used for these estimates are indicated in Table 5. The maximum precipitation flux of 5.6 Tg yr^{-1} corresponds an average maximum concentration of 11.7 ppb which is in reasonable agreement with the observations reported by Barnard and Nordstorm (1981) and those of Mahadevan et al. (1986). Barnard and Nordstrom (1981) found an average of 8.1 ppb (range of 1-24 ppb) in rainwater samples obtained in eastern U.S. Mahadevan et al. (1986) found averages for marine, coastal, inland and deep inland regions of India and the Bay of Bengal unaffected by pollution of 6.5 ppb, 16.0 ppb, 16.0 ppb and 3.3 ppb respectively. These will be further discussed below.

Table 5a. Maximum fluorine emission fluxes (Tg yr^{-1})

Sea salt to atmosphere	1
Volcanos to atmosphere	6
Soil	0.5
Anthropogenic	0.5
Total	8

Table 5b. Dry deposition fluxes (Tg yr^{-1})

Sea salt (80%)	0.8
Soil dust (50%)	0.25
Volcanic and anthropogenic (20%)	1.3
Total	2.35
Precipitation F needed to balance	≤ 5.6

To summarize the natural fluorine cycle, the total flux is in the range 0.5 - 7.5 Tg yr^{-1} with volcanoes able to account for as much as 6, but as little as 0.06 Tg yr^{-1}. This leaves sea salt F^- as a likely second in importance, with as much as 1 Tg yr^{-1} and as little as 0.4 Tg yr^{-1}. However, over the continents, blowing soil dust can be a major contributor to aerosol fluoride. The cycle is in reasonable balance with known sources and sinks. The estimates of fluxes are, however, based on very limited sampling and analyses of flourine in the atmosphere and in precipitation which may or may not be representative of global abundances.

2. DISTRIBUTIONS

Chlorine

a. Abundances in reservoirs

1. *Gaseous organic chlorine.* The average tropospheric concentrations of CH_3Cl were found by Singh et al.(1983) to be 633 ppt (volumetric mixing ratio). They also found that the surface oceans averaged 11.5 ng L^{-1} which represents 275% saturation. By using a thin film model (cf Liss and Slater, 1974) they estimate a global flux of 4.9 Tg yr^{-1}. Logan et al. (1981) used a tropospheric chemistry model which simulated the OH radical concentrations and accounted for the reaction of CH_3Cl with OH. They computed a global loss rate of CH_3Cl of 5.2 Tg yr^{-1} which is in excellent agreement with the estimate of Singh et al.(1983). Both computations of flux involve the assumption that CH_3Cl is in steady state balance between emission to and loss from the atmosphere. The good agreement of the two results lends credibility to the concept of a global steady state of CH_3Cl abundance as a balance between emission from the ocean and destruction by reaction with OH. Singh et al.(1983) found that the Eastern Pacific Ocean is the dominant source region and estimated that it could conceivably account for the entire atmospheric burden of CH_3Cl.

2. *Gaseous inorganic chlorine.* From the reviews of Cicerone (1981), the NRC (1976), and the discussion in Warneck (1988), the various findings of several investigators form a somewhat consistent picture as seen in the items below.

i. Total aerosol samples in marine atmospheres and precipitation collected in maritime air show depletions of Cl relative to Na of about 2 - 20%.
ii. The submicrometer (diameter) particles display depletions of up to 90% and the larger particle fractions have depletions of less than 10%.
iii. Cl/Na ratios in precipitation are relatively close to that in sea water near the coasts of continents and tend to decrease toward the interiors. Some urban areas of the U.S. were found even in the early 1960's to have notably higher ratios.
iv. The only gaseous inorganic Cl-species identified in the troposphere is HCl (Farmer et al., 1976). His results yielded estimated concentrations in the lower tropospheric that are in general agreement with measurements of total inorganic Cl gas made by others in maritime air.

Farmer et al.'s measurements showed column abundances of HCl that were substantially the same for inland desert and for a coastal region with overall variability of about a factor of 2. As Cicerone (1980) points out, these results raise the question about whether sea salt is the dominant source of HCl and if it is, why was there no gradient with distance from the coast? The answer that can be inferred is that over the continents (at least North America and Europe) pollution sources of HCl contribute significantly to its concentrations. This is supported by the item iii above which notes the higher Cl/Na ratios in urban regions.

Comparison of the inorganic chlorine gas contents with the aerosol chlorine contents of maritime air indicates they are of the same magnitude, viz. about 1-2 $\mu g\ m^{-3}$ and 5 $\mu g\ m^{-3}$ respectively. It would appear that more than 15% of the inorganic chlorine in maritime air is in gaseous form. This finding is consistent with the larger values of observed chlorine depletions of marine aerosols which have an upper limit of 20%. However, if the lifetime of gaseous HCl is longer than that of aerosol Cl^- as may be possible, then lower values of chlorine depletions would be favored. The specification of a reliable average value of chlorine depletion awaits more intensive and extensive measurements of the global distributions in space and time of the Cl-species than are now available.

3. *Aerosol inorganic chlorine.* Raemdonck et al (1986) found sea salt concentrations over the Eastern Tropical and Equatorial Pacific to range from 2.6 to 8.2 $\mu g\ m^{-3}$ and that the average enrichment factor of Cl referred to Na was -0.08 on one type of sample and was -0.06 on another type. This corresponds to Cl^- concentrations of 1.3 to 4.2 $\mu g\ m^{-3}$. These recent results can be compared to earlier chemical measurements of Cl^- in aerosols over the central Atlantic Ocean as summarized by Warneck (1988) which average to 4.6 $\mu g\ m^{-3}$.

Talbot et al (1988) sampled and analyzed aerosols over Amazonia by aircraft and found that both in the mixed layer and the free troposphere virtually all of the Cl^- resided in the coarse particle mode ($d > 1\mu m$). They found average aerosol Cl^- atmospheric concentrations of 43 $ng\ m^{-3}$ in the mixed layer and 29 $ng\ m^{-3}$ in the free troposphere. These results are commensurate with those of Artaxo et al. (1988) who studied natural aerosols at two sites in Amazonia which were found to contain concentrations of Cl of 60 ± 45 $ng\ m^{-3}$ and 90 ± 30 $ng\ m^{-3}$. Most of the Cl was found in the coarse particle mode ($d \geq 2\ \mu m$) but was not of marine origin since the sites are more than 1000 km from the coast. Principal factor analysis led the authors to conclude that the Cl and other elements included in the group (mostly S, K and Ca) originated from plant material such as waxes, abraded leaves, etc. The authors conclude that over forested areas of the world which are large, the aerosols have a predominantly biogenic component compared to soil dust and sea salt. Aside from the potential importance of this aerosol to global mass loadings, it is evident that the small Cl-contents, though small in the global balance which is dominated by sea salt, may be a significant natural continental source of aerosol chlorine.

Vong et al (1988) reported that the average mass ratio of Na/Cl of 41 rainwater samples taken at a single site (found to be suitable for Northern Hemisphere background precipitation measurements) on the coast of the Pacific Northwest was 1.96 ± 0.43 while that for 14 submicrometer aerosol samples was 1.39. This latter figure represents a 20% depletion of Cl relative to sea water. The variability of the ratio in rainwater is due predominantly to meteorological and/or emission source factors. The depletion of Cl in the small particle fraction is consistent with the original observations of Duce (1969) and many others since. Multivariate analyses ascribed all of the Cl in both rainwater and submicrometer aerosol to a sea salt aerosol source. Average rainwater Cl concentrations were 98 $\mu eq\ L^{-1}$ (3500 $\mu g\ L^{-1}$) and average aerosol Cl concentrations were 390 $ng\ m^{-3}$.

Fluorine

Fluorine in soil.

A survey of 30 U.S. soil types (National Research Council, 1971) showed fluoride concentrations of 20 - 500 ppm in samples taken from 0 - 3 inch depths yielding an average concentration of 190 ppm. Samples taken to 12-inch depths ranged to 1620 ppm with an average of 292 ppm.

Fluorine in water.

The fluoride concentrations in the oceans are probably governed by equilibrium relationships among the species F^- (48-50%), MgF^+(47-49%), CaF^+(2%), NaF(1%) and the solids MgF_2 and CaF_2. The percentages in parentheses are the relative amounts of dissolved fluorine in each species (Dahlem Conference, 1975). The mass ratio of F/Cl in seawater is 6.7×10^{-5}. The average fluoride concentration in sea water is 1.3 mg/kg and, as indicated above is governed by equilibrium with Ca and Mg species. Natural fresh waters have fluoride contents that depend on the soil or rocks with which they associated. African lakes of volcanic origin have F^- contents as high as 67 ppm while most fresh waters have been found to have contents in the range 0.1 - 2 ppm. The lower limit of detection is about 0.1 ppm which prevents understanding the lowest natural levels. (See Faust and Aly, 1981).

Fluorine in air.

Gregory et al. report a few measurements of fluoride in aerosols over the tropical forest of Guyana. They found a free tropospheric concentration of 0.74 ng/std m^3 at 3.5 km height and a forest boundary layer concentration of 5.1 ng/std m^3. They also report a coastal boundary layer concentration of 3.8 ng/std m^3.

Fluorine and Chlorine in precipitation.

Barnard and Nordstrom (1982) found F^- concentrations in precipitation in a coastal site in Delaware and an inland site in Virginia that varied over similar ranges from 0 - 18 ppb with a mean of 8.1 ppb. The difference in mean concentrations between the two sites was not statistically different from zero.

Mahadevan et al. (1986) have reported precipitation fluoride data from India and the Bay of Bengal that give perhaps the best insight to the natural background concentrations. These are summarized in Table 7 where it is to be noted that the values for the Indian data are geometric means and the quantities in parentheses are the geometric standard deviations, all reflecting the approximate log-normality of the distributions of concentration values. The sites chosen for sampling are remote from any known pollution sources including volcanos. The study found concentrations upwards of about 1 μM for polluted urban locations in Bombay.

The following tables are given for reference. Some of the entries and references come from review articles or books rather than the original work. The measurements by Gregory et al. (1986) were made in a single day aboard an aircraft over the tropical forest of Guyana. The measurements of Galloway et al. (1982) were on samples of precipitation collected in several locations around the world deemed to be remote from pollution sources. Both sets of results can be considered to be representative of natural abundances of the substances measured.

Table 6. Concentrations of Cl and F in Air ($\mu g\ m^{-3}$).

	Continental	Maritime	Reference
	Range	Average	
Cl(aerosol)	0.08 - 0.14	0.114.6	Warneck (1988)
Cl(gas)inorganic	1.6 - 3.3[a]	1 - 2[b]	a. Farmer et al. (1976) b. Cicerone (1981)
CH_3Cl(gas)		0.9 - 1.3	Singh et al. (1983)
F(aerosol)	$(1 - 5) \times 10^{-3}$		Gregory et al. (1986)

Table 7. Concentrations of Cl and F in Precipitation (∼M). (1ppb F is equivalent to 0.053 μM)

		Continental	Maritime	Reference
Cl^-		0.0 - 22.9	12.6 - 1780	Galloway et al (1982)
F^-	U.S.A.[a]	0 - 0.56(0-0.95)	0.43(0 - 0.74)	Barnard and Nordstrom (1982)
	Indian[b]		0.27(2.0)	Mahadevan et al. (1986)
	Coastal		0.69(1.8)	
	120 km inland	0.26(1.0)		
	1200 km inland	0.14(.20)		

Notes: a. Entries are arithmetic means (90 percentile ranges); b. All data on and below this line pertain to the same reference. Entries are geometric means (geometric standard deviations).

XII. BIOLOGICAL AND HEALTH EFFECTS

Combined Summary and Conclusions

Toxicology of Atmospheric Degradation Products of Selected Hydrochlorofluorocarbons

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Assessment of Effects on Vegetation of Degradation Products from Alternative Fluorocarbons

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COMBINED SUMMARY AND CONCLUSIONS

There is a need for more information on exposure, especially to organic breakdown products. This should include estimates of ground level concentrations, modes of deposition (wet & dry) and should extend to identification of half-lives in soil and water, and the products of microbial transformation.

Nothing is known of the toxicology to humans, animals or plants of any of the organic breakdown products other than trifluoroacetic acid. It was considered dubious to extrapolate from analogous compounds (e.g. trichloroacetic acid). The limited work on toxicology of TFA was with very high concentrations compared with those potentially arising from HCFC's and CFC's. Studies should aim to determine the long-term threshold level for toxicological effects.

One of the major uncertainties is the fate of -CF_3 as there is conflict of opinion about the stability of the C-F bond. The biological evidence (from toxicology and pesticide biochemistry) indicates that- CF_3 is recalcitrant and may persist in the environment but an opinion was expressed that there may be significant chemical defluorination at room temperature. Because of the mammalian toxicity of monofluoracetate, the possibility of defluorination of trifluoro- to monofluoro- needs to be firmly clarified.

In contrast with position regards organic products, and notwithstanding uncertainties about rates of deposition, it can be stated with a high degree of confidence that inorganic fluoride (HF) does not present a significant risk to human, animals, plants, or soil.

Likewise HCl is of no direct risk to humans, animals or plants. Acidity from inorganic acids or as a result of mineralization of organic products does not add any significant burden to the environment in the form of acide deposition.