

## **X. IMPACT ON PHOTOCHEMICAL OXIDANTS INCLUDING TROPOSPHERIC OZONE**

*An Assessment of Potential Impact of Alternative Fluorocarbons on Tropospheric Ozone*

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## EXECUTIVE SUMMARY

One type of tropospheric impact of the alternative halocarbons may arise from their possible contribution as precursors to the formation of O<sub>3</sub> and other oxidants on urban and global scales. In the present assessment the following specific issues related to tropospheric oxidants are 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<sub>3</sub> precursors?

Since almost all CFCs are emitted in urban environments, the first question deals primarily with urban "smog" formation. Salient features of chemical relationships between oxidants and their precursors as well as the relevant terminologies are described briefly in order to provide a framework for the discussion of these two issues.

Based on an analysis of the atmospheric concentrations of various O<sub>3</sub> precursors, and their atmospheric reactivity and O<sub>3</sub> forming potential, the maximum projected contributions of the alternative fluorocarbons to O<sub>3</sub> production in both urban and global atmospheres have been derived as follows:

- 1: Urban Atmosphere (values in parenthesis in units of 10<sup>-3</sup>% of the total contribution of all O<sub>3</sub> precursors):

HFCs: CH<sub>3</sub>CHF<sub>2</sub>-152a (59), CH<sub>2</sub>FCF<sub>3</sub>-134a (8), CHF<sub>2</sub>CF<sub>3</sub>-125 (4)

HCFCs: CHClF<sub>2</sub>-22 (8), CH<sub>3</sub>CClF<sub>2</sub>-142b (6), CH<sub>3</sub>CHClF-124 (16),

CH<sub>3</sub>CCl<sub>2</sub>F-141b (13), CHClCF<sub>3</sub>-123 (59)

- 2: Global Atmosphere (values in parenthesis in units of 10<sup>-3</sup>% of the total contribution of all O<sub>3</sub> precursors):

HFCs: CH<sub>3</sub>CHF<sub>2</sub>-152a (92), CH<sub>2</sub>FCF<sub>3</sub>-134a (11), CHF<sub>2</sub>CF<sub>3</sub>-125 (7)

HCFCs: CHClF<sub>2</sub>-22 (11), CH<sub>3</sub>CClF<sub>2</sub>-142b (10), CH<sub>3</sub>CHClF-124 (25),

CH<sub>3</sub>CCl<sub>2</sub>F-141b (20), CHClCF<sub>3</sub>-123 (92)



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## 1. INTRODUCTION

While the chlorofluorocarbons (CFCs) such as CFC-11 ( $\text{CFCl}_3$ ) and CFC-12 ( $\text{CF}_2\text{Cl}_2$ ) 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 ( $\text{CF}_3\text{CHCl}_2$ ), 141b ( $\text{CFCl}_2\text{CH}_3$ ), 142b ( $\text{CF}_2\text{ClCH}_3$ ), 22 ( $\text{CHF}_2\text{Cl}$ ) and 124 ( $\text{CF}_3\text{CHFCl}$ ) and the hydrofluorocarbons (HFCs) 134a ( $\text{CF}_3\text{CH}_2\text{F}$ ), 152a ( $\text{CHF}_2\text{CH}_3$ ) and 125 ( $\text{CF}_3\text{CHF}_2$ ). 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 HFCs 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  $\text{O}_3$ , 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  $\text{O}_3$  and other oxidants on urban and global scales. In the present assessment the following specific issues related to tropospheric oxidants will be 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  $\text{O}_3$  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  $\text{O}_3$  distribution via changes in climate and emission rates of natural precursors of  $\text{O}_3$ . The latter topic is discussed elsewhere in the AFEAS report.

## 2. BACKGROUND

### 2.1. Photochemical Oxidants

The present assessment deals specifically with issues concerning  $\text{O}_3$  rather than "oxidants" in general. The term "oxidant" is often used loosely and deserves clarification. Very often, it refers implicitly to  $\text{O}_3$ , 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 ( $\text{H}_2\text{O}_2$ ), peroxyacetyl nitrate (PAN), and formic acid ( $\text{HCOOH}$ ). As already discussed elsewhere in the AFEAS report [cf. "Degradation Products

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**Table 1** Rate Constants for the HO Reaction of Alternative Fluorocarbons

Compound		A-Factor $\times 10^{-12}$	E/R	k(298 K) <sup>(a)</sup> $\times 10^{-15}$	Lifetime <sup>(d)</sup> (yr)
HFCs <sup>(b)</sup>					
CH <sub>3</sub> CHF <sub>2</sub>	152a	1.20	1100 ± 200	37.0	1.7
CH <sub>2</sub> FCF <sub>3</sub>	134a	1.70	1750 ± 300	4.8	13.2
CHF <sub>2</sub> CF <sub>3</sub>	125	0.38	1500 ± 500	2.5	25.4
HCFCs <sup>(b)</sup>					
CHClF <sub>2</sub>	22	1.20	1650 ± 150	4.7	3.5
CH <sub>3</sub> CClF <sub>3</sub>	142b	0.96	1600 ± 150	3.8	16.7
CH <sub>3</sub> CHClF	124	0.66	1205 ± 300	10.0	6.3
CH <sub>3</sub> CCl <sub>2</sub> F	141b	0.27	1050 ± 300	8.0	7.9
CHCl <sub>2</sub> CF <sub>3</sub>	123	0.64	850 ± 150	34.0	1.7
Other <sup>(c)</sup>					
CO		0.15 (1 + 0.6 P <sub>atm</sub> )	0 ± 300	150.0 (1 + 0.6 P <sub>atm</sub> )	0.3
CH <sub>4</sub>		2.30	1700 ± 200	7.7	8.2
C <sub>2</sub> H <sub>6</sub>		11.00	1100 ± 200	280.0	0.2
CH <sub>3</sub> CCl <sub>3</sub>		5.00	1800 ± 200	12.0	5.3

(a) k in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>

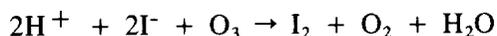
(b) Taken from Hampson, Kurylo and Sander (AFEAS Report, 1989)

(c) Taken from NASA Kinetic Data (1987)

(d) Lifetime = 1/k[HO]; k at 298 K; [HO] taken to be 5x10<sup>5</sup> molecule cm<sup>-3</sup> (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  $I_2$ :

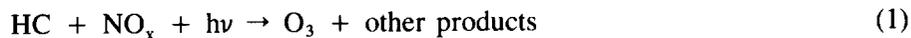


This technique of measuring and reporting total oxidants was used almost exclusively until the mid-1970s. In addition, the U.S. Federal Air Quality Standard was written in terms of “total oxidant” (0.08 ppm oxidant for 1 h) rather than  $O_3$  specifically. A variety of air pollutants give a positive 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:



where HC denotes various reactive carbon-containing compounds, particularly hydrocarbons, and  $h\nu$  is

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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  $O_2$ :



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  $NO_2$ :



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,

$$[O_3] = J[NO_2]/k[NO] \quad (5)$$

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).



One of the principal sources of  $HO$  radicals is the photolysis of  $O_3$  in the presence of  $H_2O$ :



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  $CO$ :



In these reactions,  $\text{NO}_x$  and odd hydrogen ( $\text{HO} + \text{HO}_2$ ) are not consumed directly and thus act as catalysts in the production of  $\text{O}_3$ . The overall reaction (1) for the formation of  $\text{O}_3$  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  $\text{O}_3$ , "O<sub>3</sub> precursors" can be appropriately defined as reactive HCs and CO, since the atmospheric role of the alternative halocarbons in  $\text{O}_3$  production is chemically analogous to that of HCs and CO in that their HO radical initiated oxidation produces  $\text{RO}_2$  radicals capable of converting NO to  $\text{NO}_2$ .

### 2.3. Ozone Forming Potential

A prerequisite to the assessment of the contribution of the alternative halocarbons to tropospheric  $\text{O}_3$  is a quantitative knowledge of the relationship between photochemical  $\text{O}_3$  production and the concentrations of its precursors, i.e. HCs and  $\text{NO}_x$ . This issue has been addressed extensively using detailed model calculations, and its key features will be described briefly below. Notably, the  $\text{O}_3$  forming potential defined in terms of  $\text{O}_3$  production for each HC molecule consumed is known to be nonlinearly dependent on the absolute and relative concentrations of  $\text{NO}_x$  and HCs, and on the HC composition. In certain circumstances  $\text{O}_3$  production even decreases with increasing concentrations of the precursors.

This nonlinear phenomenon can be readily discerned in the  $\text{O}_3$  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; Dimitriadis and Dodge 1983] (cf. Fig. 1a). The series of  $\text{O}_3$  isopleths shown in this figure correspond to daily maximum hourly average  $\text{O}_3$  concentrations produced in mixtures with various initial HC and  $\text{NO}_x$  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  $\text{O}_3$  on the initial NMHC and  $\text{NO}_x$  concentrations and their ratio. Model calculations of  $\text{O}_3$  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  $\text{O}_3$  when sufficient NO is present [Crutzen, 1988]. In fact, at very low  $\text{NO}_x$  concentrations, these carbon-containing compounds can serve as a sink for  $\text{O}_3$ . For instance, CO oxidation can proceed via



rather than via the  $\text{O}_3$  forming channel for CO oxidation in the presence of NO, i.e. reactions 9, 10, 11, 2, and 3, as discussed earlier. Namely,  $\text{HO}_2$  radicals can react with either NO or  $\text{O}_3$  leading to either  $\text{O}_3$  production or destruction, respectively, depending on the concentration ratio  $[\text{NO}]/[\text{O}_3]$ . Since the rate

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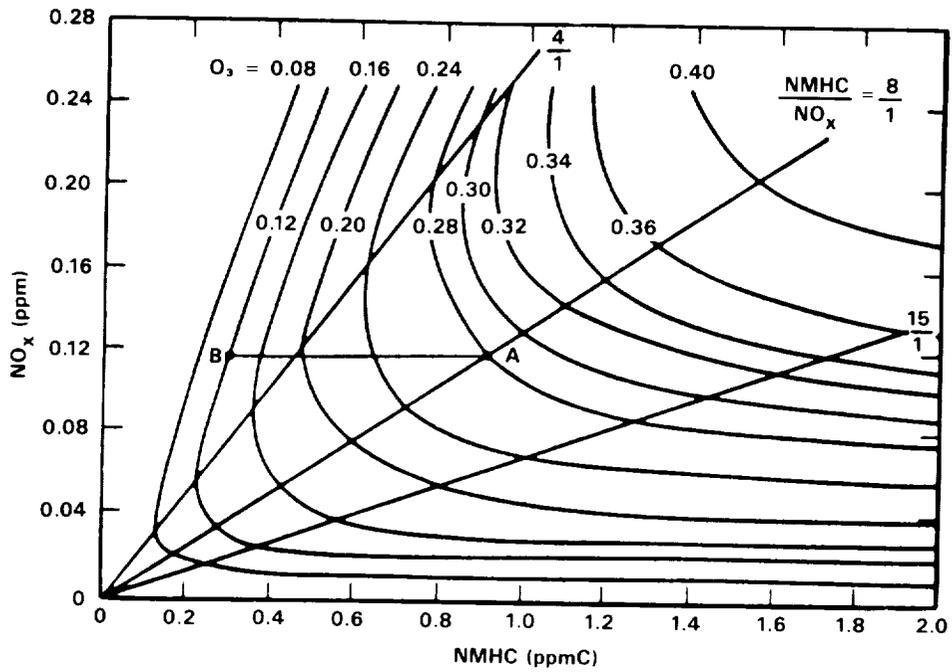


Figure 1a: Ozone Isopleths used in EKMA Approach (from Dodge, 1977a)

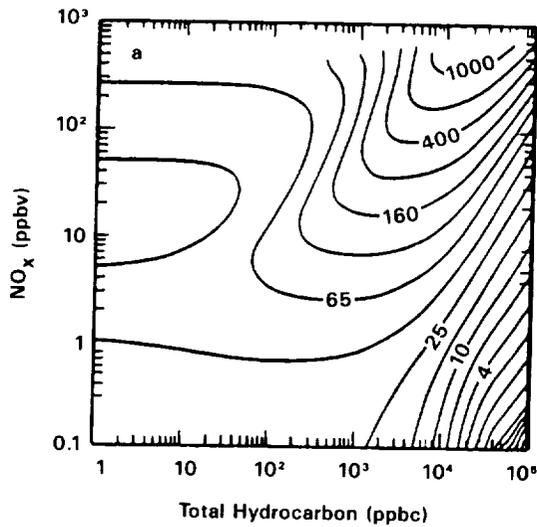


Figure 1b: Isopleth of O<sub>3</sub> mix ratio (in ppbv) calculated for regional atmospheres by Lin et al., (1988).

constant ratio  $k_6/k_{13}\omega$ ) 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

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**Table 2a** Urban Tropospheric Concentrations of CH<sub>4</sub> and CCl<sub>3</sub>F (Blake et al., 1984)

Location	Date	Concentrations				Urban Excesses				
		[CH <sub>4</sub> ] <sup>(a)</sup>		[CCl <sub>3</sub> F] <sup>(a)</sup>		(b)	Fractional			(d)
		U*	R**	U*	R**		CH <sub>4</sub>	CCl <sub>3</sub> F	(c)	
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<sub>4</sub> in ppmv (10<sup>-6</sup>) and of CCl<sub>3</sub>F in pptv (10<sup>-12</sup>).

(b) Ratio of absolute increase in CH<sub>4</sub> to absolute increase in CCl<sub>3</sub>F.

(c) Ratio of fractional increase in CH<sub>4</sub> to fractional increase in CCl<sub>3</sub>F.

(d) Ratio of (a) corrected by 10/15, the years required to emit the observed atmospheric burden for CH<sub>4</sub> divided by the years required for CCl<sub>3</sub>F.

\* U = urban      \*\*R = remote

**Table 2b** Urban Excesses of CH<sub>4</sub> versus CCl<sub>3</sub>F, CCl<sub>2</sub>F<sub>2</sub>, and CH<sub>3</sub>CCl<sub>3</sub> (Blake et al., 1984)

Concentrations in pptv (10 <sup>-12</sup> )	CH <sub>4</sub>	CCl <sub>3</sub> F	CCl <sub>2</sub> F <sub>2</sub>	CH <sub>3</sub> CCl <sub>3</sub>
London, England (7/25/80)	2.02x10 <sup>6</sup>	509	817	638
Remote Location Background	1.62x10 <sup>6</sup>	184	330	120
Absolute Concentration Excess	0.41x10 <sup>6</sup>	325	487	518
Molar Excess Ratio CH <sub>4</sub> /Halocarbon)		1260	840	790
Estimated 1980 Release (kilotons)		265	393	504
Estimated 1980 CH <sub>4</sub> Emissions (megatons)		39	44	48
Excess Ratio (Urban/Remote-1.00)	0.25	1.77	1.48	4.32
Ratio of Excess Ratios (CH <sub>4</sub> /X)		1.77	1.48	4.32
Corrected Ratio of Excess Ratios		0.10 <sup>3</sup>	0.11	0.12

(a) Corrected for total atmospheric burden divided by yearly release in 1980: CH<sub>4</sub>, 10; CCl<sub>3</sub>F, 15; CCl<sub>2</sub>F<sub>2</sub>, 16; CH<sub>3</sub>CCl<sub>3</sub>, 4.8.

Table 3 Urban Halocarbons and Other Trace Gases<sup>(a)</sup>: Los Angeles

Compounds	Concentrations		Average	Std. Dev.
	Maximum	Minimum		
	(ppt)			
CCl <sub>2</sub> F <sub>2</sub>	2,476.6	225.5	860.4	599.4
CCl <sub>3</sub> F	6,953.3	98.4	617.1	636.6
CHCl <sub>2</sub> F	90.0	21.0	38.1	16.4
CCl <sub>2</sub> FCClF <sub>2</sub>	398.0	29.0	119.1	77.5
CClF <sub>2</sub> CClF <sub>2</sub>	150.0	7.5	39.8	32.2
CHCl <sub>3</sub>	877.8	23.1	103.1	103.4
CH <sub>3</sub> Cl	943.9	707.9	833.8	80.2
CH <sub>3</sub> CCl <sub>3</sub>	7,663.2	100.4	1,539.3	1,574.7
CCl <sub>2</sub> CCl <sub>2</sub>	2,267.3	60.8	674.4	498.4
CHClCCl <sub>2</sub>	1,772.3	25.5	312.6	302.3
COCl <sub>2</sub>	61.1	21.1	31.8	8.3
	(ppb)			
NO	259.1	0.5	49.0	60.9
NO <sub>2</sub>	302.4	16.9	82.7	68.8
CH <sub>4</sub>	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 <sub>3</sub>	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<sub>3</sub> 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<sub>3</sub> 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

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Table 4 Ambient Air Hydrocarbons in 39 U.S. Cities<sup>(a)</sup>

Compound	Formula	Concentration (ppbC)	
		Median	Maximum
Isopentane	C <sub>5</sub> H <sub>12</sub>	45.3	3,393
n-Butane	C <sub>4</sub> H <sub>10</sub>	40.3	5,448
Toluene	C <sub>7</sub> H <sub>8</sub>	33.8	1,299
Propane	C <sub>3</sub> H <sub>8</sub>	23.5	393
Ethane	C <sub>2</sub> H <sub>6</sub>	23.3	475
n-Pentane	C <sub>5</sub> H <sub>12</sub>	22.0	1,450
Ethylene	C <sub>2</sub> H <sub>4</sub>	21.4	1,001
m-, p-Xylene	C <sub>8</sub> H <sub>10</sub>	18.1	338
2-Methylpentane	C <sub>6</sub> H <sub>14</sub>	14.9	647
Isobutane	C <sub>6</sub> H <sub>10</sub>	14.8	1,433
Acetylene	C <sub>2</sub> H <sub>2</sub>	12.9	114
Benzene	C <sub>6</sub> H <sub>6</sub>	12.6	273
n-Hexane, 2-Ethyl-1-butene	C <sub>6</sub> H <sub>14</sub> , C <sub>6</sub> H <sub>12</sub>	11.0	601
3-Methylpentane	C <sub>6</sub> H <sub>14</sub>	10.7	351
1,2,4-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	10.6	81
Propylene	C <sub>3</sub> H <sub>6</sub>	7.7	455
2-Methylhexane	C <sub>7</sub> H <sub>16</sub>	7.3	173
o-Xylene	C <sub>8</sub> H <sub>10</sub>	7.2	79
2,2,4-Trimethylpentane	C <sub>8</sub> H <sub>18</sub>	6.8	106
Methylcyclopentane	C <sub>7</sub> H <sub>12</sub>	6.4	293
3-Methylhexane	C <sub>7</sub> H <sub>16</sub>	5.9	168
2-Methylpropene, 1-butene	C <sub>7</sub> H <sub>8</sub>	5.9	365
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	5.9	159
m-ethyltoluene	C <sub>9</sub> H <sub>12</sub>	5.3	83
n-Heptane	C <sub>7</sub> H <sub>16</sub>	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  $O_3$  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  $1 \times 10^7$  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.

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**Table 5** Relative Removal Rates of Urban Hydrocarbons by HO Radicals<sup>(a)</sup>

Compound	k (x10 <sup>-12</sup> ) at 25 C cm <sup>3</sup> /molec s	Concentration (x 10 <sup>10</sup> ) molec/cm <sup>3</sup>	Rate (x10 <sup>-2</sup> ) Second <sup>-1</sup>	% 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, 1-butene	(52.3) (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<sub>3</sub>. 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<sub>3</sub> production. Nevertheless, the global O<sub>3</sub> forming potential, (i.e. the maximum possible global O<sub>3</sub> 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<sub>2</sub> 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<sub>3</sub>. 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) <sup>(a)</sup> x 10 <sup>-15</sup>	Relative Rate (x10 <sup>-4</sup> ) s <sup>-1</sup>	Percentage Rate <sup>(e)</sup> %
HFCs <sup>(b,d)</sup>				
CH <sub>3</sub> CHF <sub>2</sub>	152a	37.0	87.9	0.059
CH <sub>2</sub> FCF <sub>3</sub>	134a	4.8	11.4	0.008
CHF <sub>2</sub> CF <sub>3</sub>	125	2.5	5.9	0.004
HCFCs <sup>(b)</sup>				
CHClF <sub>2</sub>	22	4.7	11.2	0.008
CH <sub>3</sub> CClF <sub>2</sub>	142b	3.8	9.0	0.006
CH <sub>3</sub> CHClF	124	10.0	23.8	0.016
CH <sub>3</sub> CCl <sub>2</sub> F	141b	8.0	19.0	0.013
CHCl <sub>2</sub> CF <sub>3</sub>	123	37.0	87.9	0.089
Other <sup>(c)</sup>				
CH <sub>4</sub>		7.7	4,430.0	2.961
CH <sub>3</sub> CCl <sub>3</sub>		12.0	23.0	0.015
CCl <sub>2</sub> CCl <sub>2</sub> <sup>(f)</sup>		170.0	97.7	0.065
CHClCCl <sub>2</sub>		2,460.0	1,107.0	0.740

(a) k in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>

(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<sup>-1</sup>) given in Table 5.

(f) Taken from the maximum concentration of CH<sub>3</sub>CCl<sub>3</sub> in Table 3.

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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<sub>3</sub> 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<sub>3</sub>CCl<sub>3</sub> 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<sub>AF</sub> for a given alternative fluorocarbon (AF) is taken to be the sum of R<sub>CFC-11</sub> and R<sub>CFC-12</sub> on a molar rather than weight basis. In Table 7, R<sub>CFC-11</sub> and R<sub>CFC-12</sub> in 1982 are shown to be 310 x 10<sup>6</sup> and 444 x 10<sup>6</sup> kg/yr (or 2.3 x 10<sup>9</sup> and 3.7 x 10<sup>9</sup> mole/yr), and hence, R<sub>AF</sub> = 6.0 x 10<sup>9</sup> 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<sub>CFC-11</sub> and C<sub>CFC-12</sub> shown in Table 7, i.e. C<sub>AF</sub> ≤ 0.6 ppbV. This value of C<sub>AF</sub> 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<sub>3</sub>CCl<sub>3</sub> are all comparable despite great differences in their atmospheric lifetimes (τ), i.e. τ<sub>CFC-11</sub> = 65 yr, τ<sub>CFC-12</sub> = 120 yr, and τ<sub>CH<sub>3</sub>CCl<sub>3</sub></sub> = 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<sub>3</sub>CCl<sub>3</sub> 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 τ<sub>CH<sub>3</sub>CCl<sub>3</sub></sub> 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<sub>CH<sub>4</sub></sub> = (500 ± 145) x 10<sup>9</sup> kg/yr or (33 ± 9) x 10<sup>12</sup> mole/yr. The detailed global distribution and seasonal variation of CH<sub>4</sub>, (C<sub>CH<sub>4</sub></sub>), is now available. The latitudinal distribution of annual mean C<sub>CH<sub>4</sub></sub> in 1985 ranges from 1.6 ppm in the Southern Hemisphere to 1.7 ppm in the Northern Hemisphere. Thus, C<sub>CH<sub>4</sub></sub> = 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<sub>4</sub>. The approximate value of τ<sub>CH<sub>4</sub></sub> = 8.2 yr given in Table 1 is close to this value. This value of τ<sub>CH<sub>4</sub></sub> is judged to be one of the better known quantities in the global CH<sub>4</sub> budget, as it is tied to the empirical determination of the lifetime for CH<sub>3</sub>CCl<sub>3</sub>. An accurate value of τ<sub>CH<sub>4</sub></sub> is needed to estimate the oxidation rate of CH<sub>4</sub> 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<sub>4</sub> and other natural HCs, and direct emissions from fossil fuel combustion, with an estimated total production R<sub>CO</sub> of 1060 x 10<sup>9</sup> kg as carbon/yr (or 88 x 10<sup>12</sup> mole/yr). CO reacts rather rapidly with HO radicals (τ<sub>CO</sub> ≈ 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 10 <sup>6</sup> kg	Year	Reference	Est. atmospheric lifetime <sup>(a)</sup> years (NAS 1984)
CFC 11 (CCl <sub>3</sub> F)	200	1983	310	1982	1,8	65
CFC 12 (CCl <sub>2</sub> F <sub>2</sub> )	320	1983	444	1982	1,8	120
CFC 13 (CF <sub>3</sub> Cl)	~ 3.4	1980	—	—	10	400
CFC 22 (CHCl <sub>2</sub> F)	~ 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
CH <sub>3</sub> CCl <sub>3</sub>	~ 120	1983	545	1983	3,11	6.5
CFC 116	~ 4	1980	—	—	10	>500
CCl <sub>4</sub>	~ 140	1979	~830	1983	3,12	50
CH <sub>3</sub> Cl	630	1980	~830	1984	3,6	~ 1.5
CH <sub>3</sub> I	~ 1	1981	—	—	9	0.02
CBrClF <sub>2</sub>	~ 1.2	1984	(~5?)‡	—	4	25
CBrF <sub>3</sub>	~ 1	1984	7-8	1984	2,4	110
CH <sub>3</sub> Br	9.0	1984	—	—	4	2.3
CH <sub>2</sub> BrCl	3.2	1984	—	—	4	—
CHBr <sub>2</sub> Cl	0.9	1984	—	—	4	—
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	~ 1	1984	—	—	4	~ 1
CHBr <sub>3</sub>	~ 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

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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<sub>3</sub>-CO global distributions are also strongly influenced by natural non-methane hydrocarbons (NMHC), particularly isoprene, terpenes, and the C<sub>2</sub>-C<sub>5</sub> alkenes. The most recent estimate for an annual global NMHC emission flux gives 3.7 x 10<sup>11</sup> kg C/yr (or 3.1 x 10<sup>13</sup> 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<sub>2</sub>-C<sub>5</sub>) 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<sub>3</sub> precursors, i.e. CH<sub>4</sub>, 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<sub>3</sub> precursors shown in the last column have been derived from the corresponding production rates multiplied by their relative O<sub>3</sub> forming potentials. The O<sub>3</sub> 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<sup>(a)</sup>

Compound	Production (x10 <sup>12</sup> )	% Contribution
HCFs & HCFCs	0.006	0.0056
CH <sub>4</sub>	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.

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**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)	$k_{\text{HO}}(298 \text{ K})^{(a)}$ $\times 10^{-15}$	Relative Rate ( $\text{s}^{-1}$ ) ( $\times 10^{-4}$ )	Percentage Contribution
<u>HFCs</u>					
CH <sub>3</sub> CHF <sub>2</sub>	152a	0.6 <sup>(b)</sup>	37.0	5.6	0.092
CH <sub>2</sub> FCF <sub>3</sub>	134a	0.6	4.8	0.7	0.011
CHF <sub>2</sub> CF <sub>3</sub>	125	0.6	2.5	0.4	0.007
<u>HCFCs</u>					
CHClF <sub>2</sub>	22	0.6	4.7	0.7	0.011
CH <sub>3</sub> CClF <sub>3</sub>	142b	0.6	3.8	0.6	0.010
CH <sub>3</sub> CHClF	124	0.6	10.0	1.5	0.025
CH <sub>3</sub> CCl <sub>2</sub> F	141b	0.6	8.0	1.2	0.020
CHCl <sub>2</sub> CF <sub>3</sub>	123	0.6	37.0	5.6	0.092
<u>NOPs</u>					
CH <sub>4</sub>		1,600	7.7	3,080.0	50.522
CO		100	240.0	3,000.0	49.210

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

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

to be 0.0056% of total natural O<sub>3</sub> 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<sub>4</sub> (cf. Table 8b).

The results of an analysis of the relative oxidation rates of individual AF vs. natural O<sub>3</sub> precursors are summarized in Table 8b. The global mean concentration of each AF is assumed to be 0.6 ppbV (or  $1.5 \times 10^{10}$  molecule/cm<sup>3</sup> 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<sub>3</sub> precursors, i.e. CH<sub>4</sub> and CO, have been calculated, in turn, from these relative rates corrected for their O<sub>3</sub> forming efficiencies. As before, the O<sub>3</sub> 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<sub>3</sub> 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

The author wishes to thank G. Yarwood and C. Francis for their assistance in the preparation of this manuscript.

