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Potential impact of iodine on tropospheric levels of ozone and other critical oxidants

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Abstract. A new analysis of tropospheric iodine chemistry suggests that under certain conditions this chemistry could have a significant impact on the rate of destruction of tropospheric ozone. In addition, it suggests that modest shifts could result in the critical radical ratio HO_2/OH. This analysis is based on the first ever observations of CH_3I in the middle and upper free troposphere as recorded during the NASA Pacific Exploratory Mission in the western Pacific. Improved evaluations of several critical gas kinetic and photochemical rate coefficients have also been used. Three iodine source scenarios were explored in arriving at the above conclusions. These include: (1) the assumption that the release of CH_3I from the marine environment was the only iodine source with boundary layer levels reflecting a low-productivity source region, (2) same as scenario 1 but with an additional marine iodine source in the form of higher molecular weight iodocarbons, and (3) source scenario 2 but with the release of all iodocarbons occurring in a region of high biological productivity. Based on one-dimensional model simulations, these three source scenarios resulted in estimated I_x (I_x =I + IO + HI + HOI + $2I_2O_2$ +INO_x) yields for the upper troposphere of 0.5, 1.5, and 7 parts per trillion by volume (pptv), respectively. Of these, only at the 1.5 and 7 pptv level were meaningful enhancements in O_3 destruction estimated. Total column O_3 destruction for these cases averaged 6 and 30%, respectively. At present we believe the 1.5 pptv I_x source scenario to be more typical of the tropical marine environment; however, for specific regions of the Pacific (i.e., marine upwelling regions) and for specific seasons of the year, much higher levels might be experienced. Even so, significant uncertainties still remain in the proposed iodine chemistry. In particular, much uncertainty remains in the magnitude of the marine iodine source. In addition, several rate coefficients for gas phase processes need further investigating, as does the efficiency for removal of iodine due to aerosol scavenging processes.

Introduction

Of the trace gases in the troposphere, ozone, together with the free radicals generated by its photolysis, is most responsible for defining the oxidizing capacity of the troposphere. Within the troposphere, the mixing ratio of this trace gas is influenced by both transport and photochemical processes [e.g., *Fabian and Pruchniewicz*, 1977; *Mahlman et al.*, 1980; *Chameides and Walker*, 1973; *Fishman and Crutzen*, 1977; *Liu et al.*,1980]. Conventional thinking suggests that it is the reaction of peroxy radicals, (e.g. HO_2 CH_3O_2, and RO_2, where "R" is any organic grouping) with NO to produce the product species NO_2 that forms the basis of photochemical O_3 formation. Photolysis of NO_2

leads to the release of an O atom which, via reaction with O_2, results in the formation of one net O_3 molecule. Photochemical destruction occurs when the O_3 photolysis product $O(^1D)$ reacts with H_2O to produce two hydroxyl radicals, OH, or when hydroperoxyl HO_2 and OH radicals react with O_3. Less certain is the suggestion that halogen species might also provide a photochemical destruction channel for tropospheric O_3 [e.g., *Chameides and Davis*, 1980; *Singh and Kasting*, 1988; *Barrie et al.*, 1988; *Bottenheim et al.*, 1990; *Chatfield and Crutzen*, 1990; *Keene et al.*, 1990; *Jenkin*, 1993; *Jobson et al.*, 1994; *Le Bras and Platt*, 1995].

Being the most abundant of the halogens, chlorine has undergone the most intense investigation. Both the OH-initiated oxidation of natural and man-made chlorocarbons and the heterogeneous sea-salt reactions have been explored as possible sources of reactive chlorine [e.g., *Singh and Kasting*, 1988; *Keene et al.*, 1990; *Pszenny et al.*, 1993; *Singh*, 1995, and references therein]. However, because of the absence of documented high-altitude sources of chlorine, its high affinity for hydrogen abstraction, and the low reaction probability for converting the product HCl back to reactive chlorine, it now seems unlikely that this halogen by itself represents a significant loss of O_3. A possible exception to this conclusion might involve chemistry within

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the marine boundary layer (BL) [*Singh et al.,* this issue]. (The possibility of interhalogen reactions serving as a sink for O_3 is discussed below in the text.)

Investigations of bromine have also focused on the marine BL, but in this case the region of interest has been polar latitudes. Direct measurements of BrO radicals at levels as high as 17 pptv during Arctic springtime conditions [*Hausmann and Platt,* 1994] have indicated the presence of a significant BL source of reactive bromine.   These measurements were also found to coincide with dramatic decreases in ambient ozone levels (e.g., from 40 to <0.5 parts per billion by volume (ppbv)) [*Anlauf et al.,* 1994]. These observations have led to considerable speculation about possible O_3 destruction mechanisms, but in most cases these have been difficult to quantify due to the uncertainties associated with complex heterogeneous sources of bromine [*Finlayson-Pitts et al.,* 1990; *McConnell et al.,* 1992; *Fan and Jacob,* 1992]. Even so, the polar observations of BrO would seem to suggest that under some conditions, bromine could provide an important BL sink for O_3.

The impact of iodine in the troposphere, like chlorine and bromine, has also received attention in the context of marine BL chemistry [*Chameides and Davis,* 1980; *Chatfield and Crutzen,* 1990; *Jenkin et al.,* 1985; *Jenkin,* 1993]. More recently, it has been proposed as a sink for O_3 in the lower stratosphere [*Solomon et al.,* 1995]. Unlike bromine and chlorine, the production of reactive iodine requires no complex heterogeneous mechanism. For example, of the companion methyl halides, CH_3I is the only species that readily photolyzes within the troposphere. In fact, its photochemical lifetime is roughly 4 to 5 times shorter than the most photosensitive bromine compound $CHBr_3$.

The objective of this study will be to reexamine the role of iodine as a tropospheric sink for O_3 and to also explore its ability to modulate the centrally important radical ratios HO_2/OH and NO_2/NO. This analysis has been motivated by both the availability of new CH_3I data for the middle and upper free troposphere and the updated values for several critical photochemical/gas kinetic rate coefficients. The CH_3I observations are the first of their kind and were recorded as part of NASA's western Pacific Exploratory Mission (PEM-West A).

2. Iodine Sources and Transport

2.1 Marine Observations of Iodine

As previously reviewed by *Chameides and Davis* [1980], there is now ample evidence showing that the methyl halide CH_3I is a metabolic byproduct of many species of marine algae. This iodocarbon alone was estimated to provide a global source of iodine of the order of 1-2 Tg/yr. By comparison, industrial sources of volatile iodine were indicated to be less than 10% of the natural biogenic source. Yet other marine sources such as the direct photolysis of iodine compounds in ocean surface waters were listed as potentially important but still nonquantifiable.

More recently, *Solomon et al.* [1995] have provided an update of global marine iodine sources. The most significant additions have been those reported by *Moore and Tokarczyk* [1992], *Klick and Abrahamsson* [1992], and *Schall and Heumann* [1993].   Collectively, these investigators' observations indicate that the source strength for other iodocarbons (e.g., CH_2I_2, C_2H_5I, and CH_2ICl) could possibly

exceed that for CH_3I. For example, Schall and Heumann's measurements in the Arctic suggest that CH_3I may only represent 26% of the total marine iodine released to the atmosphere. (Note that because of an expected red shift in the absorption spectrum for species such as CH_2I_2 and C_2H_5I relative to CH_3I, one would expect the lifetimes for these species to be even shorter than that for CH_3I.)

Atmospheric measurements of CH_3I have primarily been confined to the marine BL with average mixing ratios ranging from 1 to 3 pptv [*Liss and Slater,* 1974; Singh et al., 1983; *Rasmussen et al.,* 1982; *Reifenhauser and Heumann,* 1992]; but for regions characterized as having high biological productivity, much higher mixing ratios have been reported (i.e., 10-20 pptv), with one recent observation in the coastal waters of England reaching as high as 43 pptv [*Oram and Penkett,* 1994]. Marine areas nominally labeled as high-productivity regions are those typically found at high latitudes during springtime or those characterized as experiencing marine upwelling. In the latter regard, the equatorial upwelling in the Pacific could define an important area for the atmospheric influence of iodine. This conclusion reflects the fact that not only would this region be a potentially rich source of iodine but also would be a region that experiences considerable deep convection.

As noted earlier in the text, the CH_3I observations recorded during PEM-West A are unique in that both marine BL and free tropospheric measurements were recorded. These measurements were based on whole air samples collected with preconditioned stainless steel canisters. The contents were typically analyzed within 7 days using standard gas chromatograph (GC)/electron capture analysis techniques [*Blake et al.,* 1994, this issue]. Among the problems that may have impacted on the integrity of these samples was the extremely dry conditions (i.e., specific humidity <2 g/kg) experienced in the upper troposphere. Previous experience has shown that in some cases, loss of halocarbons to canister walls could occur. (Following PEM-West A, it was determined that adding 5 torr of purified H_2O prior to use typically alleviated the above problem.) Since there have been no previous studies indicating increases of CH_3I during storage, this suggests that the results reported here most likely represent a lower limit to the true CH_3I level.

Two different calibration methods were used in an effort to establish the accuracy of the reported CH_3I measurements. In the first approach to verify the dilution procedure, a low pptv CH_3Br standard, prepared by NIST, was compared against CH_3I and CH_3Br standards made from each of the pure compounds. In addition, permeation tubes for methyl iodide and methyl bromide were diluted in ultrapure air as a means of calibrating working reference gases.   Good agreement was observed between the two methods. To estimate the precision of the CH_3I measurements, 11 samples collected consecutively during a BL run and 7 consecutive samples collected around 7 km were analyzed. For the BL run the results were 1.3±0.08; whereas, at 7 km the mean and standard deviation were 0.13±0.03 pptv. (A more detailed description of the analytical technique used in the analysis of methyl halides can be found in the work of *T.-Y. Chen et al.,* manuscript in preparation, 1996.)

As still a further check on the reliability of these field data, we have compared the observed PEM-West A values for dimethyl sulfide (DMS) against those of CH_3I. (We note here that the GC-mass spec technique used during PEM West

A to measure DMS included independent calibration runs for each individual measurement of DMS.)   Since both compounds have predominantly marine sources, to a first approximation one might expect that the ratio of concentration for these two species should be similar at both high and low altitudes, provided their atmospheric lifetimes were not too dissimilar.   In fact, at low altitudes some difference exists because DMS is controlled by OH oxidation and CH_3I by photolysis (e.g., DMS <1 day versus CH_3I 3-4 days); whereas at upper free tropospheric altitudes, reduced levels of OH and an enhanced UV flux result in nearly the same lifetime (i.e., ~2 days). For the PEM West A data set, a comparison of matched BL observations of DMS and CH_3I (all above the limit of detection) gave a median ratio value for DMS/CH_3I of 25. By comparison, for the highest-altitude data blocks, the value of this ratio was estimated at 43. Given the shift in lifetimes with altitude, one might actually expect that the high-altitude ratio should have been lower than that at low altitudes. However, upon reflecting on the fact that frequently there was a high degree of natural variability in the levels of both species and that the sampling integration times differed significantly (e.g., DMS, 3-4 min; CH_3I, 10-60 s), one could argue that the level of agreement cited above still suggests that the high-altitude measurements of CH_3I were probably not seriously compromised. Further evidence supporting this conclusion can be found in the level of correspondence between the DMS and CH_3I measurements shown in Figure 1. This figure shows a scatterplot of these two species under conditions for which their lifetimes would be somewhat similar, i.e., data recorded for altitudes above 4 km. In this case a regression analysis, based on data taken from all latitudes, gave a Pearson R correlation coefficient of

0.71. Still the possibility of "offset" errors cannot be totally ruled out. At this time, therefore, our assessment is that the CH_3I measurements are probably good to within a factor of 2 to 3.

The range and median values for the CH_3I observations recorded during PEM-West A are shown in Figures 2a and 2b. These data have been binned every 2 km except for low altitudes where the height was confined to 1 km. In addition, both the upper and the lower 5% of the observations have been trimmed in the "range" display. The latitudinal zones shown are those designated elsewhere as "western tropical North Pacific," $0°-18°N$, and "western North Pacific rim," $18°-42°N$.   This division reflects the PEM-West A O_3 tendency analysis reported by *Davis et al.* [this issue].

The data displayed in Figures 2a and 2b show marine BL values of CH_3I reaching as high as 1.5 to 1.8 pptv. For the tropics these levels are then observed to decrease to < 0.5 pptv. In contrast to the tropics, the Pacific rim data reveal the presence of many elevated CH_3I observations at high altitude, with values at 10-12 km reaching >1 pptv. These high-altitude values reflect the influence of observations recorded during PEM-West A flight 9. This mission was unique in that the flight profile was designed to sample the low-altitude inflow and high-altitude outflow from Typhoon Mireille. The strong vertical pumping action from this typhoon produced enhanced high-altitude levels of both CH_3I as well as DMS [*Newell et al.*, this issue; *Thornton et al.*, this issue] Median values of CH_3I are seen to range from highs of 0.6 to 1 pptv in the marine BL to lows of 0.1 to 0.15 at middle and high-altitudes. The Pacific rim region is seen as having the largest range in median values (e.g., 1 to 0.1 pptv) with the minimum coming at middle altitudes. The
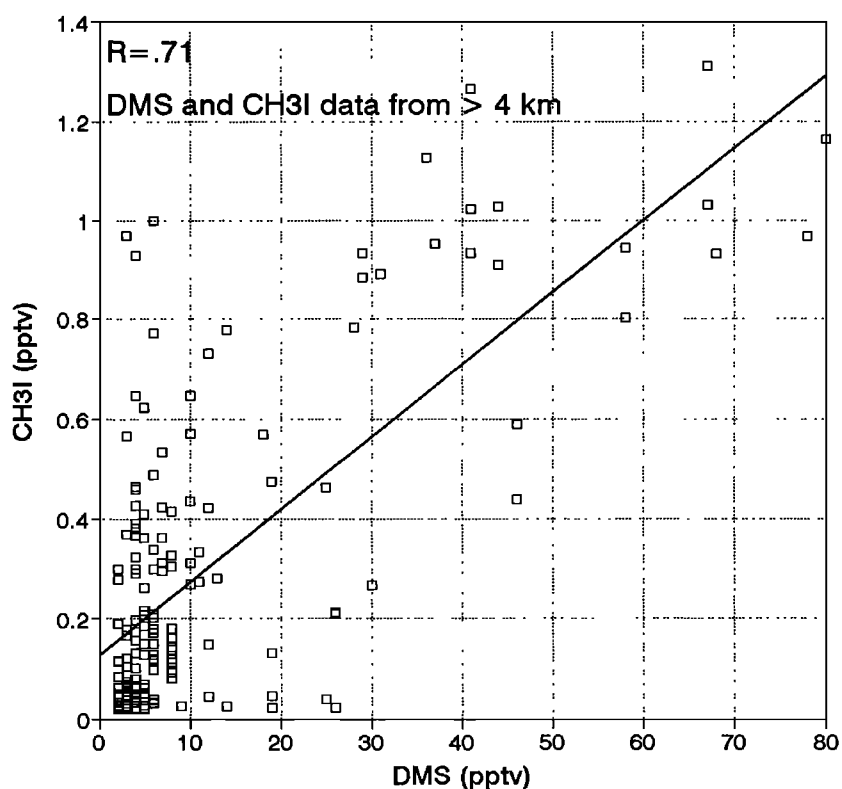

Figure 1. Scatterplot of CH_3I versus DMS. Data have been restricted to simultaneous measurements of CH_3I and DMS above 4 km. The solid line indicates the best fit to the data.
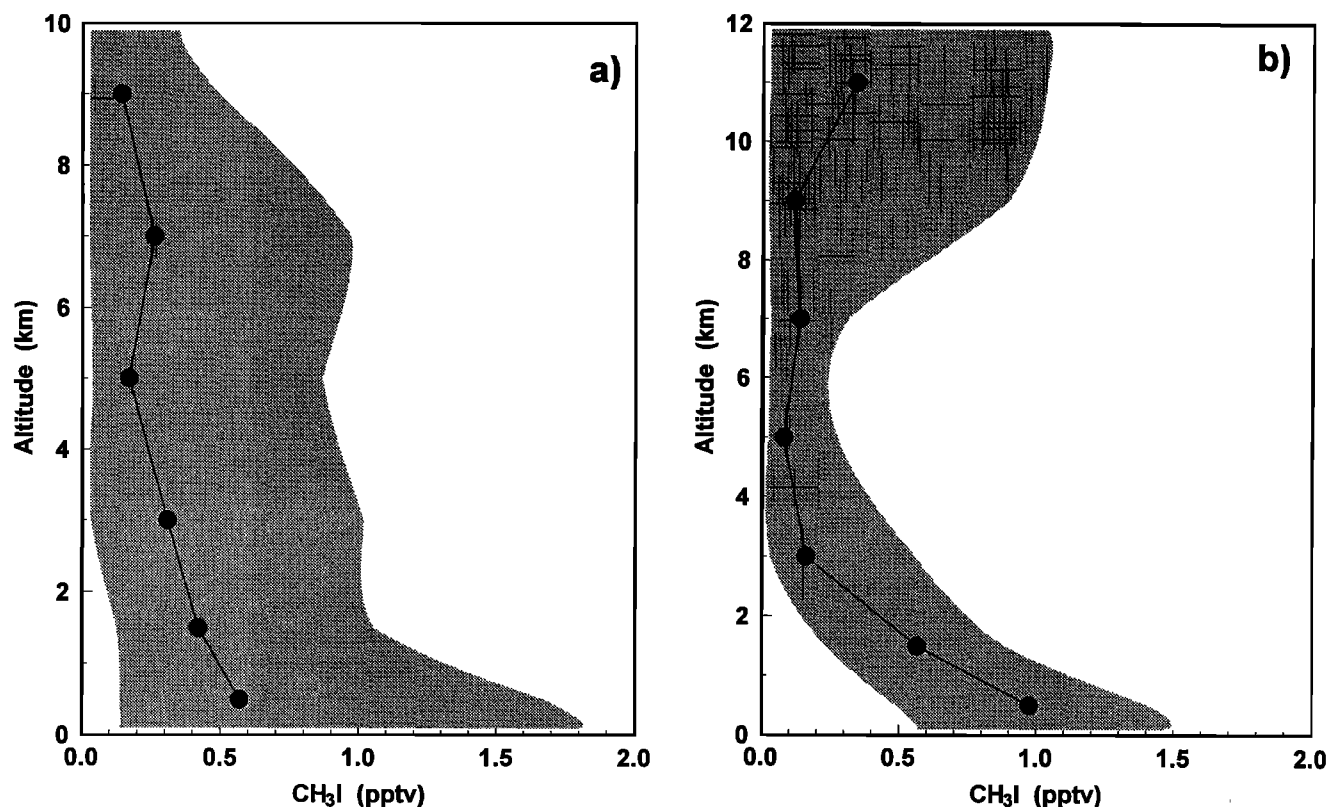
Figure 2. Altitude distributions for CH_3I as measured during PEM-West A for the latitude ranges: (a) 0°-18°N and (b) 18°-42°N. Circles indicate the median values for altitude bins: 0-1 km, 1-2 km, 2-4 km, 6-8 km, 8-10 km, and 10-12 km. Shaded regions indicate the range of CH_3I observations within each bin after trimming the upper and lower 5% of the data within each bin.

resulting hour glass shaped profile is thus seen to be similar to those for several other PEM-West A trace gases whose distributions were strongly influenced by deep convection [e.g., *Blake et al.*, this issue]. By contrast, in the tropics, although BL values start lower (i.e., 0.6 pptv), a rather steady roll-off in CH_3I median values occurs from the BL to altitudes of 8-10 km, resulting in a high-altitude median value of ~0.15 pptv.

2.2. Vertical Transport and I_x Distributions

As discussed below in the text with reference to the photochemistry of tropospheric iodine, the abundance of total reactive iodine I_x (I_x= I +IO + HOI + HI + $2I_2O_2$ + INO_x) in the middle and upper troposphere has been assessed in terms of a photochemical source, e.g., photolysis of CH_3I and/or other iodocarbons, and losses in the form of surface deposition and heterogeneous uptake by cloud droplets, precipitation, and possibly aerosols. Thus given the stochastic nature of these loss processes in the middle and upper troposphere, one can estimate that the timescales involved could be significantly longer than that for vertical transport. We have investigated this question in this study by using a simple one-dimensional model [*McKeen et. al.*, 1989] that incorporates a first-order diffusion process to describe vertical transport.

A particular concern in employing the one-dimensional formulation is that it is difficult to envision how such a

representation might adequately simulate deep convective processes that obviously are a major contributor to the relatively high mixing ratios of CH_3I in the upper troposphere. In this regard we have assumed that the entrainment and detrainment of air by convective processes has been effective at nearly all altitudes. In other words, the combination of deep and shallow convection effectively mix boundary layer air to various altitudes. Moreover, we assume that the ensemble of air masses sampled during PEM-West A were representative of the ambient environment. As discussed in the above text, for the case of the tropics an examination of the median profile of CH_3I (e.g., Figure 2a) as well as that of DMS does show a gradual decrease with altitude. Thus this is consistent with the above assumptions, and suggests that the median profile can be simulated with the eddy diffusion formulation.

For this investigation a single value of the diffusion coefficient (K_z) was used from 50 meters above the surface to the highest altitudes of the model at 12 km. Below 50 m a very stable layer was assumed with I_x being immediately deposited at the surface upon contact. The initial concentrations of I_x and CH_3I were assumed to be zero. An integration time of 20 days was chosen so as to permit CH_3I to reach a steady state condition at high-altitudes.

The key features of this one-dimensional transport simulation are illustrated in Figure 3. Also shown are the median values estimated for CH_3I as given in Figure 2a. With photolysis acting as the only loss mechanism for CH_3I,
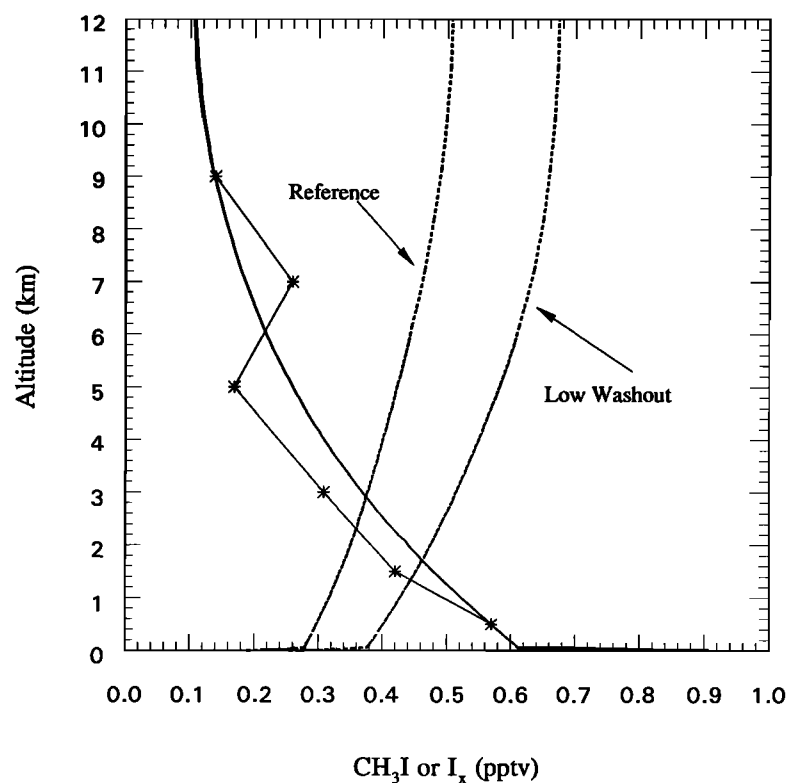
CH$_3$I or I$_x$ (pptv)

Figure 3. Altitude profiles of CH$_3$I and I$_x$ based on one-dimensional model simulations. Asterisks indicate the median values of CH$_3$I for the PEM-West A tropical zone 0°-18°N. The solid line indicates the simulated profile for CH$_3$I assuming an emission flux of 2×10^{11} molecules/m^2/s and an eddy diffusion coefficient K$_z$ of 80 m^2/s. Dotted lines indicate I$_x$ levels for: (1) K$_z$ value of 80 m^2/s and washout rates according to Table 1, ("reference" curve), and (2) K$_z$ value of 80 m^2/s with washout rates from Table 1 decreased by one half below 5 km and zero for altitudes above 5 km ("low washout").

a reasonable fit to the CH$_3$I experimental observations was found when K$_z$ was assigned a value of 80 m^2/s and the surface emission rate was given a value of 2×10^{11} molecules/m^2/s. In this case, the value of K$_z$, relative to the photolysis loss rate, defines the vertical gradient for CH$_3$I, while the flux value simply shifts the vertical profile along the abscissa. We note that our value for K$_z$ of 80 m^2/s is only slightly larger than the value used by *Liu et al.* [1984] (i.e., 50-70 m^2/s). These authors based their value on observations of ^{222}Rn over the continental United States during summertime. Like CH$_3$I, the tracer ^{222}Rn has only a surface source and during the summer season is probably also dynamically forced by convection to high-altitudes.

The I$_x$ "reference" profile shown in Figure 3 was obtained using the same K$_z$ value together with an altitude dependent washout rate for all soluble species as defined by *Logan et al.* [1981] (see Table 1). The resulting I$_x$ profile shows a maximum of ~ 0.5 pptv for altitudes approaching 12 km. To explore the magnitude of influence of the assumed value for the washout rate on I$_x$, a simulation was also carried out in which this rate was reduced by a factor of ½ for altitudes below 5 km and to zero above 5 km. As shown in Figure 3, I$_x$ is enhanced by only 0.2 pptv, yielding a maximum value of 0.7 pptv. The effect resulting from assuming a much faster I$_x$ removal rate than that employed for the "reference" profile is discussed below in the text.

For purposes of exploring the tropospheric impact of iodine in this investigation, we have selected three I$_x$ source

scenarios. The low scenario, involving 0.5 pptv of I$_x$ at 10 km, assumes CH$_3$I to be the only source of iodine and uses the "reference" value of K$_z$ of 80 m^2/s and a CH$_3$I flux of 2×10^{11} molecule/m^2/s, e.g. low productivity marine water. A somewhat more realistic scenario, we believe, is one involving 1.5 pptv of I$_x$ which reflects the inclusion of source compounds like CH$_2$I$_2$ and C$_2$H$_5$I that could more than double the iodine flux to the atmosphere. The final scenario explored here involves a high-altitude value of I$_x$ of 7 pptv. This scenario considers possibilities such as CH$_3$I defining only 26% of the marine iodine flux to the troposphere (see earlier discussion of iodine sources), lower loss rates for I$_x$, and higher marine primary productivity relative to that observed during PEM-West A. We note that vertical profiles of I$_x$ for scenarios 2 and 3 were obtained here by scaling the above cited 10-km values according to the I$_x$ reference profile in Figure 3.

3. Tropospheric Iodine Chemistry and Model Results

3.1 Description of Model

The basic photochemical model used in this study is similar to that described by *Davis et al.* [this issue], *Crawford et al.* [this issue], and *Davis et al.* [1993]. Iodine chemistry was added to this basic model as per the reactions shown in Table 1. Once the level of I$_x$ was established, as per the discussion in the above text, the partitioning of I$_x$ and

Table 1. Tropospheric Iodine Reactions in the Evaluation of Iodine Phochemistry

Reaction	J or K Values	Reference
(R1) $CH_3I+h\nu \rightarrow CH_3+I$	7.9×10^{-6} [a]	cross sections from *Calvert and Pitts* [1963]
(R2) $I+O_3 \rightarrow IO+O_2$	$2.0 \times 10^{-11} \exp(-890/T)$	*Atkinson et al.* [1993]
(R3) $I+HO_2 \rightarrow HI+O_2$	$1.5 \times 10^{-11} \exp(-1090/T)$	*Atkinson et al.* [1993]
(R4) $I+NO_2+M \rightarrow INO_2+M$	$k_o=3.0 \times 10^{-31}(T/300)^{-1}[N_2]^b$ $k_{inf}=6.6 \times 10^{-11}$ $F_c=[\exp(-T/650)+\exp(-2600/T)]$	*Atkinson et al.* [1993]
(R5) $INO_2+h\nu \rightarrow .5(I+IO+NO+NO_2)$	2.9×10^{-3}	assumed same as $IONO_2+h\nu$
(R6) $IO+h\nu \rightarrow I+O$	2.2×10^{-1} [a]	cross sections from *Stickel et al.* [1990] and *Laszlo et al.* [1995]
(R7) $IO+NO \rightarrow I+NO_2$	$7.3 \times 10^{-12} \exp(330/T)$	*Atkinson et al.* [1993]
(R8) $IO+HO_2 \rightarrow HOI+O_2$	8.4×10^{-11}	*DeMore et al.* [1994]
(R9) $IO+IO \rightarrow .2(2I+O_2)+.8(I_2O_2)$	$1.7 \times 10^{-12} \exp(1020/T)$	*Atkinson et al.* [1993]/ products *Jenkin et al.* [1985]
(R10) $IO+NO_2+M \rightarrow IONO_2+M$	$k_o=7.7 \times 10^{-31}(T/300)^{-5}[N_2]^b$ $k_{inf}=1.6 \times 10^{-11}$ $F_c=0.4$	*Atkinson et al.* [1993]
(R11) $IONO_2+h\nu \rightarrow .5(I+IO+NO_2+NO_3)$	2.9×10^{-3} [a]	cross sections from *Atkinson et al.* [1993] products assumed, this work
(R12) $IONO_2 \rightarrow IO+NO_2$	$2.07 \times 10^{-15} \exp(-11859/T)$	*Chatfield and Crutzen.* [1990]
(R13) $HI+OH \rightarrow I+H_2O$	3.0×10^{-11}	*Atkinson et al.* [1993]
(R14) $HOI+h\nu \rightarrow I+OH$	5.9×10^{-3} [a]	cross sections from *Atkinson et al.* [1993]
(R15) $HOI+OH \rightarrow IO+H_2O$	2.0×10^{-13}	*Chameides and Davis* [1980]
(R16) $I_2O_2+h\nu \rightarrow 2I+O_2$	1.3×10^{-2} [a]	assumed $9 \times (Cl_2O_2+h\nu)$ cross sections from *DeMore et al.* [1994]
(R17) $HI \rightarrow$ deposition	1.16×10^{-5}	estimated
(R18) $HOI \rightarrow$ deposition	1.16×10^{-5}	estimated
(R19) $I_2O_2 \rightarrow$ deposition	1.16×10^{-5}	estimated
(R20) $HI \rightarrow$ rainout/washout	see footnote c	*Logan et al.* [1981]
(R21) $HOI \rightarrow$ rainout/washout	see footnote c	*Logan et al.* [1981]
(R22) $I_2O_2 \rightarrow$ rainout/washout	see footnote c	*Logan et al.* [1981]
(R23) $HI \rightarrow$ aerosol	see text	estimated
(R24) $HOI \rightarrow$ aerosol	see text	estimated
(R25) $I_2O_2 \rightarrow$ aerosol	see text	estimated

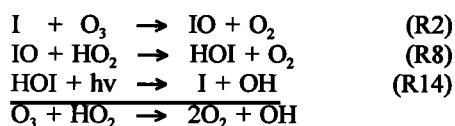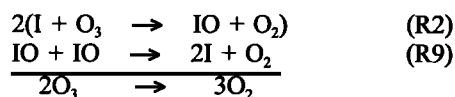[a]Photolysis rates have been calculated for a solar zenith angle of 30° at the surface.

[b]$k=(k_o k_{inf}/(k_o+k_{inf}))F_c$.

[c]2.31×10^{-6} (0-4 km), $2.31 \times 10^{-6} \exp(1.6-4z)$ (4-12 km).

the interaction of iodine species with O_3 and other HO_x species was defined by our iodine-modified box model.

Figure 4 shows our current iodine chemistry in schematic form, thus illustrating the extensive cycling among the individual iodine species I, IO, I_2O_2, HOI, and INO_x. Model-estimated vertical profiles for each of these species are shown in Figure 5. These profiles are based on a high-altitude I_x level of 1.5 pptv. They tend to show that at all altitudes but 8-10 km, HOI is the dominant iodine species. For the latter altitude range, the concentration levels of I, HI, IO, and HOI are seen to all lie within a factor of 2.5 of each other. By comparison, the species I_2O_2, INO_2, and $IONO_2$ are 1 to 2 orders of magnitude lower in concentration.

From a detailed analysis of the chemistry presented in Figure 4, two O_3 destruction sequences can be identified:

$$2(I + O_3 \rightarrow IO + O_2) \quad (R2)$$
$$IO + IO \rightarrow 2I + O_2 \quad (R9)$$
$$\overline{2O_3 \rightarrow 3O_2}$$

$$I + O_3 \rightarrow IO + O_2 \quad (R2)$$
$$IO + HO_2 \rightarrow HOI + O_2 \quad (R8)$$
$$HOI + h\nu \rightarrow I + OH \quad (R14)$$
$$\overline{O_3 + HO_2 \rightarrow 2O_2 + OH}$$

Quite noteworthy here is that the rate-controlling step in each sequence involves the reaction of IO, either with itself or with HO_2. In this regard, the proposed iodine chemistry differs from that outlined for the lower stratosphere by *Solomon et al.* [1995]. These investigators have suggested that interhalogen/IO reactions involving BrO and ClO radicals were probably the dominant O_3 loss processes in the lower stratosphere. This reflects the fact that *Solomon et al.* [1995] estimate much higher levels of bromine and chlorine for the lower stratosphere than those predicted by our standard model for the upper troposphere. In our standard model only gas phase species such as CH_3Cl, CH_3Cl_3, and C_2Cl_4 have been considered as sources of Cl_x. This results in only a few pptv of Cl_x, most of which is tied up in the form of HCl and therefore of little chemical consequence.

To further explore the possible importance of interhalogen chemistry in the upper troposphere, we have examined two other possible Cl_x sources. The first of these considered transport of a Cl_x source from the stratosphere. An upper limit to the amount of Cl_x from this source can be estimated by assuming that both O_3 and Cl_x are inert tracers in the lower stratosphere and upper troposphere. We believe this should be a reasonably good assumption for O_3 as its production and loss rates are very small [e.g., *Davis et al.*, this issue]. For Cl_x, one would intuitively expect that soluble

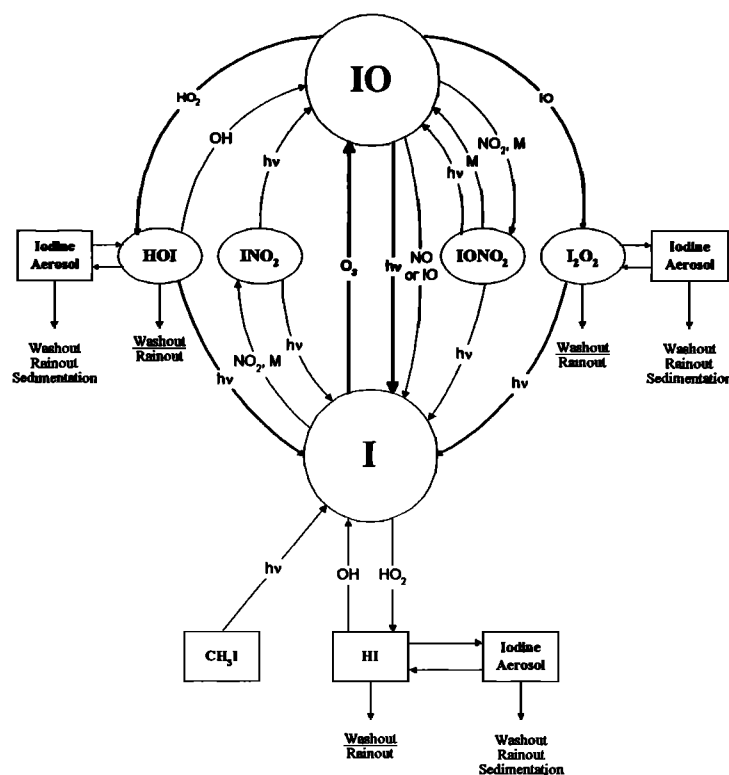**Tropospheric Iodine Photochemical Reaction Scheme**

Figure 4. Tropospheric iodine photochemical reaction scheme. The relative flux strength for each pathway is indicated by the width of each connecting line. Stable species are those shown as rectangles. Short-lived species are indicated as circles and ellipses.

species like HCl would be effectively scavenged by high-altitude clouds. However, extensive observations of similar species (i.e., NO_y) suggests that it might tend to behave as if it were nearly inert [e.g., *Murphy et al.*, 1993; *Liu et al.*, this issue; and *Smyth et al.*, this issue]. Given that the assumption of inertness of Cl_x and O_3 is correct, the ratio Cl_x/O_3 should be approximately constant for the lower stratosphere and upper troposphere. Thus using values near 20 km [*World Meteorological Organization (WMO)*, 1989], we have estimated a value for Cl_x/O_3 of $\sim 5 \times 10^{-4}$. For the tropical zone $0°-18°N$, where the median level of O_3 was 32 ppbv, this gives an estimated value for the mixing ratio of Cl_x of 16 pptv. Similarly, for the Pacific rim region ($18°-42°N$) where the median value of O_3 was 45 ppbv, the estimated mixing ratio for Cl_x would be 23 pptv. Thus we estimate that these Cl_x levels could provide no more than a 10^5 molecules/cm^3 source of ClO, assuming only gas phase chemistry to be important. At this level the concentration is more than 2 orders of magnitude less than that for HO_2 and hence would render any interhalogen O_3 sink reaction unimportant.

The other high-altitude source of Cl_x considered here involves the reaction of sulfuric or nitric acid with sea-salt aerosols, the latter being transported to the upper troposphere via deep convection. This source, together with HCl released from the gas phase oxidation of chlorocarbons (see above text), has been suggested as a possible contributor to the 400 pptv levels of HCl reported for the tropical tropopause by *Tuck et al.* [1995]. Our assessment of this alternate source suggests that if only gas phase chemistry is invoked, the

resulting ClO level gives a rate for the IO + ClO ozone sink reaction that is still only a few percent of that for (R8). Thus we conclude that if interhalogen O_3 sink reactions are to be important in the troposphere, a significant yet unidentified source of reactive chlorine will need to be found. This could potentially be some form of heterogeneous process which might not only release chlorine but also bromine.

Although some uncertainty still remains concerning aspects of the gas phase chemistry of iodine, the issue of I_x heterogeneous reactions encompasses perhaps an even greater uncertainty. As indicated in Table 1, washout/rainout and surface deposition are major components of the current model. In the marine BL this results in an approximate 1-day lifetime for I_x. By comparison, for middle free tropospheric altitudes these processes lead to an I_x lifetime that ranges from 5 to 10 days, thus being comparable to that for reasonably fast vertical mixing. For the upper free troposphere, as evaluated by equations 20-23, washout/rainout rates are factors of 5 to 15 times slower than vertical mixing. Thus further enhancements in the removal rate due to microphysical processes operating within deep convection or, alternatively, to other noncloud related aerosol heterogeneous losses could potentially lead to significant decreases in the high-altitude levels of I_x. To explore this possibility, simulations were carried out using the previously described one-dimensional model in which removal times of 7 and 14 days were assumed. The results showed that I_x was decreased at the highest altitudes by 50% and 30%, respectively.
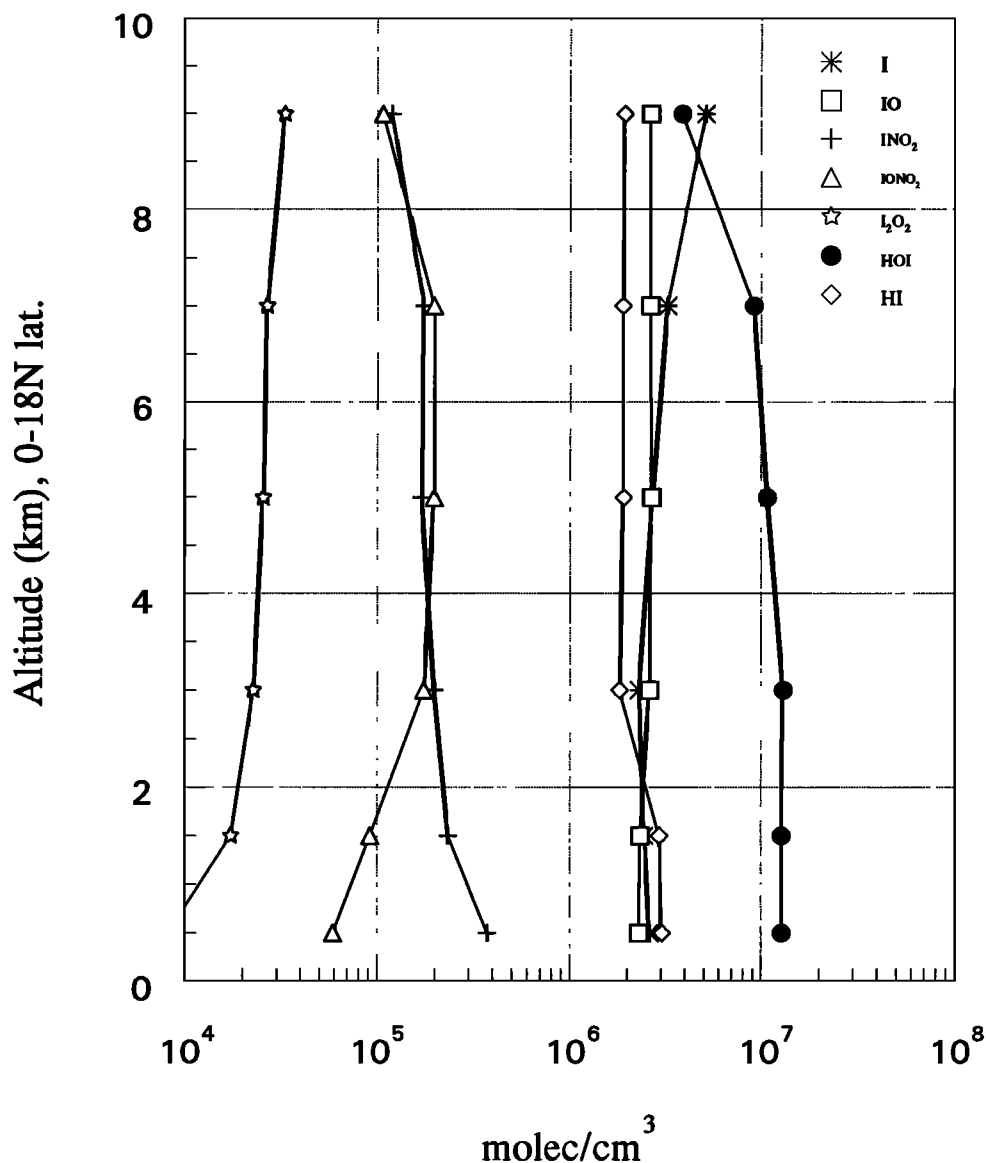
Figure 5. Altitude profiles of reactive iodine species for 0°-18°N based on the "reference" altitude trend given in Figure 2, scaled to give 1.5 pptv of I_x at high-altitude.

Solomon et al. examined the issue of aerosol sinks for iodine as related to the lower stratosphere. The chemical nature of these aerosols was taken to be predominantly sulfate and/or sulfuric acid, as are probably also aerosols for the upper troposphere. Although very little information is now available on heterogeneous reactions of iodine, Solomon and co-workers have argued from analogy with chlorine chemistry [e.g., *Hanson et al.*, 1994] that because of the high reactivity of iodine, it would most likely not be permanently removed but would simply be recycled. Furthermore, these investigators suggest that the partitioning of iodine between the aerosol and gas phases would tend to favor most iodine being in the gas phase. However, given the impact of a 14-day aerosol sink, it would seem prudent to more fully explore the issue of heterogeneous loss of iodine.

3.2 Ozone Destruction

As discussed earlier in the text, the two most significant iodine-related O_3 sinks involve the reaction sequences (R2),

(R8), (R14), and (R2), and (R9). Ozone destruction due to the IO self-reaction (R9) is found to be strongly dependent on both the altitude and the absolute I_x level selected. Thus only for I_x levels at 7 pptv are IO levels found to be sufficiently high that this reaction contributes greater than 10% to the total iodine-related O_3 destruction; for example, see Table 2. In addition, even at 7 pptv of I_x, (R9) does not become significant until reaching altitudes >6 km. For example, from Table 2 it can be seen that only at 10 to 12 km is approximately 30% of the iodine-related O_3 destruction due to the IO self-reaction.

As shown in Table 2 (top), for the case of 0.5 pptv I_x the predicted O_3 destruction $D(O_3)$ due to iodine never exceeds that estimated from HO_x alone by more than 8%. This leads to a relatively small 0 to 12-km column $D(O_3)$ effect of only 2%. Based on what we believe to be a more typical source scenario, involving 1.5 pptv I_x, Table 2 (middle) indicates that for some altitude/latitude ranges, as much as a 24% increase in $D(O_3)$ might occur. In all cases the general trend in $D(O_3)$ is seen as involving increasing iodine effects with

Table 2. Diurnally Averaged, Column Integrated Ozone Destruction from Iodine

Latitude	Altitude	Without I_x, molec/cm²/s	With .5 pptv I_x*, molec/cm²/s	%Effect
0-18	0-1	4.84E+10	4.91E+10	1.41
0-18	1-2	4.57E+10	4.65E+10	1.74
0-18	2-4	8.86E+10	9.01E+10	1.74
0-18	4-6	5.57E+10	5.72E+10	2.62
0-18	6-8	3.70E+10	3.82E+10	3.27
0-18	8-10	0.85E+10	0.91E+10	7.81
		(28.4E+10)[b]	(29.0+10)[b]	(2.24)[b]
18-42	0-1	5.10E+10	5.17E+10	1.31
18-42	1-2	7.69E+10	7.77E+10	1.04
18-42	2-4	9.01E+10	9.15E+10	1.57
18-42	4-6	5.98E+10	6.12E+10	2.27
18-42	6-8	2.36E+10	2.47E+10	4.46
18-42	8-10	1.33E+10	1.40E+10	5.64
18-42	10-12	0.39E+10	0.41E+10	6.81
		(31.9E+10)[b]	(32.5E+10)[b]	(1.98)[b]

Latitude	Altitude	Without I_x, molec/cm²/s	With 1.5 pptv I_x*, molec/cm²/s	% Effect
0-18	0-1	4.84E+10	5.05E+10	4.24
0-18	1-2	4.57E+10	4.81E+10	5.22
0-18	2-4	8.86E+10	9.32E+10	5.20
0-18	4-6	5.57E+10	6.01E+10	7.84
0-18	6-8	3.70E+10	4.06E+10	9.80
0-18	8-10	0.85E+10	1.05E+10	23.81
		(28.4E+10)[b]	(30.3E+10)[b]	(6.71)[b]
18-42	0-1	5.10E+10	5.30E+10	3.94
18-42	1-2	7.69E+10	7.93E+10	3.11
18-42	2-4	9.01E+10	9.43E+10	4.71
18-42	4-6	5.98E+10	6.39E+10	6.82
18-42	6-8	2.36E+10	2.68E+10	13.51
18-42	8-10	1.33E+10	1.156E+10	17.44
18-42	10-12	0.39E+10	0.47E+10	21.30
		(31.9E+10)[b]	(33.8E+10)[b]	(5.98)[b]

Latitude	Altitude	Without I_x, molec/cm²/s	With 7 pptv I_x*, molec/cm²/s	%Effect
0-18	0-1	4.84E+10	5.80E+10	20
0-18	1-2	4.57E+10	5.67E+10	24
0-18	2-4	8.86E+10	11.0E+10	24
0-18	4-6	5.57E+10	7.60E+10	36
0-18	6-8	3.70E+10	5.40E+10	46
0-18	8-10	0.85E+10	1.89E+10	123
		(28.4E+10)[b]	(37.3E+10)[b]	(32)[b]
18-42	0-1	5.10E+10	6.04E+10	18
18-42	1-2	7.69E+10	8.80E+10	14
18-42	2-4	9.01E+10	11.0E+10	22
18-42	4-6	5.98E+10	7.89E+10	32
18-42	6-8	2.36E+10	3.93E+10	66
18-42	8-10	1.33E+10	2.60E+10	95
18-42	10-12	0.39E+10	0.85E+10	122
		(31.9E+10)[b]	(41.1E+10)[b]	(29)[b]

Read 4.84E+10 as 4.84×10^{10}.
* I_x levels at all altitudes have been scaled to the "reference" curve given in Figure 3.
[b] Column integrated numbers

increasing altitude. However, it must be recognized that this trend is strongly influenced by the rapidly decreasing contribution to $D(O_3)$ from HO_x chemistry alone. As a result, although the percent change in $D(O_3)$ is largest for high-altitudes, the total column effect on $D(O_3)$ is actually more influenced by middle free tropospheric altitudes.

A similar trend in $D(O_3)$ is seen for I_x levels of 7 pptv, e.g., Table 2 (bottom). In this case, the upper altitude values of $D(O_3)$ are shifted by factors of 2 or more due to the inclusion of iodine chemistry. The resulting enhancement in total column O_3 destruction is approximately 30%. If this evaluation of the PEM-West A tropical regime is further extended to the tropopause (based on generic high-altitude tropical trace gas compositions), we find that total O_3 column destruction is increased by only an additional 2% over that cited above for 0-10 km. This result once again makes the point that although very large effects can be found from iodine at high-altitudes, these altitudes tend to contribute less to the total column $D(O_3)$ effect.

Taking for the moment the most extreme case for the impact of iodine on the troposphere (e.g., I_x levels of 7 pptv), the total-column $D(O_3)$ results from Table 2 (8×10^{10} molecules/cm²/s) indicate that this photochemical destruction flux would be nearly 1.5 times larger than the O_3 deposition flux to the ocean [e.g., *Kawa and Pearson*, 1989; *Lenschow et al*, 1982]. Equally noteworthy is the fact that, as discussed by *Davis et al.* [this issue], even before adding iodine, the PEM-West A tropical regime has been evaluated as having an imbalance between O_3 photochemical production and destruction of between 3 and 12×10^{10} molecules/cm²/s. (The lower deficit number assumes significant high-altitude (e.g., 10-17 km) production of O_3 due the presence of high levels of lightning-generated NO_x.) If, however, this region is at steady state for O_3 as suggested by *Davis et al.*, [this issue, 1995] then an additional 8×10^{10} molecules/cm²/s O_3 loss due to iodine raises still further questions concerning our level of understanding of the tropical ozone budget. Most likely, it means that during the time period of PEM-West A, I_x levels were much closer to those labeled earlier as "typical," i.e., 1.5 pptv. Quite clearly, the optimum location for seeing a maximum iodine effect was not that defined by the PEM-West A mission as evidenced by the low primary productivity levels estimated from the low observed levels of CH_3I.

3.3. Modulation of HO_2/OH and NO_2/NO Ratios

Based on (R8), (R14), and (R7), one would predict that with increasing levels of I_x, shifts should occur in both the ratios HO_2/OH and the NO_2/NO. But, as seen in Tables 3 (top) and 3 (middle) only minor changes are seen in these ratios when I_x levels are limited to 0.5 and 1.5 pptv. By comparison, for I_x levels of 7 pptv the HO_2/OH ratio is observed to shift by as much as -18 to -24%, depending on latitude and altitude. The trend in this ratio is one which shows increasing negative values with increasing altitude. The average for all altitudes and latitudes is estimated here to be -15%. This leads to an average increase in the level of OH by 9%; for example, the OH effect typically defines 60% of the total change in the HO_2/OH ratio. Given this shift in OH, if I_x levels were to persist at the 7 pptv level for an extended period of time, one would also estimate a correspondingly 9% shorter lifetime for OH-controlled long-lived trace gases such as CH_4 and CH_3CCl_3.

Concerning changes in the ratio NO_2/NO, from Table 3 (bottom) it can be seen that 7 pptv of I_x shifts the value of this ratio by a maximum of 11%. Furthermore, this shift is only observed for the highest altitudes examined. The average shift over all altitudes and latitudes is approximately 5%. Thus on average, the magnitude of the iodine shift in

Table 3. Tropospheric Impact of Iodine on Ratios HO_2/OH and NO_2/NO

Latitude	Altitude	HO_2/OH, Without I_x	HO_2/OH, With 0.5 pptv I_x[a]	HO_2/OH, % Effect[b]	NO_2/NO, Without I_x	NO_2/NO, With 0.5 pptv I_x[a]	NO_2/NO, % Effect[b]
0-18	0-1	109	108	-0.7	1.30	1.31	0.2
0-18	1-2	105	104	-0.9	1.20	1.21	0.2
0-18	2-4	78	77	-1.1	1.21	1.21	0.2
0-18	4-6	81	80	-1.4	0.87	0.88	0.2
0-18	6-8	76	75	-1.5	0.68	0.68	0.2
0-18	8-10	66	64	-2.2	0.32	0.32	0.5
18-42	0-1	91	90	-0.7	1.55	1.55	0.2
18-42	1-2	82	82	-0.7	2.00	2.00	0.1
18-42	2-4	85	84	-0.9	1.46	1.46	0.1
18-42	4-6	71	70	-1.2	1.14	1.14	0.2
18-42	6-8	64	63	-1.5	0.70	0.70	0.3
18-42	8-10	41	40	-1.5	0.47	0.47	0.5
18-42	10-12	32	32	-0.9	0.19	0.19	0.8

Latitude	Altitude	HO_2/OH, Without I_x	HO_2/OH, With 1.5 pptv I_x[a]	HO_2/OH, % Effect[b]	NO_2/NO, Without I_x	NO_2/NO, With 1.5 pptv I_x[a]	NO_2/NO, % Effect[b]
0-18	0-1	109	106	-2.2	1.30	1.31	0.7
0-18	1-2	105	103	-2.7	1.20	1.21	0.6
0-18	2-4	78	75	-3.2	1.21	1.22	0.7
0-18	4-6	81	77	-4.0	0.87	0.88	0.6
0-18	6-8	76	73	-4.3	0.68	0.69	0.6
0-18	8-10	66	61	-6.4	0.32	0.32	1.5
18-42	0-1	91	89	-2.1	1.55	1.56	0.7
18-42	1-2	82	81	-2.1	2.00	2.01	0.4
18-42	2-4	85	83	-2.6	1.46	1.46	0.4
18-42	4-6	71	68	-3.5	1.14	1.15	0.5
18-42	6-8	64	62	-4.5	0.70	0.71	0.9
18-42	8-10	41	39	-4.3	0.47	0.48	1.6
18-42	10-12	32	31	-2.7	0.19	0.19	2.3

Latitude	Altitude	HO_2/OH, Without I_x	HO_2/OH, With 7 pptv I_x[a]	HO_2/OH, % Effect[b]	NO_2/NO, Without I_x	NO_2/NO, With 7 pptv I_x[a]	NO_2/NO, % Effect[b]
0-18	0-1	109	98	-9.4	1.30	1.34	3.3
0-18	1-2	105	93	-11.4	1.20	1.24	2.9
0-18	2-4	78	67	-13.3	1.21	1.25	3.1
0-18	4-6	81	67	-16.5	0.87	0.90	3.2
0-18	6-8	76	63	-17.3	0.68	0.70	3.2
0-18	8-10	66	50	-24.2	0.32	0.34	7.5
18-42	0-1	91	83	-9.1	1.55	1.59	3.1
18-42	1-2	82	75	-9.2	2.00	2.04	2.1
18-42	2-4	85	76	-11.1	1.46	1.49	2.1
18-42	4-6	71	60	-14.6	1.14	1.17	2.5
18-42	6-8	64	53	-18.0	0.70	0.73	4.3
18-42	8-10	41	34	-17.2	0.47	0.50	7.4
18-42	10-12	32	29	-11.6	0.19	0.21	10.9

For reference purposes the OH levels for $0°-18°N$ latitude and $30°$ zenith angle are 3.6E+6 for 0-1 km and 3.8E+6 for 6-8 km. For all altitudes and I_x levels, increases in OH contribute roughly 60% to the total change in the HO_2/OH ratio.
[a] I_x levels at all altitudes have been scaled to the "reference".
[b] Based on steady state modeling conditions.

this ratio does not appear to provide a satisfactory explanation for the total enhancement in NO_2 levels observed during PEM-West A although it might have been one of the contributing factors (for further details, see *Crawford et al.* [this issue]).

4. Comparison With Previous Studies

The two most relevant tropospheric iodine modeling studies that have preceded this work have been those reported by *Chameides and Davis* [1980] and *Chatfield and Crutzen* [1990]. Chameides and Davis (C&D) only examined the

case of the marine BL but did so for a wide range of median values of CH_3I. Since only the total source of iodine is important, not the specific form, we have here been able to backout the level of CH_3I for BL conditions that corresponds to our high-altitude 7 pptv I_x scenario. For this specific case, BL levels of CH_3I would be in the range of 10 to 13 pptv. Based on this input, we find that the C&D standard model predicts an approximate 25% enhancement in $D(O_3)$ over that estimated from HO_x related chemistry alone. As shown in Table 2 (bottom), this is basically the same enhancement predicted from this work (i.e., 20%) for BL conditions in the tropics. Although this agreement appears to be quite good,

it turns out that it is actually quite fortuitous. For example, on closer inspection one finds that C&D estimated IO levels are nearly 1 order of magnitude higher than those estimated in this work. As a result, both the IO self-reaction and the reaction with HO_2 are found to contribute significantly to $D(O_3)$. The reason for C&D's high IO levels now appears to be largely due to a major difference in the assignment of k values to the three critical processes (R6), (R8), and (R9). All three processes represent loss reactions for IO; and all three have now been assigned new k values based on more reliable kinetic and photochemical data. The new values are nearly 1 order of magnitude higher than the C&D values.

Chatfield and Crutzen [1990] (C&C) also explored the question of tropospheric destruction of ozone by iodine although the main thrust of the study of these investigators was the possible impact of iodine on the oxidation of marine DMS. These authors concluded that iodine was probably an insignificant sink for ozone; however, this conclusion, was based on BL CH_3I levels of only 3 pptv. In addition, C&C based their assessment on a k value for (R8) which has recently been reevaluated based on new kinetic data as being 1½ orders of magnitude higher [*DeMore et al.*, 1994]. The J value for (R16) was also taken to be nearly 3 orders of magnitude lower than that estimated here. All 3 factors have been found to significantly minimize the tropospheric effects of iodine. This point was demonstrated here by carrying out simulations using PEM-West A median values for all photochemical species but invoking the C&C CH_3I, (R8), and (R16) values. The $D(O_3)$ results in this case were within a factor of 1.5 of C&C, thus agreeing with the C&C evaluation in showing no significant effect on ozone from iodine chemistry.

As noted above, the availability of new kinetic data was the basis for the k value assigned to (R8) in this study. However, in the case of (R16) no spectroscopic data are available from which to evaluate this J value [*Sander*, 1986; *Jenkin*, 1993]. C&C assumed values ranging from 3×10^{-4} to 2×10^{-5} s^{-1}, but this is 2 orders of magnitude lower than the J value calculated from the recently reported absorption spectrum for Cl_2O_2 [*DeMore et al.*, 1994]. We have taken what we believe is a rather conservative value for (R16), $9\times J(Cl_2O_2)$ which is approximately 3 orders of magnitude greater than C&C. This estimate is still 1 order of magnitude lower than the J value for (R6), involving the photolysis of IO.

5. Summary and Conclusions

The CH_3I observations from PEM-West A, in conjunction with updated J and k values for several tropospheric iodine reactions, suggest that under certain conditions the addition of iodine chemistry to current models leads to predicted enhancements in the rate of destruction of ozone. It also predicts shifts in the critical free radical ratio HO_2/OH. Although the percent effect on $D(O_3)$ was found to increase steadily with increasing altitude, the mid-troposphere was found to be the major contributor to the 0 to 12 km column-integrated value of $D(O_3)$. The total column effect on $D(O_3)$ was estimated to be only 6% for I_x levels of 1.5 pptv; however, this increased to 30% at tropical latitudes for the high I_x scenario involving 7 pptv. A potential enhancement in $D(O_3)$ of 30% represents a major impact on the O_3 budget at tropical latitudes. In fact, it is difficult to reconcile with

the findings of *Davis et al.* [this issue] who report that for the time period of PEM-West A this region displayed significant net-photochemical column destruction even in the absence of iodine chemistry. This most likely suggests that during PEM-West A, I_x never reached the 7 pptv level. This conclusion would seem to be in agreement with the observations that BL levels of CH_3I were also low indicating a marine region having low primary productivity.

The influence of iodine on the radical ratio HO_2/OH was found to be most significant for the upper free troposphere and for I_x levels of 7 pptv. For this I_x level the average effect for all altitudes was approximately 15%. The effect of iodine on the NO_2/NO ratio was also found to maximize at high-altitude but never exceeded 11% even for the highest I_x scenario. If the maximum estimated shift in the HO_2/OH ratio were to be realized, this would result in a 9% increase in atmospheric levels of OH and thus lead to an approximate 9% decrease in the lifetimes of OH-controlled trace gases such as CH_4 and CH_3CCl_3.

Of interest also is the fact that median levels of CH_3I in the 8-10 km altitude range (e.g., for the western tropical Pacific) reached 0.15 pptv, with individual observations reaching 0.3 to 0.7 pptv. Although these altitudes are still significantly removed from the tropical tropopause, if the mixing ratios observed for CH_3I represent only a fraction of the total iodine being convectively pumped into the upper troposphere, it is still possible that *Solomon et al.'s* [1995] requirement of a few tenths of one pptv of iodine in the lower stratosphere might be reached on some occasions. In this context, because of the high sensitivity for detection of iodine species like CH_3I, together with its short lifetime of 2-4 days, CH_3I would appear to be an excellent tracer for the transport of marine BL air into the upper troposphere and lower stratosphere.

Major uncertainties in the proposed iodine chemistry include the total marine iodine source strength as well as the reliability of several k and J values. In particular, it will be important in future field studies to include not only measurements of CH_3I but also those for other iodocarbons. In addition, both the critical IO reaction involving HO_2 (R8) and the self-reaction (R9) should be further investigated, as should the photochemical cross section for the species I_2O_2. Finally, the efficiency for removal of iodine species due to high-altitude aerosol must be resolved. Quite significant to gaining more direct insight into all aspects of the proposed iodine chemistry would be direct observations of the radical species I and IO.

References

Anlauf, K. G., R. E. Mickle, and N. B. A. Trivett, Measurement of ozone during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, 99, 24,345-25,353, 1994.

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A.

Kerr, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry, Supplement IV, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data, 21*, 1125-1568, 1992.

Barrie, L. A., J. W. Bottenheim, R. C. Shnell, P. J. Crutzen, and R. A. Rasmussen, Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, *Nature, 334*, 138-141, 1988.

Blake, D. R., T. W. Smith Jr., T. -Y. Chen, W. J. Whipple, and F. S. Rowland, Effects of biomass burning on summertime nonmethane hydrocarbons concentrations in the Canadian wetlands, *J. Geophys. Res., 99*, 1699-1719, 1994.

Blake, D. R., T. -Y. Chen, T. W. Smith, Jr., C. J.-L. Wang, O. W. Wingenter, N. J. Blake, F. S. Rowland, and E. W. Mayer, Three-dimensional distribution of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.*, this issue.

Bottenheim, J. W., L. A. Barrie, E. Atlas, L. E. Heidt, H. Niki, R. A. Rasmussen, and P. B. Shepson, Depletion of lower-tropospheric ozone during Arctic spring: Polar Sunrise Experiment 1988, *J. Geophys. Res., 95*, 18,555-18,568, 1990.

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

Chameides, W. L., and J. C. G. Walker, A photochemical theory of tropospheric ozone, *J. Geophys. Res., 78*, 8751-8760, 1973.

Chatfield, R. B., and P. J. Crutzen, Are there interactions of iodine and sulfur species in marine air photochemistry?, *J. Geophys. Res., 95*, 22,319-22,341, 1990.

Crawford, J., et al., Photostationary state analysis of the NO_2-NO system based on airborne observations from the western and central North Pacific, *J. Geophys. Res.*, this issue.

Davis, D. D., et al., Photostationary state analysis of the NO_2-NO system based on airborne observations from the subtropical /tropical North and South Atlantic, *J. Geophys. Res., 98*, 23,501-23,523, 1993.

Davis, D. D., et al., Assessment of the ozone photochemistry tendency in the western North Pacific as inferred from PEM-West A observations during the fall of 1991, *J. Geophys. Res.*, this issue.

DeMore, W. B., S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ. 94-26*, Jet Propul. Lab., Pasadena, Calif., 1994.

Fabian, P., and P. G. Pruchniewicz, Meridional distribution of ozone in the troposphere and its seasonal variation, *J. Geophys. Res., 82*, 2063-2073, 1977.

Fan, S.-M., and D. J. Jacob, Surface ozone depletion in the Arctic spring sustained by bromine reactions on aerosols, *Nature, 359*, 522-524, 1992.

Finlayson-Pitts, B. J., F. E. Livingston, and H. N. Berko, Ozone destruction and bromine photochemistry in the Arctic spring, *Nature, 343*, 622-625, 1990.

Fishman, J., and P. J. Crutzen, A numerical study of tropospheric photochemistry using a one-dimensional model, *J. Geophys. Res., 82*, 5897-5906, 1977.

Hanson, D. H., A. R. Ravishankara, and S. Solomon, Heterogeneous reactions in sulfuric acid aerosols: A framework for model calculations, *J. Geophys. Res., 99*, 3615-3629, 1994.

Hausmann M., and U. Platt, Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res., 99*, 25,399-25,413, 1994.

Jenkin, M. E., A comparative assessment of the role of iodine photochemistry in tropospheric ozone depletion in *The Tropospheric Chemistry of Ozone in the Polar Regions*, edited by H. Niki and K. H. Becker, Springer-Verlag, New York, 1993.

Jenkin, M. E., R. A. Cox, and D. E. Candeland, Photochemical aspects of tropospheric iodine behaviour, *J. Atmos. Chem., 2*, 359-375, 1985.

Jobson, B. T., H. Niki, Y. Yokouchi, J. Bottenheim, F. Hopper, and R. Leaitch, Measurements of C_2-C_6 hydrocarbons during Polar Sunrise 1992 Experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res., 99*, 25,355-25,368, 1994.

Kawa, S. R., and R. Pearson Jr., Ozone budgets from the dynamics and chemistry of marine stratocumulus experiment, *J. Geophys. Res., 94*, 9809-9817, 1989.

Keene, W. C., A. A. P. Pszenny, D. J. Jacob, R. A. Duce, J. N. Galloway, J. J. Schultz-Tokos, H. Sievering, and J. F. Boatman, The geochemical cycling of reactive chlorine through the marine troposphere, *Global Biogeochem. Cycles, 4*, 407-430, 1990.

Klick, S., and K. Abrahamsson, Biogenic volatile iodated hydrocarbons in the ocean, *J. Geophys. Res., 97*, 12,683-12,687, 1992.

Laszlo, B., M. Kurylo, R. Huie, Absorption cross sections, kinetics of formation, and self reaction of the IO radical produced via the laser photolysis of $N_2O/I_2/N_2$ mixtures, *J. Phys. Chem., 99*, 11,701, 1995.

LeBras, G., and U. Platt, A possible mechanism for combined chlorine and bromine catalyzed destruction of tropospheric ozone in the Arctic, *Geophys. Res. Lett., 22*, 599-602, 1995.

Lenschow, D. H., R. Pearson Jr., and B. B. Stankor, Measurements of ozone vertical flux to ocean and forest, *J. Geophys. Res., 87*, 8833-8837, 1982.

Liss, P. S., and P. G. Slater, Flux of gases across the air-sea interface, *Nature, 247*, 181-184, 1974.

Liu, S. C., D. Kley, M. McFarland, J. D. Mahlman, and H. Levy II, On the origin of tropospheric ozone, *J. Geophys. Res., 85*, 7546-7552, 1980.

Liu, S. C., J. R. McAfee, and R. J. Cicerone, Radon 222 and tropospheric vertical transport, *J. Geophys. Res., 89*, 7291-7297, 1984.

Liu, S. C., et al., Model study of tropospheric trace species distribution during PEM-West A, *J. Geophys. Res.*, this issue.

Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res., 86*, 7210-7254, 1981.

Mahlman, J. D., H. Levy II, and W. J. Moxim, Three-dimensional tracer structure and behavior as simulated in two ozone precursor experiments, *J. Atmos. Sci., 37*, 655-685, 1980.

McConnell, J. C., G. S. Henderson, L. A. Barrie, J. W. Bottenheim, H. Niki, C. H. Langford, and E. M. J. Templeton, Photochemical bromine production implicated in Arctic boundary-layer ozone depletion, *Nature, 355*, 150-152, 1992.

McKeen, S. A., D. Kley, and A. Volz, The historical trend of tropospheric ozone over western Europe: A model perspective, in *Proc. of the 1988 Quadrennial Ozone Symposium*, edited by R. Bojkov and P. Fabian, A. Deepak, Hampton, VA, 1989.

Moore, R. M., and R. Tokarczyk, Chloroiodomethane in N. Atlantic waters: A potentially significant source of atmospheric iodine, *Geophys. Res. Lett., 19*, 1779-1782, 1992.

Murphy, D. M., D. W. Fahey, M. H. Proffitt, S. C. Liu, C. S. Eubank, S. R. Kawa, and K. K. Kelly, Reactive nitrogen and its correlation with ozone in the lower stratosphere and upper troposphere, *J. Geophys. Res., 98*, 8751-8774, 1993.

Newell, R. E, et al., Atmospheric sampling of supertyphoon Mireille with the NASA DC-8 aircraft on September 27, 1991, during PEM-West A, *J. Geophys. Res.*, this issue.

Oram, D. E., and S. A. Penkett, Observations in eastern England of elevated methyl iodide concentrations in air of Atlantic origin, *Atmos. Environ., 28*, 1159-1174, 1994.

Pszenny, A. A. P., W. C. Keene, D. J. Jacob, S. Fan, J. R. Maben, M. P. Zetwo, M. Springer-Young, and J. N. Galloway, Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air, *Geophys. Res. Lett., 20*, 699-702, 1993.

Rasmussen, R. A., M. A. K. Khalil, R. Gunawardena, and S. D. Hoyt, Atmospheric methyl iodide, *J. Geophys. Res., 87*, 3086-3090, 1982.

Reifenhauser, W., and K. G. Heumann, Determinations of methyl iodide in the Antarctic atmosphere and the south Polar Sea, *Atmos. Environ., 26(A)*, 2905-2912, 1992.

Sander, S.P., Kinetics and mechanism of the IO + IO reaction, *J. Phys. Chem., 90*, 2194-2199, 1986.

Schall C., and K. G. Heumann, GC determination of volatile organoiodine and organobromine compounds in Arctic seawater and air samples, *Fresnius J. Anal. Chem., 346*, 717-722, 1993.

Singh, H. B., Halogens in the atmospheric environment, in *Composition, Chemistry, Climate of the Atmosphere*, edited by

H.B. Singh, pp. 216-250, Van Nostrand Reinhold, New York, 1995.

Singh, H.B., and J.F. Kasting, Chlorine-hydrocarbon photochemistry in the marine troposphere and lower stratosphere, *J. Atmos. Chem.*, *7*, 261-285, 1988.

Singh, H.B., L.J. Salas, and R.E. Stiles, Methyl halides in and over the eastern Pacific (40°N-32°S), *J. Geophys. Res.*, *88*, 3684-3690, 1983.

Singh, H. B., et al., Low ozone in the marine boundary layer of the tropical Pacific Ocean: Photochemical loss, chlorine atoms, and entrainment, *J. Geophys. Res.*, this issue.

Smyth, S., et al., Comparison of free tropospheric western Pacific air mass classification schemes for the PEM-West A experiment, *J. Geophys. Res.*, this issue.

Solomon, S., R. R. Garcia, and A. R. Ravishankara, On the role of iodine in ozone depletion, *J. Geophys. Res.*, *99*, 20,491-20,499, 1995.

Thornton, D. C., A. R. Bandy, B. W. Blomquist, D. D. Davis, and R. W. Talbot, Sulfur dioxide as a source of condensation nuclei in the upper troposphere of the Pacific Ocean, *J. Geophys. Res.*, this issue.

Tuck, A. F., C. R. Webster, R. D. May, D. C. Scott, S. J. Hovde, J. W. Elkins, and K. R. Chan, Time and temperature dependence of fractional HCl abundances from airborne data in the southern hemisphere during 1994, *Faraday Discuss.*, in press, 1995.

World Meteorological Organization (WMO), Scientific assessment of stratospheric ozone: 1989, Global ozone research and monitoring project, *WHO Rep. 20*, Geneva, 1989.

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