ASSESSMENT OF POTENTIAL IMPACT OF ALTERNATIVE FLUOROCARBONS ON TROPOSPHERIC OZONE

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1. INTRODUCTION

While the chlorofluorocarbons (CFCs) such as CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) are chemically inert in the troposphere, the hydrogen-containing halocarbons being considered as their replacements can, to a large extent, be removed in the troposphere by the HO radical. These alternative halocarbons include the hydrochlorofluorocarbons (HCFCs) 123 (CF_3CHCl_2), 141b ($CFCl_2CH_3$), 142b (CF_2ClCH_3), 22 (CHF_2Cl) and 124 (CF_3CHFCl) and the hydrofluorocarbons (HCFs) 134a (CF_3CH_2F), 152a (CHF_2CH_3) and 125 (CF_3CHF_2). Listed in Table 1 are the rate constants (k) for the HO radical reaction of these compounds [Hampson, Kurylo and Sander, 1989] and their estimated chemical lifetimes in the troposphere [Prather, 1989; Derwent and Volz-Thomas, 1989]. In this table, values of the lifetimes of these selected HCFCs and HCFs are seen to vary by more than a factor of more than ten ranging from 1.6 years for HFC 152a and HCFC 125 to as long as 28 years for HFC 125. Clearly, from the standpoint of avoiding or minimizing impact on stratospheric O_3, those halocarbons with short tropospheric lifetimes are the desirable alternates. However, potential environmental consequences of their degradation in the troposphere should be assessed and taken into account in the selection process.

One type of tropospheric impact of the alternative halocarbons may arise from their possible contribution as precursors to the formation of O_3 and other oxidants on urban and global scales. In the present assessment the following specific issues related to tropospheric oxidants will addressed:

1. Is it likely that the HFCs and HCFCs would contribute to production of photochemical oxidants in the vicinity of release?

2. On a global basis, how would emissions of HCFCs and HFCs compare to natural sources of O_3 precursors?

Since almost all CFCs are emitted in urban environments, the first question deals primarily with urban "smog" formation. In the following section, salient features of chemical relationships between oxidants and their precursors as well as the relevant terminologies will be described briefly first in order to provide a framework for the subsequent discussion of these two issues. It should be mentioned that the present report deals only with possible direct chemical effects and not with indirect climate-chemical interactions [cf. Wang 1986; Ramanathan et al. 1987; Wuebbles et al. 1989]. Namely, the alternative halocarbons and/or their degradation products may act as "green-house" gases and alter the global tropospheric O_3 distribution via changes in climate and emission rates of natural precursors of O_3. The latter topic is discussed elsewhere in the AFEAS report.

2. BACKGROUND

2.1. Photochemical Oxidants

The present assessment deals specifically with issues concerning O_3 rather than "oxidants" in general. The term "oxidant" is often used loosely and deserves clarification. Very often, it refers implicitly to O_3, the most abundant oxidant in the troposphere. However, there are many other trace atmospheric gases which are also known as "oxidants," e.g. hydrogen peroxide (H_2O_2), peroxyacetyl nitrate (PAN), and formic acid (HCOOH). As already discussed elsewhere in the AFEAS report [cf. "Degradation Products

Table 1 Rate Constants for the HO Reaction of Alternative Fluorocarbons

Compound		A-Factor x 10^{-12}	E/R	k(298 K)[a] x 10^{-15}	Lifetime[d] (yr)
HFCs[b]					
CH_3CHF_2	152a	1.20	1100 ± 200	37.0	1.7
CH_2FCF_3	134a	1.70	1750 ± 300	4.8	13.2
CHF_2CF_3	125	0.38	1500 ± 500	2.5	25.4
HCFCs[b]					
$CHClF_2$	22	1.20	1650 ± 150	4.7	3.5
CH_3CClF_3	142b	0.96	1600 ± 150	3.8	16.7
CH_3CHClF	124	0.66	1205 ± 300	10.0	6.3
CH_3CCl_2F	141b	0.27	1050 ± 300	8.0	7.9
$CHCl_2CF_3$	123	0.64	850 ± 150	34.0	1.7
Other[c]					
CO		0.15 ($1 + 0.6\ P_{atm}$)	0 ± 300	150.0 ($1 + 0.6\ P_{atm}$)	0.3
CH_4		2.30	1700 ± 200	7.7	8.2
C_2H_6		11.00	1100 ± 200	280.0	0.2
CH_3CCl_3		5.00	1800 ± 200	12.0	5.3

(a) k in cm^3 $molecule^{-1}$ s^{-1}

(b) Taken from Hampson, Kurylo and Sander (AFEAS Report, 1989)

(c) Taken from NASA Kinetic Data (1987)

(d) Lifetime = 1/k[HO]; k at 298 K; [HO] taken to be 5×10^5 molecule cm^{-3} (Crutzen and Gidel, 1983; Volz et al., 1981)

of Alternative Fluorocarbons in the Troposphere''], the alternative halocarbons can lead to the formation of a variety of products which can be considered as ''oxidants.'' Some of the halogen/carbon-containing oxidants derived from the alternative halocarbons may play important roles in atmospheric environments and their potential tropospheric impact must be assessed.

Broadly speaking, the term ''oxidant'' simply refers to the oxidizing ability of a reagent, i.e. to remove electrons from, or to share electrons with, other molecules or ions [Finlayson-Pitts and Pitts, 1986]. The ability of a chemical species to oxidize or reduce other chemical species is termed its ''redox potential'' and is expressed in volts. For example, O_3 has a standard potential of +2.07 volts in the redox pair of O_3/H_2O, and hydrogen peroxide +1.776 volts in the redox pair, H_2O_2/H_2O [Weast, 1977]. Historically, the term ''oxidant'' has been defined by a wet chemical technique; that is, an oxidant is any species giving a positive response in the KI method. The basis of this method is the oxidation of the colorless iodide ion in solution to form brown I_2:

$$2H^+ + 2I^- + O_3 \rightarrow I_2 + O_2 + H_2O$$
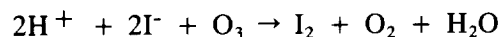
This technique of measuring and reporting total oxidants was used almost exclusively until the mid-1970s. In addition, the U.S. Federal Air Quality Standard was written in terms of ''total oxidant'' (0.08 ppm oxidant for 1 h) rather than O_3 specifically. A variety of air pollutants give a positive response, but some interfere negatively. Namely, ''total oxidants'' will include a weighted combination of various pollutants such as O_3, NO_2, and PAN, but SO_2 gives a 100% negative response and must therefore be removed with the use of a scrubber, e.g. Cr_2O_3, from the gas stream prior to analysis.

The recognition of the problems with the wet chemical KI technique and the simultaneous development of physical techniques for monitoring the major oxidant O_3 specifically, led to a change in the Federal Air Quality Standard from oxidant to O_3; simultaneously the standard was relaxed to higher concentrations, 0.12 ppm O_3 for 1 hr. Today, the UV method is most commonly used to monitor O_3 in ambient air, and is accepted as an ''equivalent method'' by the EPA [Finlayson-Pitts and Pitts 1986]. In any case, the term ''photochemical oxidant'' must be defined in a species-specific manner depending upon the particular context.

2.2 Ozone Precursors

Within the context of the present assessment, the term ''ozone precursor'' can be equated with carbon monoxide and various volatile organic compounds, particularly hydrocarbons, for reasons stated briefly below. Namely, it is now well-established that significant in-situ photochemical production and destruction of O_3 takes place on urban, regional and global scales [WMO 1985; Logan 1985; Finlayson-Pitts and Pitts 1986; Crutzen 1988]. Tropospheric O_3 production occurs via carbon monoxide and hydrocarbon oxidation, with NO_x (= NO + NO_2) acting as a catalyst. A large number of molecular and free radical species participate interactively in these chemical processes. The overall reaction mechanism can be represented as:

$$HC + NO_x + h\nu \rightarrow O_3 + \text{other products} \tag{1}$$
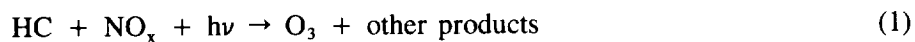
where HC denotes various reactive carbon-containing compounds, particularly hydrocarbons, and $h\nu$ is

solar radiation reaching the earth's surface in the wavelength region from 280 to 430 nm. Tropospheric production of O_3 is due entirely to the photodissociation of NO_2 at these wavelengths into NO and O followed by the recombination of O with O_2:

$$NO_2 + h\nu(\leq 430 \text{ nm}) \rightarrow NO + O \tag{2}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{3}$$

where M is any third body, such as O_2 and N_2, that removes the energy of the reaction and stabilizes O_3. Thus, strictly speaking, O atoms are the primary precursor of O_3. NO_2 can act as both the source and sink for O_3, since NO produced in reaction 2 removes O_3 and regenerates NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{4}$$

Reactions 2-4 alone do not provide a net production of O_3 but are largely responsible for controlling the formation and destruction of O_3, thus establishing a steady O_3 concentration governed by the so-called photostationary state relation,

$$[O_3] = J[NO_2]/k[NO] \tag{5}$$

where k is the rate constant for reaction 4 and $J[NO_2]$ is the NO_2 photodissociation rate.

According to the above relationship among O_3, NO and NO_2, photochemical production of O_3 can be attributed to the occurrence of reactions which reduce NO by oxidizing it to NO_2 without removing O_3. Such oxidation paths are provided by peroxy radicals (RO_2; R = H atom or organic group) which are, in turn, produced primarily in the HO-radical initiated oxidation of various hydrocarbons and their degradation products (e.g. CO and organic carbonyl compounds derived from RO radicals).

$$RO_2 + NO \rightarrow RO + NO_2 \tag{6}$$
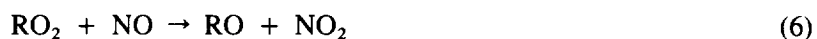
One of the principal sources of HO radicals is the photolysis of O_3 in the presence of H_2O:

$$O_3 + h\nu(\leq 310 \text{ nm}) \rightarrow O(^1D) + O_2 \tag{7}$$

$$O(^1D) + H_2O \rightarrow 2HO \tag{8}$$
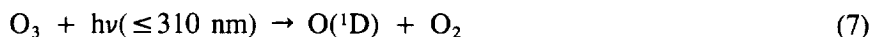
Namely, O_3 can serve as its own precursor in the HO-radical initiated oxidation of hydrocarbons via reaction 6. Note also that reaction 6 can regenerate HO radicals via reaction 6 for R = H atom, thereby providing a chain reaction. To illustrate this in its simplest form, the conversion of NO to NO_2 and the formation of O_3 can take place in the HO radical initiated chain oxidation of CO:

$$HO + CO \rightarrow CO_2 + H \tag{9}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{10}$$

$$HO_2 + NO \rightarrow HO + NO_2 \tag{11}$$

$$NO_2 + h\nu(\leq 430 \text{ nm}) \rightarrow NO + O \tag{2}$$

$$\underline{O + O_2 + M \rightarrow O_3 + M} \tag{3}$$

Net: $CO + 2O_2 \rightarrow CO_2 + O_3 \tag{12}$

In these reactions, NO_x and odd hydrogen ($HO + HO_2$) are not consumed directly and thus act as catalysts in the production of O_3. The overall reaction (1) for the formation of O_3 involves a much larger number of mutually interactive free radicals and molecular species than those encountered in CO oxidation. In the present assessment of the potential impact of the alternative halocarbons on tropospheric O_3, "O_3 precursors" can be appropriately defined as reactive HCs and CO, since the atmospheric role of the alternative halocarbons in O_3 production is chemically analogous to that of HCs and CO in that their HO radical initiated oxidation produces RO_2 radicals capable of converting NO to NO_2.

2.3. Ozone Forming Potential

A prerequisite to the assessment of the contribution of the alternative halocarbons to tropospheric O_3 is a quantitative knowledge of the relationship between photochemical O_3 production and the concentrations of its precursors, i.e. HCs and NO_x. This issue has been addressed extensively using detailed model calculations, and its key features will be described briefly below. Notably, the O_3 forming potential defined in terms of O_3 production for each HC molecule consumed is known to be nonlinearly dependent on the absolute and relative concentrations of NO_x and HCs, and on the HC composition. In certain circumstances O_3 production even decreases with increasing concentrations of the precursors.

This nonlinear phenomenon can be readily discerned in the O_3 isopleths calculated for urban atmospheres using so-called the EKMA technique (Empirical Kinetic Modeling Approach) which is used in formulating control strategies [Dodge 1977a,b; Dimitriades and Dodge 1983] (cf. Fig. 1a). The series of O_3 isopleths shown in this figure correspond to daily maximum hourly average O_3 concentrations produced in mixtures with various initial HC and NO_x concentrations. Among various assumptions made in deriving the results shown in Fig. 1a, the total non-methane hydrocarbons (NMHC) are taken to be a lumped parameter mixture [Hogo and Gery, 1988]. Although a single plot such as that in figure 1a is an oversimplification of urban chemistry and meteorological conditions, it clearly illustrates the highly nonlinear dependence of O_3 on the initial NMHC and NO_x concentrations and their ratio. Model calculations of O_3 isopleths corresponding to rural and regional atmospheres are shown in Fig. 1b for comparison [Liu et al. 1987; Lin, Trainer and Liu 1988].

In the global atmosphere, the oxidation of CO and hydrocarbons leads to the production of O_3 when sufficient NO is present [Crutzen, 1988]. In fact, at very low NO_x concentrations, these carbon-containing compounds can serve as a sink for O_3. For instance, CO oxidation can proceed via

$$CO + HO \rightarrow CO_2 + H \tag{9}$$

$$H + O_2 + M \rightarrow HO_2 + M \tag{10}$$

$$\underline{HO_2 + O_3 \rightarrow HO + 2O_2} \tag{13}$$

$$Net: CO + O_3 \rightarrow CO_2 + O_2 \tag{14}$$

rather than via the O_3 forming channel for CO oxidation in the presence of NO, i.e. reactions 9, 10, 11, 2, and 3, as discussed earlier. Namely, HO_2 radicals can react with either NO or O_3 leading to either O_3 production or destruction, respectively, depending on the concentration ratio [NO]/[O_3]. Since the rate
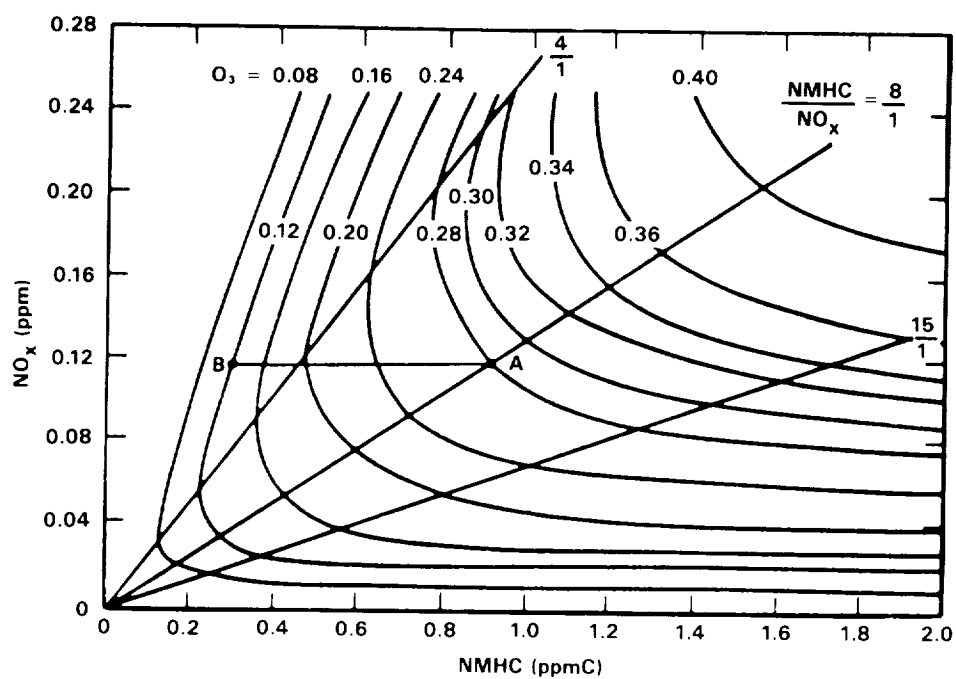
Figure 1a: Ozone Isopletes used in EKMA Approach (from Dodge, 1977a)
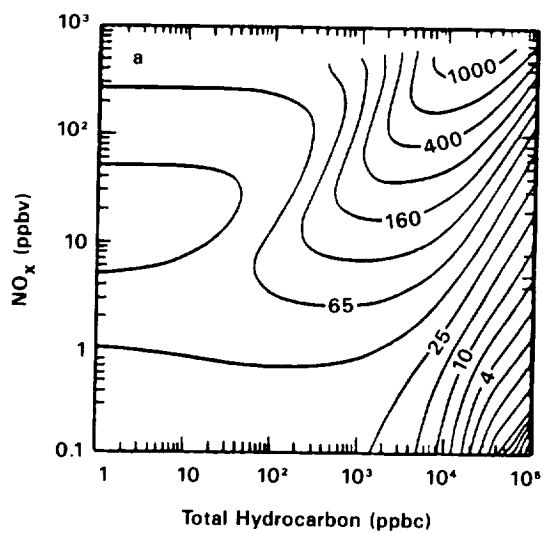
Figure 1b: Isoplete of O_3 mix ratio (in ppbV) calculated for regional atmospheres by Lin et al., (1988).

constant ratio $k_6/k_{13} \simeq$) 4000, the transition from O_3 destruction to production occurs at $[NO]/[O_3]$ = 1/4000, typically corresponding to [NO] $\simeq$ 5-10 ppt. Values of [NO] at this level or even below are known to occur in the lower atmosphere in remote marine environment [McFarland et al., 1979; Davis et al., 1987; Ridley et al., 1987]. Model calculations suggest that in NO-rich environments two O_3 molecules can be produced for each carbon atom in any NMHC [Liu et al., 1987]. According to the tropospheric O_3 budget analysis by Crutzen [1988], at most only 10% of the O_3 forming potential of HCs is actually realized at the present time, due to insufficient NO_x in the background troposphere.

3. CONTRIBUTION OF THE HFCs AND HCFCs TO THE PRODUCTION OF PHOTOCHEMICAL OXIDANTS IN THE VICINITY OF RELEASE

3.1. Approach

The major technological uses of the alternative halocarbons mean that almost all of their release will occur in urban surroundings [WMO 1985]. Thus, the O_3 forming potential of the alternative fluorocarbons in urban atmospheres will be assessed specifically in this section. In order to address this issue properly, the crucial observational data that will be required are:

1. How much HFCs or HCFCs will be present in a typical urban atmosphere?

2. How much HCs are currently present in a typical urban atmosphere, and what is the representative composition of urban HCs?

3. What is the O_3 forming potential of the alternative fluorocarbons as compared with that of urban HCs?

Each question is dealt with separately in the following sub-sections. Note that a plausible approach to answering Question #1 is to use the available data on urban concentrations of CFC-11 and CFC-12, since calculation of the actual absolute emission strength and the resulting ambient concentration for a particular source region is a difficult task for any atmospheric species.

3.2. Urban Chlorofluorocarbons

There are a number of recent measurements of urban concentrations of CFC-11 and CFC-12 together with those of other atmospherically important trace gases. For instance, summarized in Table 2a are the measured concentrations of CH_4 and CFC-11 reported by Blake et al. [1984] for 22 urban samples collected over a four year period from many different geographical locations. Approximate background concentrations are given for contemporary samples collected away from these urban locations. Table 2b shows a more detailed analysis of the London data given in Table 2a, for CH_4, CFC-11, CFC-12 and CH_3CCl_3. It can be noted from the ambient air data in these two tables that urban tropospheric concentrations of CFC-11 and CFC-12 are typically less than 1 ppbV and are up to three times higher than the corresponding background concentrations.

Extensive measurements of halocarbons and other trace gases in several U.S. cities have been made over the past decade by Singh et al. [1977,1986]. Table 3 shows a set of data from Los Angeles obtained by these authors in 1976. Concentrations of various trace gases indicated in this table are in the highest range reported from all cities. For the purpose of deriving a realistic upper limit of the contribution of

Table 2a Urban Tropospheric Concentrations of CH_4 and CCl_3F (Blake et al., 1984)

| Location | Date | Concentrations | | | | | Urban Excesses Fractional | | | |
| | | $[CH_4]^{(a)}$ | | $[CCl_3F]^{(a)}$ | | | | | | |
		U*	R**	U*	R**	(b)	CH_4	CCl_3F	(c)	(d)
Santiago, Chile	1/20/80	1.59	1.51	204	165	2100	0.053	0.24	0.22	0.15
Rio de Jan., Brazil	1/26/80	1.72	1.51	236	165	3000	0.14	0.43	0.32	0.22
Paramaribo, Surinam	2/01/80	2.44	1.61	474	165	2700	0.52	1.87	0.28	0.18
Cracow, Poland	5/08/80	3.42	1.65	599	180	4200	1.07	2.33	0.46	0.31
Warsaw, Poland	5/09/80	1.96	1.65	422	180	1300	0.19	1.34	0.14	0.09
London, England	7/25/80	2.03	1.62	564	184	1200	0.25	2.07	0.12	0.08
London, England	7/25/80	2.03	1.62	509	184	1300	0.25	1.77	0.14	0.09
Copenhagen, Denmark	8/01/80	1.68	1.60	455	182	300	0.05	1.50	0.03	0.02
Copenhagen, Denmark	8/01/80	1.69	1.60	570	182	200	0.06	2.13	0.03	0.02
Sao Paulo, Brazil	8/13/80	1.66	1.52	226	175	2700	0.09	0.29	0.32	0.22
Santiago, Chile	8/21/80	1.69	1.52	251	175	2200	0.11	0.43	0.26	0.17
Beijing, China	9/16/80	1.65	1.62	197	182	2000	0.02	0.08	0.25	0.16
Dalian, China	9/22/80	1.67	1.62	209	182	1900	0.03	0.15	0.02	0.13
Ketchikan, Alaska	11/22/80	1.92	1.63	329	189	2100	0.17	0.68	0.25	0.17
New York City	2/20/81	1.91	1.64	590	193	700	0.17	2.06	0.08	0.03
Rio de Jan., Brazil	6/14/81	1.62	1.53	192	175	5000	0.06	0.10	0.60	0.04
Hamburg, Germany	8/22/83	1.83	1.67	353	210	1100	0.10	0.68	0.14	0.10
Hamburg, Germany	8/24/83	1.82	1.67	317	210	1400	0.09	0.51	0.18	0.12
London, England	9/09/83	1.75	1.67	318	210	700	0.05	0.51	0.09	0.06
Brussels, Belgium	9/16/83	1.70	1.67	378	210	200	0.03	0.80	0.04	0.03
Rome, Italy	11/09/83	2.16	1.67	894	210	700	0.29	3.26	0.09	0.06
Rome, Italy	11/10/83	1.93	1.67	837	210	400	0.16	2.99	0.05	0.03

(a) Concentrations of CH_4 in ppmv (10^{-6}) and of CCl_3F in pptv (10^{-12}).
(b) Ratio of absolute increase in CH_4 to absolute increase in CCl_3F.
(c) Ratio of fractional increase in CH_4 to fractional increase in CCL_3F.
(d) Ratio of (a) corrected by 10/15, the years required to emit the observed atmospheric burden for CH_4 divided by the years required for CCl_3F.
* U = urban   **R = remote

Table 2b Urban Excesses of CH_4 versus CCl_3F, CCl_2F_2, and CH_3CCl_3 (Blake et al., 1984)

Concentrations in pptv $(10^{-*}12)$	CH_4	CCl_3F	CCl_2F_2	CH_3CCl_3
London, England (7/25/80)	2.02×10^6	509	817	638
Remote Location Background	1.62×10^6	184	330	120
Absolute Concentration Excess	0.41×10^6	325	487	518
Molar Excess Ratio CH_4/Halocarbon)		1260	840	790
Estimated 1980 Release (kilotons)		265	393	504
Estimated 1980 CH_4 Emissions (megatons)		39	44	48
Excess Ratio (Urban/Remote-1.00)	0.25	1.77	1.48	4.32
Ratio of Excess Ratios (CH_4/X)		1.77	1.48	4.32
Corrected Ratio of Excess Ratios		0.10^3	0.11	0.12

(a) Corrected for total atmospheric burden divided by yearly release in 1980: CH_4, 10; CCl_3F, 15: CCl_2F_2, 16; CH_3CCl_3, 4.8.

Table 3 Urban Halocarbons and Other Trace Gases[a]: Los Angeles

Compounds	Concentrations Maximum	Minimum	Average	Std. Dev.
(ppt)				
CCl_2F_2	2,476.6	225.5	860.4	599.4
CCl_3F	6,953.3	98.4	617.1	636.6
$CHCl_2F$	90.0	21.0	38.1	16.4
CCl_2FCClF_2	398.0	29.0	119.1	77.5
$CClF_2CClF_2$	150.0	7.5	39.8	32.2
$CHCl_3$	877.8	23.1	103.1	103.4
CH_3Cl	943.9	707.9	833.8	80.2
CH_3CCl_3	7,663.2	100.4	1,539.3	1,574.7
CCl_2CCl_2	2,267.3	60.8	674.4	498.4
$CHClCCl_2$	1,772.3	25.5	312.6	302.3
$COCl_2$	61.1	21.1	31.8	8.3
(ppb)				
NO	259.1	0.5	49.0	60.9
NO_2	302.4	16.9	82.7	68.8
CH_4	5,202.0	1,402.3	2,299.2	1,188.6
TNMHC	4,491.3	570.1	1,706.5	1,106.1
CO	5,740.0	76.7	1,530.2	1,354.1
O_3	213.4	0.0	38.0	53.1

(a) Measured during 4/29-5/4/76 (Singh et al., 1977)

the alternative fluorocarbons to urban O_3 formation, the most appropriate concentration to be used is a sum of the maximum concentrations of CFC-11 and CFC-12 shown in Table 3, i.e. (6,953.3 pptV + 2,476.6 pptV) $\simeq$ 9.5 ppbV. Thus, in the calculations that follow, the maximum concentration of total alternative fluorocarbons anticipated in a given urban atmosphere will be assumed to be 9.5 ppbV.

3.3 Urban Hydrocarbons

The feature that distinguishes the chemistry of urban atmospheres from that of the natural troposphere is the greater variety, and higher concentrations of HCs due to anthropogenic sources. In order to assess the O_3 forming potential of urban hydrocarbons, the concentrations of individual hydrocarbons must be known so that the vast difference in their atmospheric reactivity can be properly taken into account. Table 4 gives a summary of urban hydrocarbon composition measured by Seila and Lonneman [1988] in 39

Table 4 Ambient Air Hydrocarbons in 39 U.S. Cities[a]

Compound	Formula	Concentration (ppbC)	
		Median	Maximum
Isopentane	C_5H_{12}	45.3	3,393
n-Butane	C_4H_{10}	40.3	5,448
Toluene	C_7H_8	33.8	1,299
Propane	C_3H_8	23.5	393
Ethane	C_2H_6	23.3	475
n-Pentane	C_5H_{12}	22.0	1,450
Ethylene	C_2H_4	21.4	1,001
m-, p-Xylene	C_8H_{10}	18.1	338
2-Methylpentane	C_6H_{14}	14.9	647
Isobutane	C_6H_{10}	14.8	1,433
Acetylene	C_2H_2	12.9	114
Benzene	C_6H_6	12.6	273
n-Hexane, 2-Ethyl-1-butene	C_6H_{14},C_6H_{12}	11.0	601
3-Methylpentane	C_6H_{14}	10.7	351
1.2,4-Trimethylbenzene	C_9H_{12}	10.6	81
Propylene	C_3H_6	7.7	455
2-Methylhexane	C_7H_{16}	7.3	173
o-Xylene	C_8H_{10}	7.2	79
2,2,4-Trimethylpentane	C_8H_{18}	6.8	106
Methylcyclopentane	C_7H_{12}	6.4	293
3-Methylhexane	C_7H_{16}	5.9	168
2-Methylpropene,1-butene	C_7H_8	5.9	365
Ethylbenzene	C_8H_{10}	5.9	159
m-ethyltoluene	C_9H_{12}	5.3	83
n-Heptane	C_7H_{16}	4.7	233
		378.3	19,411

(a) Ambient air hydrocarbons in 39 U.S. cities - the 25 most abundant based on median concentration (Seila and Lonneman, 1988; quoted by Seinfeld, 1989)

U.S. cities which was quoted recently by Seinfeld [1989]. Listed in this table are the 25 most abundant compounds based on median concentration in terms of ppbC. Methane is normally the most abundant and least reactive among the urban HCs, and is seldom reported in air quality data such as those in Table 4. The median concentrations, rather than the maximum, for individual compounds will be used in the following calculations.

3.4 Contribution of Hydrocarbons vs. Alternative Fluorocarbons to Urban Ozone Production

To a good first-order approximation, relative contributions of individual hydrocarbons to overall O_3 production in a given urban air mass can be evaluated based on their removal rates by HO radicals, i.e. $-d[HC]/dt = k_i[HO][HC]_i$ where k_i is the rate constant for the HO radical reaction of the i-th hydrocarbon [Winer et al., 1979; Finlayson-Pitts and Pitts, 1986]. Namely, as stated in Sections 2.2 and 2.3, attack by HO is primarily responsible for the consumption of most hydrocarbons, and this process leads to the free radicals, e.g. HO_2 and RO_2, that oxidize NO to NO_2, which then forms O_3. While this approach is useful for some hydrocarbons, it has significant disadvantages as well [Finlayson-Pitts and Pitts, 1986]. This arises because the HC removal rates by HO do not necessarily reflect important mechanistic aspects of atmospheric reactions of HC-NO_x mixtures leading to the formation of O_3. For instance, the long chained alkanes and some aromatics produce nitrates which do not contribute significantly to the O_3 production. However, despite the potential deficiencies, the O_3 forming potential of organic mixtures in ambient air assessed using the HO reaction rates, has been shown to give results which are generally consistent with those based on experimentally observed O_3 formation in irradiation of urban air samples [Uno et al., 1985]. Presented below are the results of calculations based on the HO reaction rates.

Table 5 shows relative removal rates, i.e. $k_i[HC]_i$, computed from the HC composition (median) given in Table 4, in combination with the respective HO rate constants. Concentrations of HCs in Table 5 are given in units of molecules cm^{-3} and relative rates in $seconds^{-1}$. Since CH_4 is not included among the HCs listed in Table 4, its concentration is taken from the average value given in Table 3. The contribution of CO is not included in Table 5 because of its large variability in ambient urban air. However, it should be noted that with an average value of CO = 1.53 ppm (cf. Table 2), the relative removal rate of CO can be as much as 40% of those of the total HCs. Thus, the exclusion of CO in the above calculations leads to a conservative estimate for the O_3 forming potential of urban atmospheres.

Similarly, relative removal rates of the alternative fluorocarbons were calculated from their HO-reactivity and the assumed concentrations of individual fluorocarbons present at 9.5 ppbV each together with the HC composition given in Table 5. Results of these calculations are summarized in Table 5. According to the percentage rates shown in the last column of this table, all the fluorocarbons listed contribute less than 0.1% each to the O_2 forming potential of the total HCs, and less than 2% of that of CH_4. It is also to be noted in this table that other urban halocarbons reported in Table 3 such as $CCl_2 = CCl_2$ and $CHCl = CCl_2$ surpass the alternative fluorocarbons in their O_3 forming potential.

Additionally, an upper limit for the fractional conversion of the alternative fluorocarbons can be calculated to be 7% in two successive "smoggy" days with daily average concentration of HO radicals assumed to be as high as 1×10^7 molecule cm^{-3}. Thus, if an oxidant is formed which contains all the carbon atoms in the parent fluorocarbon, its concentration can reach at most 0.7 ppbV in urban air.

Table 5 Relative Removal Rates of Urban Hydrocarbons by HO Radicals[a]

Compound	k (x10⁻¹²) at 25 C cm³/molec s	Concentration (x 10¹⁰) molec/cm³	Rate (x10⁻²) Second⁻¹	% Rate
Methane	0.0077	5,748.0	44.3	3.0
Isopentane	3.9	22.7	88.8	5.9
n-Butane	2.7	25.2	68.0	4.5
Toluene	6.4	12.1	77.3	5.2
Propane	1.1	19.6	21.5	1.4
Ethane	0.3	29.1	8.7	0.6
n-Pentane	4.1	11.0	45.1	3.0
Ethylene	8.8	26.8	235.4	15.7
m-Xylene	(20.6)			
p-Xylene	(13.0)AV 16.8	5.7	95.0	6.4
2-Methylpentane	5.5	6.2	34.1	2.3
Isobutane	2.2	9.3	20.4	1.4
Acetylene	0.9	16.1	14.5	1.0
Benzene	1.0	5.3	0543	
n-Hexane,	(5.3)			
2-Ethyl-1-butene	(60.1)AV 32.7	4.6	149.9	10.0
3-Methylpentane	5.5	4.5	24.5	1.6
1.2,4-Trimethylbenzene	40.0	2.9	117.8	7.9
Propylene	24.6	6.4	157.9	10.5
2-Methylhexane	5.5	2.6	14.3	1.0
o-Xylene	14.2	2.3	32.0	2.1
2,2,4-Trimethylpentane	3.6	2.1	7.7	0.5
Methylcyclopentane	5.2	2.3	11.9	0.8
3-Methylhexane	7.1	2.1	15.0	1.0
2-Methylpropene,	(52.3)			
1-butene	(31.9)AV 42.1	3.7	155.2	10.4
Ethylbenzene	8.0	1.8	14.8	1.0
m-ethyltoluene	17.1	1.5	25.2	1.7
n-Heptane	7.4	1.7	12.4	0.8
		Total	1,496.3	100.0

(a.) The 25 most abundant compounds based on median concentration (cf. Table 4)

4. EMISSIONS OF HFCs AND HCFCs VS. NATURAL SOURCES OF OZONE PRECURSORS IN GLOBAL TROPOSPHERE

4.1 Approach

As stated in Section 2, the photochemical oxidation of CO and HCs in the presence of NO leads to the production of O_3. However, most CO and HCs emitted into the atmosphere from natural sources are oxidized in NO poor atmospheric environments, and thus do not contribute to effective O_3 production. Nevertheless, the global O_3 forming potential, (i.e. the maximum possible global O_3 production), of the alternative fluorocarbons relative to those of CO and various HCs can be assessed based on knowledge of (1) the relative reactivity of these compounds toward HO radicals, (2) the mean global distributions of these compounds, and (3) the NO-to-NO_2 conversion efficiency per molecule of these compounds consumed. Alternatively, global emission rates of these compounds can be used to derive an upper limit for the contribution of the alternative fluorocarbons to the overall budget of tropospheric O_3. Both approaches will be used in the present analysis.

Table 6 Relative Removal Rates of HFCs and HCFCs by HO Radicals in Urban Air

Compound		$k(298\ K)^{(a)}$ $\times\ 10^{-15}$	Relative Rate $(\times 10^{-4})\ s^{-1}$	Percentage Rate[e] %
HFCs[b,d]				
CH_3CHF_2	152a	37.0	87.9	0.059
CH_2FCF_3	134a	4.8	11.4	0.008
CHF_2CF_3	125	2.5	5.9	0.004
HCFCs[b]				
$CHClF_2$	22	4.7	11.2	0.008
CH_3CClF_2	142b	3.8	9.0	0.006
CH_3CHClF	124	10.0	23.8	0.016
CH_3CCl_2F	141b	8.0	19.0	0.013
$CHCl_2CF_3$	123	37.0	87.9	0.089
Other[c]				
CH_4		7.7	4,430.0	2.961
CH_3CCl_3		12.0	23.0	0.015
$CCl_2CCl_2{}^{(f)}$		170.0	97.7	0.065
$CHClCCl_2$		2,460.0	1,107.0	0.740

(a) k in cm^3 molecule⁻1 s^{-1}
(b) Taken from Hampson, Kurylo and Sander (AFEAS Report, 1989)
(c) Taken from Atkinson (1985) and NASA Kinetic Data (1987)
(d) Ambient concentrations of HFCs and HCFCs taken to be 9.5 ppbV.
(e) Fractional rate of the total rates of all HCs ($15.0\ s^{-1}$) given in Table 5.
(f) Taken from the maximum concentration of CH_3CCl_3 in Table 3.

TROPOSPHERIC OZONE

The pertinent data on sources, distribution and trends of tropospheric trace gases are taken largely from the WMO report [1985], and will be described here only briefly. Also, the projected contribution of the alternative fluorocarbons will be estimated relative to natural CO and HCs only, although the oxidation of anthropogenic HCs from polluted industrial areas is an important contribution to the global O_3 budget [Crutzen 1988].

4.2 Halocarbons

Summarized in Table 7 are the measured concentrations, estimated yearly production rates, and estimated atmospheric lifetimes of representative atmospheric halocarbons [WMO 1985]. Among these halocarbons, CFC-11, CFC-12 and CH_3CCl_3 serve as reference compounds for estimating the projected global emission rates (R) and ambient concentrations (C) of the alternative fluorocarbons. Namely, in the present analysis the value of R_{AF} for a given alternative fluorocarbon (AF) is taken to be the sum of R_{CFC-11} and R_{CFC-12} on a molar rather than weight basis. In Table 7, R_{CFC-11} and R_{CFC-12} in 1982 are shown to be 310×10^6 and 444×10^6 kg/yr (or 2.3×10^9 and 3.7×10^9 mole/yr), and hence, $R_{AF} = 6.0 \times 10^9$ mole/yr.

The projected ambient concentration of a given alternative fluorocarbon (AF) is expected to be equal to or less than the combined value of C_{CFC-11} and C_{CFC-12} shown in Table 7, i.e. $C_{AF} \leq 0.6$ ppbV. This value of C_{AF} will be used in the present assessment. It should be noted in Table 7 that values of both R and C for CFC-11, CFC-12 and CH_3CCl_3 are all comparable despite great differences in their atmospheric lifetimes (τ), i.e. $\tau_{CFC-11} = 65$ yr, $\tau_{CFC-12} = 120$ yr, and $TCH_3CCl_3 = 6.5$ yr. These estimates for τ are based on the inventory technique [Prinn et al. 1983], and not on calculated tropospheric chemical lifetimes such as those given in Table 1. In the case of CH_3CCl_3 reaction with tropospheric HO radicals as the major removal mechanism, and current models for tropospheric photochemistry appear to give a removal rate very close to the τCH_3CCl_3 given in Table 7 [Logan et al. 1981; Prather, 1989].

4.3 Methane

Methane dominates among global atmospheric hydrocarbons. The WMO report gives an estimate for the global emission rate of $R_{CH_4} = (500 \pm 145) \times 10^9$ kg/yr or $(33 \pm 9) \times 10^{12}$ mole/yr. The detailed global distribution and seasonal variation of CH_4, (C_{CH_4}), is now available. The latitudinal distribution of annual mean C_{CH_4} in 1985 ranges from 1.6 ppm in the Southern Hemisphere to 1.7 ppm in the Northern Hemisphere. Thus, $C_{CH_4} = 1.6$ ppm will be adopted for the present analysis.

An updated version of the photochemical model by Logan et al. [1981] gives a tropospheric chemical lifetime of 11 yrs for CH_4. The approximate value of $\tau_{CH_4} = 8.2$ yr given in Table 1 is close to this value. This value of τ_{CH_4} is judged to be one of the better known quantities in the global CH_4 budget, as it is tied to the empirical determination of the lifetime for CH_3CCl_3. An accurate value of τ_{CH_4} is needed to estimate the oxidation rate of CH_4 and the production rate of the ensuing product CO, as discussed below.

4.4 Carbon Monoxide

The major global sources of CO have been identified as the oxidation of CH_4 and other natural HCs, and direct emissions from fossil fuel combustion, with an estimated total production R_{CO} of 1060×10^9 kg as carbon/yr (or 88×10^{12} mole/yr). CO reacts rather rapidly with HO radicals ($\tau_{CO} \cong 0.4$ yr). The short atmospheric lifetime allows concentrations of CO to vary considerably in both space and time, mak-

Table 7 Atmospheric Halocarbons (WMO Report, 1985)

Substance	Measured concentration (pptv)	Time (year)	Est. global industrial production x 10⁶ kg	Year	Reference	Est. atmospheric lifetime [a] years (NAS 1984)
CFC 11 (CCl₃F	200	1983	310	1982	1,8	65
CFC 12 (CCl₂F₂)	320	1983	444	1982	1,8	120
CFC 13 (CF₃Cl)	∼ 3.4	1980	—	—	10	400
CFC 22 (CHCl₂F)	∼ 52	1980	206	1984	2,7	20
CFC 113	∼ 32	1/85	138-141	1984	2,5	90
CFC 114	—	—	13-14	1984	2	180
CFC 115	4	1980	—	—	10	380
CH₃CCl₃	∼ 120	1983	545	1983	3,11	6.5
CFC 116	∼ 4	1980	—	—	10	>500
CCl₄	∼ 140	1979	∼830	1983	3,12	50
CH₃Cl	630	1980	∼830	1984	3,6	∼ 1.5
CH₃l	∼ 1	1981	—	—	9	0.02
CBrClF₂	∼ 1.2	1984	(∼5?)‡	—	4	25
CBrF₃	∼ 1	1984	7-8	1984	2,4	110
CH₃Br	9.0	1984	—	—	4	2.3
CH₂BrCl	3.2	1984	—	—	4	—
CHBr₂Cl	0.9	1984	—	—	4	—
C₂H₄Br₂	∼ 1	1984	—	—	4	∼ 1
CHBr₃	∼ 2	1984	—	—	4	

‡ Estimated release from atmospheric increase, uncertain delay between industrial production and release to the atmosphere.

1. CMA, 1984.
2. DuPont, private communication, 1985.
3. ICI, private communication, 1985.
4. Khalil and Rasmussen, 1985a [mean of arctic and antarctic values, fall, 1984].
5. Khalil and Rasmussen, 1985d.
6. Rasmussen et al., 1980.
7. Khalil and Rasmussen, 1981.
8. Cunnold et al., 1982.
9. Rasmussen et al., 1982.
10. Penkett et al., 1981.
11. Prinn et al., 1983b; Khalil and Rasmussen, 1984a.
12. Simmons et al., 1983; Rasmussen and Khalil, 1981.

(a) More updated information is available in the AFEAS Report: papers by Prather; Derwent and Volz-Thomas

ing it difficult to assign a representative concentration on a global scale. Hurst and Rowland have recently reported the results of measurements of CO in remote tropospheric air samples collected quarterly in the Pacific region over a wide latitudinal range (71 °N-47 °S) since March 1986. Carbon monoxide mixing ratios in northern hemisphere samples were found to be consistently higher than those found in southern hemisphere samples. In northern temperate and arctic samples (>30 °N), CO ranged from 80 to 170 ppbV, and exhibited a large seasonal dependence. Southern hemisphere (>10 °S) CO ranged from 30 to 70 ppbV, and exhibited a smaller seasonal and latitudinal dependence. In the present analysis, the global average concentration of CO will be arbitrarily taken to be 100 ppb.

4.5 Nonmethane Hydrocarbons

Tropospheric photochemistry and $HO-O_3-CO$ global distributions are also strongly influenced by natural non-methane hydrocarbons (NMHC), particularly isoprene, terpenes, and the C_2-C_5 alkenes. The most recent estimate for an annual global NMHC emission flux gives 3.7×10^{11} kg C/yr (or 3.1×10^{13} moleC/yr) [Lamb et al. 1985], and this value will be used in the present assessment. While the global distributions of various non-methane hydrocarbons have not yet been well characterized, very large temporal and spatial variations are expected because of their short chemical lifetimes and source distributions. Measured concentrations of light HCs (C_2-C_5) in the free troposphere away from source regions are typically less than 1 ppbV [Rudolph and Ehhalt 1981; Singh and Salas 1982; Sexton and Westberg 1984; Greenberg and Zimmerman 1984; Bonsang and Lambert 1985].

4.6 Contribution of Alternative Fluorocarbons vs. Natural Sources

Table 8a gives a summary of the estimated global production of HCFs and HCFCs, and background O_3 precursors, i.e. CH_4, CO and non-methane hydrocarbons in units of mole/yr. The projected figure indicated for all HFCs and HCFCs combined is based on an estimate for the current production rates of both CFC-11 and CFC-12. The percentage contributions of various O_3 precursors shown in the last column have been derived from the corresponding production rates multiplied by their relative O_3 forming potentials. The O_3 forming potential for CO is assumed to be one half of those for all the other compounds listed [Crutzen, 1988]. The percentage contribution of all the HFCs and HCFCs is shown in this table

Table 8a Estimated Production of HCFs and HCFCs vs. Natural Ozone Precursors[a]

Compound	Production ($\times 10^{12}$)	% Contribution
HCFs & HCFCs	0.006	0.0056
CH_4	33	30.6
CO	88	40.7
NMHC	31	28.7
Total	152	100.0

(a) Ozone forming potential of CO is assumed to be one half of other compounds.

Table 8b Relative Contributions of HCFs and HCFCs vs. Natural Ozone Precursors (NOP) to Global Ozone Production: Based on HO Radical Reaction Rates

Compound		Global Mean Concentration (ppbV)	$k_{HO}(298\ K)^{(a)}$ x 10^{-15}	Relative Rate (s^{-1}) (x10^{-4})	Percentage Contribution
HFCs					
CH_3CHF_2	152a	$0.6^{(b)}$	37.0	5.6	0.092
CH_2FCF_3	134a	0.6	4.8	0.7	0.011
CHF_2CF_3	125	0.6	2.5	0.4	0.007
HCFCs					
$CHClF_2$	22	0.6	4.7	0.7	0.011
CH_3CClF_3	142b	0.6	3.8	0.6	0.010
CH_3CHClF	124	0.6	10.0	1.5	0.025
CH_3CCl_2F	141b	0.6	8.0	1.2	0.020
$CHCl_2CF_3$	123	0.6	37.0	5.6	0.092
NOPs					
CH_4		1,600	7.7	3,080.0	50.522
CO		100	240.0	3,000.0	49.210

(a) k_{HO} in cm^3 molecule^{-1} s^{-1}

(b) Upper limit value assumed for all HFCs and HCFCs.

to be 0.0056% of total natural O_3 precursors. Estimation of the relative contribution of the alternative fluorocarbons (AFs) based on their projected emission rates, such as that given in Table 8a, seems reasonable, particularly in view of the comparable atmospheric reactivity of the AFs and CH_4 (cf. Table 8b).

The results of an analysis of the relative oxidation rates of individual AF vs. natural O_3 precursors are summarized in Table 8b. The global mean concentration of each AF is assumed to be 0.6 ppbV (or 1.5 x 10^{10} molecule/cm^3 at 298 K). The relative rates given in this table have been derived from these concentrations multiplied by the rate constants for the corresponding HO radical reactions at 298 K. Percentage contributions of various AFs and major natural O_3 precursors, i.e. CH_4 and CO, have been calculated, in turn, from these relative rates corrected for their O_3 forming efficiencies. As before, the O_3 production potential of CO is taken to be one half of all the other compounds listed. The contributions of NMHCs are not included in this analysis because their global concentrations are highly uncertain. Such an omission of NMHCs should result in a slight overestimation of the percentage contributions of various AFs. In fact, the fractional contributions of the AFs given in the last column of this table are seen to be generally greater than that calculated from their estimated emission rates (cf. Table 8a). However, both methods can be considered to yield mutually consistent results on the potential contribution of the AFs to the global O_3 production. It can also be noted from a comparison of Tables 6 and 8b that the percentage contributions of individual AFs are, coincidentally, identical in both urban and global atmospheres.

5. ACKNOWLEDGEMENTS

XI. NATURAL SOURCES

Natural Chlorine and Fluorine in the Atmosphere, Water and Precipitation

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EXECUTIVE SUMMARY

The geochemical cycles of chlorine and fluorine are surveyed and summarized as framework for the understanding of the global natural abundances of these species in the atmosphere, water and precipitation. In the cycles the fluxes into and out of the atmosphere can be balanced within the limits of our knowledge of the natural sources and sinks. Sea salt from the ocean surfaces represent the predominant portion of the source of chlorine. It is also an important source of atmospheric fluorine, but volcanos are likely to be more important fluorine sources. Dry deposition or sea salt returns about 85% of the salt released there. Precipitation removes the remainder. Most of the sea salt material is considered to be cyclic, moving through sea spray over the oceans and either directly back to the oceans (about 90%) or deposited dry and in precipitation on land (about 10%), whence it runs off into rivers and streams and returns to the oceans. Most of the natural chlorine in the atmosphere is in the form of particulate chloride ion with lesser amounts as gaseous inorganic chloride (most likely HlC) and methyl chloride vapor. Fluorine is emitted from volcanos primarily as HF. It is possible that HF may be released directly from the ocean surface but this has not been confirmed by observation. HCl and mostly likely HF gases are released into the atmosphere by sea salt aerosols. The mechanism for the release is likely to be the provision of protons from the so-called excess sulfate (that which results from the oxidation of SO_2) and HNO_3. Sea salt aerosol contains fluorine as F^-, MgF^+, CaF^+ and NaF. The concentrations of the various species of chlorine and fluorine that characterize primarily natural, unpolluted atmospheres are summarized in tables and are discussed in relation to their fluxes through the geochemical cycle.