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Potential impacts of CF₃I on ozone as a replacement for CF₃Br in aircraft applications

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Abstract. Iodotrifluoromethane (CF₃I) has been considered to be a candidate replacement for bromotrifluoromethane (CF₃Br), which is used in aircraft for fuel inerting and for fire fighting. In this study, the chemical effects of aircraft-released CF₃I on atmospheric ozone were examined with the University of Illinois at Urbana-Champaign two-dimensional chemical-radiative-transport (UIUC 2-D CRT) model. Using an earlier estimate of the aircraft emission profile for tank inerting in military aircraft, the resulting equivalent Ozone Depletion Potentials (ODPs) for CF₃I were in the range of 0.07 to 0.25. As a sensitivity study, we also analyzed CF₃I emissions associated with fuel inerting if it were to occur at lower altitudes using an alternative estimate. The model calculations of resulting effects on ozone for this case gave ODPs ≤ 0.05. Furthermore, through interactions with the National Institute of Standards and Technology (NIST), we analyzed the potential effects on ozone resulting from using CF₃I in fire fighting connected with engine nacelle and auxiliary power unit applications. The scenarios evaluated using the NIST estimate suggested that the ODPs obtained by assuming aircraft flights occurring in several different latitude regions of the Northern Hemisphere are extremely low. According to the model calculation, the altitude where CF₃I is released from aircraft is a dominant factor in its ozone depletion effects. On the assumption that the CF₃I emission profile is representative of actual release characteristics, aircraft-released CF₃I has much lower impacts than CF₃Br.

depletion chemical with a lifetime of about 65 years (WMO, 1999) so that tropospheric release will make its way into the stratosphere. For this reason, substitute chemicals must be considered for replacing CF₃Br usage in aircraft uses. H-1311 has been used both as a fuel inerting agent in military aircraft and as a fire-fighting agent in a number of military and commercial aircraft. Iodotrifluoromethane (CF₃I), a close chemical cousin of CF₃Br, has been considered to be a potential replacement, even though iodine is extremely reactive with oxygen because it is photolytically reactive and easily degraded by solar radiation in the atmosphere, resulting in an atmospheric lifetime of CF₃I that is extremely short, approximately on the order of hours to days.

CF₃I photolyzes rapidly to form reactive iodine atoms even under visible light conditions. Therefore, it could be treated as a potential significant source of atmospheric iodine and its effects on atmospheric ozone depend strongly on iodine chemistry related to ozone destruction processes (e.g., Solomon, 1994a). CF₃I emissions from aircraft can occur both in the troposphere and lower stratosphere. Since the emissions, even in the troposphere, can be transported upwards by convection in the tropics and mid latitudes and spread over the stratosphere globally, both tropospheric and stratospheric chemistry and physics need to be considered for the purpose of evaluating the effects of aircraft-released CF₃I on atmospheric ozone. The possible role of iodine species in tropospheric chemistry has been previously discussed in several papers (e.g., Chameides and Davis, 1980; Davis et al., 1996). In the troposphere, iodine species generated from photolysis of many sources deplete tropospheric ozone through complex chemical cycles and are finally removed through the relatively inactive reservoir species by dry and wet depositions. Several studies have shown that iodine reaching the stratosphere can be potentially effective at destroying stratospheric ozone. Solomon et al. (1994a) first postulated the possibility that iodine-containing compounds could be transported to the stratosphere by convective transport in the tropics. Once these gases and their reaction

1 Introduction

Bromotrifluoromethane (CF₃Br), also referred to as Halon 1311 or H-1311, has been used for aircraft fire extinguishing systems because of its high fire suppression efficiency, low cost, and low toxicity. However, CF₃Br is known as an ozone

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by-products reach the stratosphere, they can release iodine atoms rapidly via photolysis. Because the reservoir species of iodine are much more photolytically unstable, iodine-containing compounds in the stratosphere are almost entirely in reactive forms (I, IO) and thus their reactions with BrO, ClO, and HO₂ can contribute significantly to the ozone depletion via chemical catalytic cycles in the lower stratosphere. However, iodine chemistry was not well understood and rate coefficients of several key reactions were not known and assumed to be quite large values at the time of the Solomon et al. (1994a) study. As a consequence, these results may have been inaccurate in estimating the impact of iodine on the ozone depletion. Recently, numerous kinetic studies on iodine compounds have been carried out and the understanding of iodine chemistry has improved considerably (e.g., Turnipseed et al., 1997; Gilles et al., 2000). As a result, in this study, we have attempted to reevaluate the role of iodine chemicals on the ozone depletion using the updated evaluations of iodine chemistry.

Several estimates of aircraft release of fire extinguishing agents with altitude have been considered. A previous study of surface CF₃I emissions (Solomon et al., 1994b) suggested that iodine compounds should not impact ozone significantly. However, as the laboratory results on iodine reactions keep being updated and the understanding of chemical processes of iodine chemistry improves, reevaluation of CF₃I emissions is a necessity. In addition, emissions from aircraft may have a larger impact than emissions from the Earth surface, because iodine species have much longer lifetimes at the higher altitudes. Moreover, the role that CF₃I emissions from aircraft play in the ozone depletion is not known yet and needs to be studied carefully using the newest available chemistry.

In this study, we have used the University of Illinois at Urbana-Champaign two-dimensional chemical-radiative-transport model. This model has the benefit of being computationally efficient and past studies have demonstrated its usefulness in studies of interactions of physical and chemical processes in the troposphere and stratosphere. However, at the same time, we recognize the limitations of two-dimensional models, particular in representing tropospheric processes. The next stage for further analysis of CF₃I impacts on ozone would be to perform similar studies with a three-dimensional chemistry-transport model of the troposphere and stratosphere.

2 Model description and updates

The University of Illinois at Urbana-Champaign two-dimensional chemical-radiative-transport (UIUC 2-D CRT) model is a zonally-averaged model of the chemistry and physics of the global atmosphere (e.g., Wuebbles et al., 2001). The model has been used extensively to study human related and natural forcings on the troposphere and strato-

sphere. However, the analysis of tropospheric processes is limited due to its zonally-averaged nature.

In Rupnik et al. (2002), an earlier 2002 version of the UIUC 2-D CRT model was used to evaluate the effects from potential using CF₃I as an fuel inerting agent. In this study, the model has been updated, referred to as the 2004 version with the latest improvements of atmospheric chemistry and dynamics. The current version of the model determines the atmospheric distribution of 89 chemically active atmospheric trace constituents with 70 photolytic reactions, 189 thermal reactions, and heterogeneous reactions. Reaction-rate constants and photochemical data in the model are primarily based on the recommendations compiled by the NASA Panel for Data Evaluation (DeMore et al., 1997; Sander et al., 2003). The model domain extends from pole to pole and from the ground to 84 km in altitude. A grid box is 5 degrees of latitude and 1.5 km in log-pressure altitude.

Recent laboratory studies have improved the understanding of atmospheric chemical processes of iodine chemistry. Table 1 summarizes chemical reactions and rate coefficients related to iodine chemistry being used in the 2004 version of the UIUC 2-D CRT model. The complete list of references for this chemistry is found also in Table 1. It should be noted that many iodine-related chemical reactions are still highly debatable (e.g., OIO photolysis). This is discussed in detail later. Reactive iodine species generated from photodissociation of CF₃I should react with atmospheric ozone. Major chemistry updates of the 2-D model that could impact effects of CF₃I on atmospheric ozone concentrations include: CF₃I and CH₃I absorption cross-sections for photochemical reactions, thermal reaction-rate coefficients of CH₃I+OH→I+H₂O+CH₂O, and of reactions of IO with ClO or BrO and I with O₃, HO₂ or O. Section 3 will further describe the effects of this chemistry on ozone.

The UIUC 2-D CRT model uses the Transformed Eulerian-Mean (TEM) formulation in log-pressure coordinates (Garcia et al., 1992) for investigations of tracer transport. The latest version of the model has some key improvements incorporated in it. Major upgrades were made through better representation of the effects of planetary waves and a more accurate method for determining residual mean meridional circulation. Planetary waves for wave numbers 1 and 2 are parameterized with better data-based boundary topography and boundary winds and stratospheric values of horizontal diffusion coefficient K_{yy} are calculated using the planetary wave dissipation rate and vorticity for both wave number 1 and 2 (Nathan et al., 2000). Values of vertical diffusion coefficient K_{zz} due to gravity waves are evaluated. Larger diffusion coefficients are specified to the troposphere to mimic fast tropospheric mixing. The model uses a seasonally varying tropospheric K_{yy} . Convective transport in the model is based on the climatology of Langner et al. (1990). Climatological latent heating and the sensible heat flux are specified based on more physically meaningful analyses. An accurate and fast longwave radiation code (Olague et al.,

Table 1. Major iodine chemical reactions in the UIUC 2-D CRT model.

Thermal Reactions	A	E/R	300K	References			
I + O ₃ = IO + O ₂	2.30e-11	870.	1.27e-12	[Sander et al.,2003]			
I + HO ₂ = HI + O ₂	1.50e-11	1090.	3.96e-13	[Sander et al.,2003]			
I + ClO = IO + Cl	4.40e-11	0.	4.40e-11	[Bedjanian et al., 1997]			
I + OCIO = IO + ClO	9.70e-12	1190.	1.84e-13	[Bedjanian et al., 1997]			
I + BrO = Br + IO	1.45e-11	0.	1.45e-11	[Bedjanian et al., 1998]			
I ₂ + O = IO + I	1.40e-10	0.	1.40e-10	[Atkinson, 1997]			
I ₂ + OH = HOI + I	1.80e-10	0.	1.80e-10	[Atkinson, 1997]			
I ₂ + NO ₃ = I + IONO ₂	1.50e-12	0.	1.50e-12	[Atkinson, 1997]			
I ₂ + Cl = I + ICl	2.10e-10	0.	2.10e-10	[Bedjanian et al., 1997]			
I ₂ + Br = I + IBr	1.20e-10	0.	1.20e-10	[Bedjanian et al., 1998]			
IO + O = I + O ₂	1.20e-10	0.	1.20e-10	[Sander et al.,2003]			
IO + HO ₂ = HOI + O ₂	8.40e-11	0.	8.40e-11	[Sander et al.,2003]			
IO + NO = I + NO ₂	9.10e-12	-240.	2.03e-11	[Sander et al.,2003]			
IO + ClO = I + OCIO	2.81e-12	-280	7.15e-12	[Bedjanian et al., 1998]			
IO + ClO = I + Cl + O ₂	1.28e-12	-280	3.26e-12	[Bedjanian et al., 1998]			
IO + ClO = ICl + O ₂	1.02e-12	-280	2.59e-12	[Bedjanian et al., 1998]			
IO + Br = I + BrO	2.30e-11	0	2.30e-11	[Bedjanian et al., 1998]			
IO + BrO = I + Br + O ₂	8.75e-12	-260	2.08e-11	[Gilles et al., 1997]			
IO + BrO = IBr + O ₂	1.63e-11	-260	3.88e-11	[Gilles et al., 1997]			
IO + IO = I ₂ + O ₂	5.00e-12	0	5.00e-12	[Harwood et al., 1997]			
IO + IO = I + OIO	3.05e-11	0	3.05e-11	[Harwood et al., 1997]			
IO + IO = 2I + O ₂	6.35e-11	0	6.35e-11	[Harwood et al., 1997]			
HI + OH = H ₂ O + I	3.00e-11	0.	3.00e-11	[Sander et al.,2003]			
INO + INO = I ₂ + 2NO	8.40e-11	2620.	1.35e-14	[Sander et al.,2003]			
INO ₂ + INO ₂ = I ₂ + 2NO ₂	2.90e-11	2600.	4.99e-15	[Sander et al.,2003]			
CH ₃ I + OH = I + H ₂ O + CH ₂ O	2.90e-12	1100.	7.41e-14	[Sander et al.,2003]			
(Three body Troe expression)	K ₀ [300]	n	K _∞ [300]	f	g		
I + NO = INO	1.80e-32	1.0	1.70e-11	0.0	0.0	[Sander et al.,2003]	
I + NO ₂ = INO ₂	3.00e-31	1.0	6.60e-11	0.0	0.0	[Sander et al.,2003]	
IO + NO ₂ = IONO ₂	5.90e-31	3.5	9.00e-12	1.5	0.0	[Sander et al.,2003]	
Photolysis reactions*	Height=0 km		Height=20 km		Height=50 km		
	Jun	Dec	Jun	Dec	Jun	Dec	
IO + hv = I + O	1.87*10 ⁻¹	1.57*10 ⁻¹	2.47*10 ⁻¹	2.33*10 ⁻¹	1.01*10 ⁻¹	7.89*10 ⁻²	[Atkinson, 1997]
HOI + hv = I + OH	3.10*10 ⁻³	1.59*10 ⁻³	8.32*10 ⁻⁴	3.19*10 ⁻⁴	3.72*10 ⁻⁴	2.03*10 ⁻⁴	[Atkinson, 1997]
INO + hv = I + NO	1.20*10 ⁻¹	9.79*10 ⁻²	8.46*10 ⁻²	6.53*10 ⁻²	3.42*10 ⁻³	2.32*10 ⁻³	[Atkinson, 1997]
INO ₂ + hv = I + NO ₂	3.07*10 ⁻²	2.57*10 ⁻²	2.17*10 ⁻²	1.67*10 ⁻²	8.23*10 ⁻⁴	5.59*10 ⁻⁴	[Atkinson, 1997]
IONO ₂ + hv = I + NO ₃	1.04*10 ⁻³	7.83*10 ⁻⁴	7.65*10 ⁻⁴	5.74*10 ⁻⁴	4.25*10 ⁻⁵	2.93*10 ⁻⁵	[Atkinson, 1997]
IONO ₂ + hv = IO + NO ₂	2.54*10 ⁻³	1.92*10 ⁻³	1.87*10 ⁻³	1.41*10 ⁻³	1.04*10 ⁻⁴	7.18*10 ⁻⁵	[Atkinson, 1997]
OIO + hv = O + IO	4.74*10 ⁻²	1.90*10 ⁻²	2.54*10 ⁻¹	2.11*10 ⁻¹	1.65*10 ⁻⁴	1.01*10 ⁻⁴	[DeMore et al., 1997]
ICl + hv = I + Cl	1.82*10 ⁻⁴	9.35*10 ⁻⁵	2.09*10 ⁻²	1.27*10 ⁻²	1.17*10 ⁻⁴	7.26*10 ⁻⁵	[DeMore et al., 1997]
IBr + hv = I + Br	2.45*10 ⁻⁴	1.28*10 ⁻⁴	2.79*10 ⁻²	1.69*10 ⁻²	1.56*10 ⁻⁴	9.64*10 ⁻⁵	[DeMore et al., 1997]
I ₂ + hv = I + I	6.80*10 ⁻⁴	3.63*10 ⁻⁴	7.71*10 ⁻²	4.66*10 ⁻²	4.31*10 ⁻⁴	2.66*10 ⁻⁴	[Tellinghuisen, 1973]
CH ₃ I + hv = CH ₃ + I	3.01*10 ⁻⁶	1.24*10 ⁻⁶	2.43*10 ⁻⁶	1.67*10 ⁻⁶	1.36*10 ⁻⁴	8.78*10 ⁻⁵	[Sander et al.,2003]
CF ₃ I + hv = CF ₃ + I	1.34*10 ⁻⁵	5.74*10 ⁻⁶	1.82*10 ⁻⁵	1.26*10 ⁻⁵	1.81*10 ⁻⁴	1.24*10 ⁻⁴	[Sander et al.,2003]

* Photochemical rates (s⁻¹) are provided at 30°N assuming evenly distributed surface CF₃I emissions at NH.

1992) for the height of surface to 60 km is adopted in the radiation part of the model. The net heating rates are thus obtained from specified latent heating and calculated long-wave and shortwave heating with the temperature and chemical species distributions. Wet deposition is incorporated for water-soluble species including the inorganic bromine/iodine species BrO/IO, HBr/HI, HOBr/HOI, and BrNO₂/IONO₂ based on the rainout rate of nitric acid. The zonally averaged temperature and wind fields are specified based on 6-year climatology of the United Kingdom meteorological Office (UKMO) reanalysis data (Swinbank and O'Neill, 1994; Coy

and Swinbank, 1997). In addition, background diffusion coefficients, which cannot be explicitly obtained in the model, are also tuned for the "leaky pipe" model in the tropics and the model barrier between mid-latitude and polar regions.

3 Atmospheric chemistry related to CF₃I

3.1 Degradation of CF₃I

CF₃I has been considered to be a potential substitute for the replacement of halon fire extinguishing agents because

Table 2. Iodine catalytic cycles.

a. Iodine self-catalytic cycles	
Cycle 1	$\begin{array}{l} I + O_3 \rightarrow IO + O_2 \\ IO + O \rightarrow I + O_2 \\ O_3 + O \rightarrow 2O_2 \end{array}$
Cycle 2	$\begin{array}{l} I + O_3 \rightarrow IO + O_2 \\ IO + IO \rightarrow 2I + O_2 \\ 2O_3 \rightarrow 2O_2 \end{array}$
Cycle 3	$\begin{array}{l} I + O_3 \rightarrow IO + O_2 \\ IO + IO \rightarrow I_2 + O_2 \\ I_2 + hv \rightarrow 2I \\ 2O_3 \rightarrow 3O_2 \end{array}$
b. Iodine catalytic cycles with HOx	
Cycle 4	$\begin{array}{l} OH + O_3 \rightarrow HO_2 + O_2 \\ I + O_3 \rightarrow IO + O_2 \\ IO + HO_2 \rightarrow HOI + O_2 \\ HOI + hv \rightarrow OH + I \\ 2O_3 \rightarrow 3O_2 \end{array}$
c. Iodine catalytic cycles with NOx	
Cycle 5	$\begin{array}{l} NO + O_3 \rightarrow NO_2 + O_2 \\ I + O_3 \rightarrow IO + O_2 \\ IO + NO_2 \rightarrow IONO_2 \\ IONO_2 + hv \rightarrow I + NO_2 \\ NO_3 + hv \rightarrow NO + O_2 \\ 2O_3 \rightarrow 3O_2 \end{array}$
d. Iodine catalytic cycles with ClO/BrO	
Cycle 6	$\begin{array}{l} I + O_3 \rightarrow IO + O_2 \\ Cl + O_3 \rightarrow ClO + O_2 \\ IO + ClO \rightarrow I + Cl + O_2 \\ 2O_3 \rightarrow 3O_2 \end{array}$
Cycle 7	$\begin{array}{l} I + O_3 \rightarrow IO + O_2 \\ Cl + O_3 \rightarrow ClO + O_2 \\ IO + ClO \rightarrow ICl + O_2 \\ ICl + hv \rightarrow I + Cl \\ 2O_3 \rightarrow 3O_2 \end{array}$
Cycle 8	$\begin{array}{l} I + O_3 \rightarrow IO + O_2 \\ Br + O_3 \rightarrow BrO + O_2 \\ IO + BrO \rightarrow I + Br + O_2 \\ 2O_3 \rightarrow 3O_2 \end{array}$

of its short atmospheric lifetime; CF₃I absorbs solar radiation efficiently in the wavelength range from 220 to 340 nm (Solomon et al., 1994b) and thus can be photodissociated rapidly in the troposphere. As a consequence, the photolysis lifetime of CF₃I is extremely short, on the order of hours to days. However, photolysis of CF₃I produces iodine atoms that can destroy ozone. We, therefore, need to further examine the products of the photodegradation process to evaluate the total impact of CF₃I release. Other chemical pathways of CF₃I degradation, such as reactions with O and OH, could further decrease its lifetime. The newest kinetics study on the reaction of CF₃I with OH has been carried out by Gilles et al. (2000). Their results showed a very small rate coefficient value and a negligible role in the atmospheric removal of CF₃I. Similarly, for the reaction of CF₃I with O, Teruel et al. (2004) showed that the rate coefficient of this reaction was quite small and would not impact the lifetime of CF₃I. As a result, only photolysis has been considered to be the degradation mechanism of CF₃I for this study.

3.2 Relevant chemical processes

Previous studies on iodine chemistry are quite limited. Most of them have concentrated on tropospheric iodine species originated from a marine environment where the major nat-

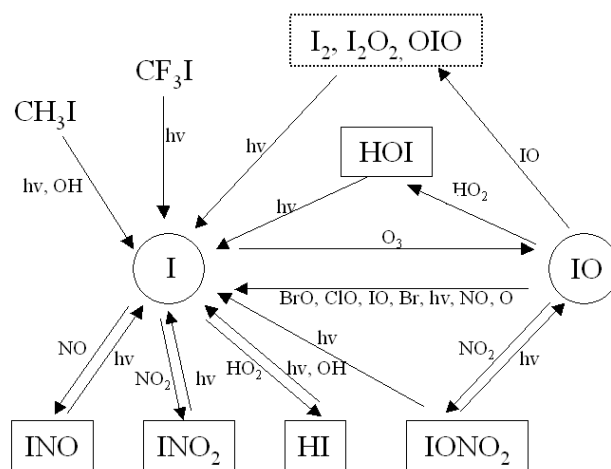


Fig. 1. Chemical processes of iodine compounds in the UIUC 2-D CRT model. Circles represent reactive iodine species, solid boxes represent reservoir species, dotted boxes represent iodine species that photolyze rapidly after formation.

ural iodine emissions occur (Alicke et al., 1999; Chameides et al., 1980; Chatfield et al., 1990; Davis et al., 1996). In the troposphere, iodine atoms generated from photolysis of iodine-containing compounds react with ozone to form iodine oxides, which are further involved in complex catalytic cycles to destroy tropospheric ozone. Iodine is removed from the troposphere through reservoir species such as IONO₂, HI and HOI by rainout and dry deposition. Due to the incomplete understanding of iodine chemistry, the study on the impact of iodine compounds in the atmosphere is still in the initial stage, especially for the stratosphere. Solomon et al. (1994b) postulated that iodine chemicals transported to the upper atmosphere are almost entirely in reactive forms I and IO, therefore impacting stratospheric ozone via chemical catalytic cycles. Since iodine reservoir species photolyze rapidly in the stratosphere, reactive iodine compounds are much more effective on ozone destruction than in the troposphere. Therefore, iodine reaching the stratosphere has the potential to impact ozone significantly. In order to evaluate the effects of CF₃I emissions from aircraft on atmospheric ozone, detailed and updated atmospheric chemistry needs to be considered and driving mechanisms of ozone depletion need to be investigated.

Figure 1 shows the current understanding of the main features of iodine chemistry. In the modeling studies presented here, chemical compounds and free radicals generated from CF₃I emissions are considered to be I, I₂, IO, OIO, HI, HOI, INO, INO₂, IONO₂, ICl, and IBr. Among these, I and IO are the reactive iodine radicals that can potentially destroy ozone and HOI, HI, INO, IONO₂ and INO₂ are the major reservoir species. The extensive cycling of these species can be evident by noting the reactions listed in Table 1. In general,

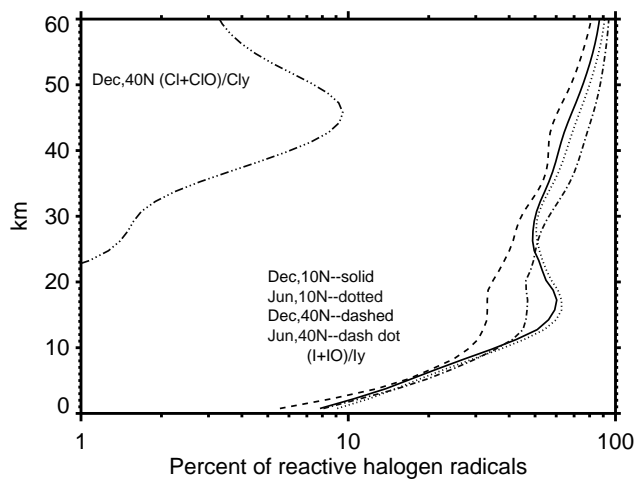


Fig. 2. The fraction of reactive free radicals (I+IO, Cl+ClO) among total iodine or chlorine species (I_y , Cl_y) based on the calculation with the UIUC 2-D CRT model for background atmosphere for the current model year (the same for Fig. 3 and 4). Results are shown for 10° N and 40° N in June and December to illustrate the latitudinal and seasonal impact.

iodine atoms released from the photodissociation of CF₃I and CH₃I as well as the reaction of CH₃I with OH act as the starting point of iodine chemistry, which in turn leads to reactions of I with oxides (O₃, ClO, BrO) to form IO and with HO₂ to form HI. IO reacts with various compounds, such as ClO/BrO/IO/Br, NO, and O, as well as photolyzes to produce O₂ and iodine atoms, which completes the chemical catalytic cycles. As a consequence, IO and I are reactants in several catalytic cycles with other species, such as HO_x, NO_x and halogen (Cl/Br/I). This is discussed in detail in Sect. 3.3. At night, I and IO react with HO₂ or NO₂ to form reservoir species, but most reservoir species of iodine are photodissociated rapidly when exposed to solar radiation. The reservoir species are then scavenged out of the atmosphere by rain or dry deposition, which is the essential sink of iodine compounds.

In terms of ozone depletion, reactive free radicals (I, IO) play the most important role among all iodine species. Figure 2 illustrates the ratio of these reactive species to total iodine species (I_y) in comparison with the ratio of reactive chlorine to total chlorine as a function of altitude. It is apparent that reactive iodine radicals are a large fraction of the total iodine in the upper troposphere and above. This is mainly because the iodine reservoir species decompose almost immediately in much of the stratosphere, where photolysis is a much more dominant pathway of degradation of iodine compounds. In the troposphere, reactive iodine species are much lower fraction of total iodine, especially at night when reservoir species could form relatively easily. In contrast, even the lowest fraction of reactive iodine radicals in the tropo-

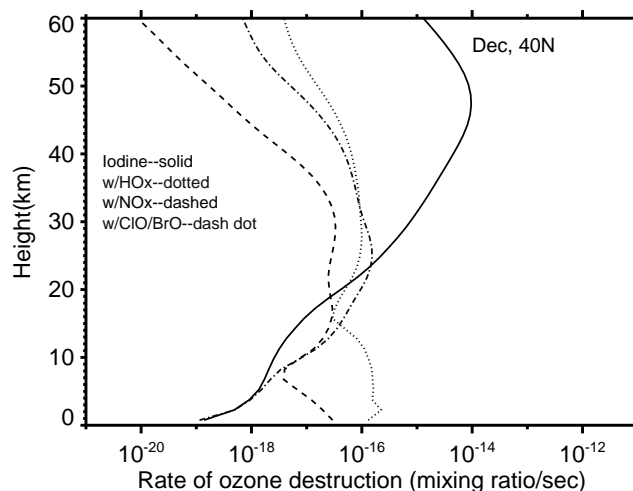


Fig. 3. The rates of ozone destruction for iodine catalytic cycles with different chemical species. In the legend, “Iodine” refers to iodine self-catalytic cycles, “w/HO_x” refers to catalytic cycles of iodine with HO_x, “w/NO_x” refers to catalytic cycles of iodine with NO_x, and “w/ClO/BrO” refers to catalytic cycles of iodine with ClO and BrO. Results are calculated by the UIUC 2-D CRT model for 40° N in December.

sphere is comparable to the highest fraction of reactive chlorine radicals in the stratosphere. The analysis above indicates that iodine is much more effective for ozone destruction than chlorine and the largest impact of iodine species on ozone should be in the stratosphere where the fraction of reactive iodine radicals is extremely high.

3.3 Iodine catalytic cycles

Catalytic cycles refer to cycles that have reactive halogen species in the atmosphere and act as catalysts in a series of reactions that are closely linked with ozone. Catalytic cycles are the primary mechanism for destruction of ozone in the stratosphere. In this section, we focus on the most important catalytic cycles of reactive iodine radicals with themselves, NO_x and HO_x, as well as halogens. An explicit list of all the major catalytic cycles related to iodine species is organized in Table 2. We categorized the iodine catalytic cycles into four groups: self-catalytic, with HO_x, with NO_x, and with ClO_x/BrO_x. This shows the individual effects of cycles with some major atmospheric reactive species. Figure 3 shows the calculated ozone loss rates due to the four groups at 40° N in December with the UIUC 2-D CRT model. For this analysis, we found that the iodine self-catalytic cycles were the dominant cycles in ozone loss from iodine in the middle and upper stratosphere at approximately 30 km and above. In contrast, the catalytic cycles with HO_x were of most importance in the troposphere, which compares well with the results by Stutz et al. (1999) and Carpenter (2003). Catalytic cycles with Cl and Br halogen were relatively less

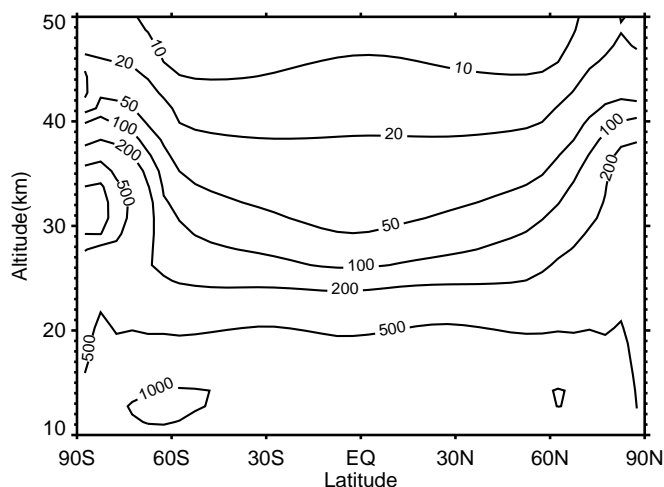


Fig. 4. Annually averaged ozone destruction efficiency of iodine chemicals relative to chlorine chemicals with latitude and altitude by the UIUC 2-D CRT model.

efficient at the latitudes in Fig. 3 but are important in the upper troposphere and lower stratosphere (UTLS) where the catalytic mechanisms are most complicated due to the competition between several categories of catalytic cycles. Figure 3 further illustrates the significant role of iodine in the stratosphere and the variability with altitude of several catalytic cycles involving iodine. It is worthy to notice that reactions of IO with itself, O, NO_x, HO_x and ClO/BrO, are all negatively dependent on temperature or independent of temperature. Therefore, the low temperature in the upper atmosphere would not decelerate the rates of iodine catalytic cycles if these reactions were rate-limiting steps. However, the reaction of I with ozone molecules, which is the initial reaction of all major iodine chemical cycles, is positively dependent on temperature. As a result, in the cold sections of UTLS with relatively low ozone abundance, iodine catalytic cycles are not very effective since IO production is limited. A previous study by Solomon et al. (1994b) suggested that iodine catalytic cycles with ClO/BrO were the dominant ozone depletion mechanism of iodine, but the chemical reaction-rate coefficients of ClO+IO and BrO+IO were unavailable at that time and assumed to be $1 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ and the self-catalytic cycles discussed in this study were not considered. New laboratory results (Bedjanian et al., 1998; Gilles et al., 1997) showed that the chemical reaction-rate coefficients of these two reactions are an order of magnitude smaller than the assumed values in the work of Solomon et al. (1994b).

3.4 Ozone Depletion Efficiency (ODE) and Ozone Depletion Potential (ODP)

CF₃I is photolytically reactive in the troposphere and can be quickly decomposed by absorption of solar radiation. Products containing iodine are removed via rainout processes if

the iodine resides in lower levels of the troposphere. Thus only about 0.1 from surface emissions. On the other hand, when reaching the stratosphere, iodine-containing chemicals can destroy ozone dramatically through catalytic ozone depletion cycles. Figure 4 shows altitude-and-latitude dependent annually averaged Ozone Depletion Efficiency (ODE) of Iodine compounds (I_y) relative to Chlorine compounds (Cl_y). The ODE here is defined to account for all the ozone loss procedures involving a chemical from thermal and photochemical reactions. Therefore, ODE is always employed to assess the instantaneous local chemical efficiency of a chemical for ozone destruction. From Fig. 4 it is obvious that iodine compounds generated by CF₃I could destroy ozone much more efficiently than chlorine compounds, especially in the lower and middle stratosphere where most of stratospheric ozone resides. Even though chlorine compounds have been considered to be the major driving forces of the past ozone depletion (e.g., WMO, 1999), chemicals with iodine such as CF₃I could potentially have large impact on stratospheric ozone. If released at the Earth's surface, only very small amount of CF₃I could be transported to the stratosphere directly. Taking the short atmospheric lifetime of CF₃I into account, more iodine is likely to reach the stratosphere indirectly from CF₃I reaction products. Much of the reactive iodine from the photolysis of CF₃I will be released at an altitude and latitude near the locations the emissions occur. In the case of CF₃I from aircraft emissions, if many of them were released in the lower stratosphere or higher troposphere above the altitude where they could be rained out efficiently, then the reactive iodine could have much stronger effects on ozone than those released near the surface.

The concept of ODPs are defined to evaluate relative cumulative effects on ozone of the emission of a gas, relative to one of the gases of most concern to ozone change, namely CFC-11 (CFCl₃) (e.g., Wuebbles et al., 1983, 1995, 2001; Solomon et al., 1992; WMO, 1995, 1999). To obtain the ODPs of a gas, a certain amount of emission perturbation that depletes 1% total ozone at steady-state needs to be put into the model run. The ODP provides a single-valued, relative evaluation for a given compound and therefore is a useful scientific index for public policy. ODPs are a vital part of the current U.S. Clean Air Act, in which 0.2 is the upper bound of ODP values of any chemical that is not controlled. Additionally, chemicals with ODPs of 0.05 or larger should be considered carefully, according to the U.S. EPA. Traditionally, ODPs have been evaluated on the basis that most chemicals evaluated for ODPs have long enough lifetime to spread all over the atmosphere globally. However, as a chemical with extremely short lifetime, on the order of several days, CF₃I is not expected to be well mixed in the atmosphere and thus has ODPs that should be dependent on location. Therefore, a more thorough study to investigate ODPs of CF₃I as a function of location (latitude, altitude, etc.) needs to be carried out using a three-dimensional model as suggested by Wuebbles et al. (2001). As a result of the temporal and

Table 3. Surface emission scenarios for CF₃I and its impact on global ozone.

Flux Scenario	$\tau_{\text{CF}_3\text{I}}$ (days)	Percent ozone depletion per mass unit (%/Tg)	ODP
Northern Hemisphere/Surface	3.7	7.158	0.013
30°–60° N/Surface	3.8	4.600	0.011
5° S–30° N/Surface	1.0	9.629	0.018

Table 4. Estimated ozone depletion effects of CF₃I using the original estimate (Rupnik et al., 2002) of the CF₃I emission profile.

Run Description	$\tau_{\text{CF}_3\text{I}}$ (days)	Ozone depletion per mass unit (Pg/Tg)	ODP
0°–10° N/aircraft emission	0.7	137.4	0.254
30°–40° N/aircraft emission	1.2	44.53	0.084
55° N–60° N/aircraft emission	7.1	37.63	0.071

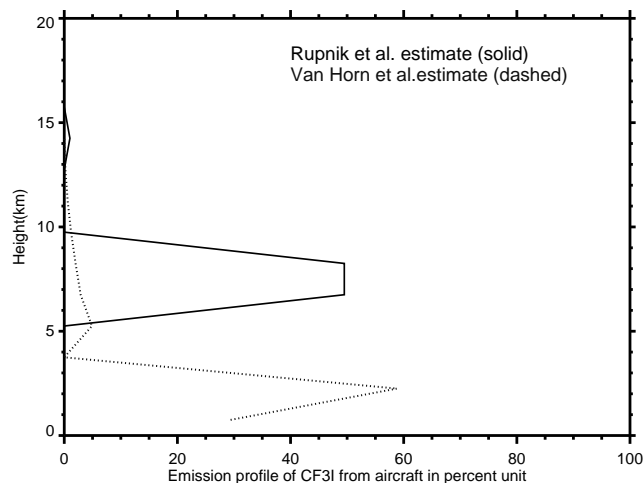
spatial variation, CF₃I emissions from aircraft are expected to have rather different ODP values from the ones derived from surface emissions.

Several earlier studies have evaluated potential effects of CF₃I on ozone, particularly stratospheric ozone in terms of ODPs. Assuming CF₃I emissions from the Earth surface only, early studies obtained extremely small ODPs of CF₃I, which were <0.008 by Solomon et al. (1994b) and 0.006 by Connell et al. (1996). Using the 2004 version UIUC 2-D CRT model, we have determined an ODP for surface emissions of CF₃I that was 0.013, based on the assumption that emissions were evenly spread throughout the Northern Hemisphere. Table 3 summarizes ODP values from several scenarios of surface emissions of CF₃I by the UIUC 2-D CRT model. In general, ODP values of CF₃I from surface emissions distribute in the range of 0.01 to 0.02.

However, as a chemical with an extremely short lifetime, the ODPs for CF₃I depend on altitude and latitude as discussed before. Therefore, emissions of CF₃I from aircraft could have rather different ODPs from the ones presented above. We discuss this in detail in Sect. 4.

4 ODP for CF₃I in different applications

“Fuel-inerting” refers to the safety action to protect fuel tank that contains highly flammable material, by pumping some inert gas or vapor, such as CF₃Br, into its air space in order to displace oxygen. As a candidate replacement of CF₃Br, CF₃I released from aircraft for fuel inerting and its relevant impact on ozone need to be assessed scientifically. The original estimate of CF₃I emissions from F-16 military aircraft by Rupnik et al. (2002) indicated that most of the emissions

**Fig. 5.** The vertical profiles of CF₃I emissions for fuel inerting in military aircraft by Rupnik et al. (2002) and Van Horn et al. (1999). Percent unit is mass-weighted.

occur in the middle upper troposphere, where a large fraction of reactive iodine could reach the stratosphere through vertical atmospheric transport processes. Specifically, the emission profile is: 99% between 21 000 and 30 000 kft (approximately 6 km–9 km), and 1% at about 45 000 kft (approximately 13.5 km), roughly even distributed (Rupnik et al., 2002). As a response to the critique of Rupnik et al. (2002) by Banister et al. (2002), we further considered a different CF₃I emission profile from F-16 military aircraft described by Van Horn et al. (1999), which we call the Van Horn estimate. The Van Horn estimate, in which most of CF₃I emissions for fuel inerting were released at much lower altitudes, was employed to do a sensitivity study by the UIUC 2-D CRT model. Figure 5 illustrates the difference between these two estimates. Note that most of CF₃I emissions in the original estimate reside near the tropopause and therefore have a better chance to survive rainout and reach the stratosphere where the reactive iodine radicals fraction is of its largest values. In contrast, in the Van Horn estimate, a large amount of CF₃I emissions is located in the middle or lower troposphere. With the goal of evaluating the effects of CF₃I emissions from aircraft comprehensively, we have done 3 case studies based on both of the original and Van Horn estimates above using the 2004 version UIUC 2-D CRT model. The three cases were designed to simulate flights occurring in three different latitude regions: 0°–10° N, 30°–40° N, and 55°–65° N, which represented tropics, lower midlatitudes and higher midlatitudes. All the model runs were scaled to deplete 1% global total ozone from the background atmosphere, which was without aircraft-released CF₃I perturbation, for the purpose of calculating ODPs of CF₃I emissions. Results of these calculations were shown in Tables 4 and 5.

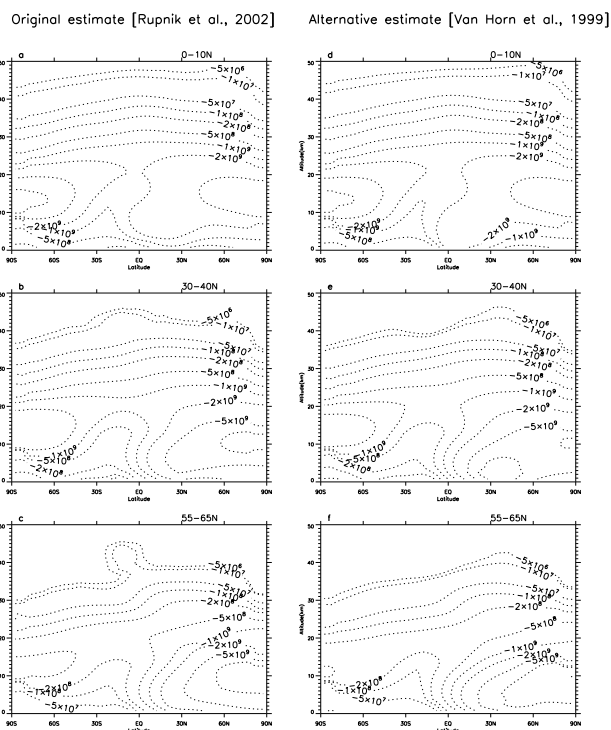
Table 5. Estimated ozone depletion effects of CF₃I using the alternative estimate (Van Horn et al., 1999) of the CF₃I emission profile.

Run Description	$\tau_{\text{CF}_3\text{I}}$ (days)	Ozone depletion per mass unit (Pg/Tg)	ODP
0°–10° N/aircraft emission	0.1	26.62	0.050
30°–40° N/aircraft emission	3.4	10.17	0.019
55°–65° N/aircraft emission	8.9	13.18	0.025

For the original estimate, the resulting ODPs were in the range of 0.07 to 0.25, above the EPA value of concern of 0.05. With respect to the Van Horn estimate, all the resulting ODPs were less than or at most equal to 0.05. Given the fact that aircraft are typically operated at mid-latitudes (case 2 and 3 in this study) in the Northern Hemisphere, where most of the population resides, CF₃I emissions following the Van Horn estimate would not have a substantial impact on ozone. Based on the comparison of the results from two different estimates, we determined that both the altitude and latitude where the CF₃I emissions from aircraft occur could play a role on the effects of CF₃I on ozone. The altitude factor may be more important since it affects the ODE of iodine compounds dramatically.

Figure 6 illustrates the ozone concentration changes in the three cases for both estimates of aircraft-released CF₃I emission profile. As shown in the figure, for the original estimate, major ozone depletion occurs in the lower stratosphere and upper troposphere. For the Van Horn estimate, the largest amount of ozone concentration decrease takes place at about the same altitudes but with a smaller amount, plus there is substantial ozone depletion near the altitudes where most of CF₃I is released. The general circulation in the atmosphere moves iodine around the world, and thus carries iodine species, which survive rainout processes, into the stratosphere from lower latitudes to higher latitudes. Because all the reactions of IO with itself, O, NO_x, HO_x and ClO/BrO are all negatively dependent or independent on temperature, iodine catalytic cycles are particularly effective in the cold regions but abundant with iodine-containing compounds. Therefore, the largest ozone destruction occurs in polar regions in the stratosphere, where iodine-containing compounds accumulate in a very cold environment. Figure 6 also indicates that iodine in the stratosphere can stay much longer than in the troposphere.

As discussed above, the major difference in the vertical profile of CF₃I emissions between estimates by Rupnik et al. (2002) and Van Horn et al. (1999) causes a large disparity in the ODPs of CF₃I aircraft emissions. Nonetheless, the ODP calculations based on both estimates showed that the ODP of CF₃I emissions would not exceed the upper limit value of 0.2 in the U.S. Clean Air Act, given the fact that most aircraft flights tend to occur at mid latitudes in the Northern Hemisphere.

**Fig. 6.** Annually averaged ozone concentration changes in unit of molecule.s⁻¹.cm⁻³ relative to background atmospheric conditions without CF₃I emissions from aircraft. Results from three cases (0°–10° N, 30°–40° N, 55°–65° N) shown here are based on two different estimates (the original estimate, Rupnik et al., 2002, left column; the alternative estimate, Van Horn et al., 1999, right column) of CF₃I emission profiles. All the model runs were scaled to deplete 1% global total ozone from background atmosphere.

Through interactions with Donald Bein at the National Institute of Standards and Technology (NIST) (unpublished data, 2005), we attempted to do an evaluation of the potential effects on ozone resulting from using CF₃I in fire fighting connected with engine nacelle and auxiliary power unit applications. Table 6 shows the CF₃I emission profile from NIST in detail. Similarly, we designed three cases (0°–10° N, 30°–40° N, 55°–65° N) for the latitudes where the emissions occur. The results are shown in Table 7. For the tropical case (0°–10° N), the resultant ODP was 0.084. The other two cases assuming mid latitudinal aircraft emissions gave ODPs smaller than 0.05. All the resulting ODPs were well below the control value of 0.2 in the U.S. Clean Air Act.

Though under different assumptions, the discussion of the effects on ozone resulting from aircraft-released CF₃I for fuel inerting could also apply here. In general, since most of CF₃I emissions in this estimate occur at lower altitudes, they do not tend to deplete atmospheric ozone. Therefore, provided the CF₃I emission profile from NIST is representative to the actual release characteristics, CF₃I released from aircraft for fire fighting should have a low impact on the ozone

Table 6. The NIST estimate of the CF₃I emission profile for fire fighting.

Flight Height	Model layer	Emission (kg)	Percent of total emissions
12–13.5 km	layer 9	8.73	0.57%
10.5–12 km	layer 8	13.34	0.87%
9–10.5 km	layer 7	77.93	5.07%
7.5–9 km	layer 6	22.39	1.46%
6–7.5 km	layer 5	142.34	9.26%
4.5–6 km	layer 4	45.00	2.93%
3–4.5 km	layer 3	61.51	4.00%
1.5–3 km	layer 2	115.62	7.52%
0–1.5 km	layer 1	1050.55	68.3%

layer and thus can be considered a qualified substitute for CF₃Br in fighting fires in engine nacelles.

5 Uncertainties in the study

Since iodine chemistry is not as well understood as that of its cousins, such as chlorine and bromine, there are still various uncertainties in the study, besides the needs for accurate estimates of the vertical profile and locations of CF₃I emissions we discussed above. For instance, the photolysis of OIO is highly debated. Hoffmann et al. (2001) proposed that self-reaction of OIO could form low-volatility iodine oxides with stable structures and thus result in a much longer lifetime. While Ashworth et al. (2002), as used in our study, suggests that OIO is unlikely to be an important reactant in iodine chemistry as a consequence of its extremely short photolysis lifetime. If self-reactions of OIO are important mechanisms for particle formation, which would lead to efficient loss through rainout processes, the effects of aircraft-released CF₃I on atmospheric ozone would be further decreased. On the other hand, heterogeneous reactions between reactive iodine and other active atmospheric reactants on the surface of aerosols could accelerate ozone destruction rate of iodine catalytic cycles (Larin et al., 2002). This mechanism could result in much larger ODPs of CF₃I. However, the role of this much faster heterogeneous process is still under further investigation. As mentioned earlier, further interest in CF₃I use in aircraft would require extensive studies using a three-dimensional global transport model of the troposphere and stratosphere. Nonetheless, recent modeling studies have been much improved by more observational data as well as improved laboratory experiments and thus the ability of models to simulate the real atmosphere has been largely enhanced.

6 Summary and conclusion

Compatibility of CF₃I as a replacement of CF₃Br in aircraft engine nacelles for fuel inerting and fire extinguishing has

Table 7. Estimated ozone depletion effects of CF₃I using the NIST estimate of the CF₃I emission profile.

Run Description	$\tau_{\text{CF}_3\text{I}}$ (days)	Ozone depletion per mass unit (Pg/Tg)	ODP
0°–10° N/aircraft emission	0.1	45.08	0.084
30°–40° N/aircraft emission	1.9	14.93	0.028
55°–65° N/aircraft emission	9.0	19.30	0.036

been evaluated using the UIUC 2-D CRT model. Iodine chemistry related to CF₃I emissions has been discussed. We find that iodine self-catalytic cycles dominate the ozone depletion mechanism in the stratosphere among the four iodine catalytic cycles groups. Due to the extremely short lifetime of CF₃I and the high ozone depletion efficiency of iodine species in the stratosphere, locations (altitudes, latitudes, etc.) where CF₃I emissions are released can impact the potential effects of iodine species on atmospheric ozone significantly. For the usage of CF₃I for fuel inerting, two estimates of CF₃I emission profile have been considered. Results showed that ODPs of CF₃I emissions should be less than 0.2 except for emissions in the troposphere. For the application of CF₃I for fire extinguishing, ODPs of CF₃I emissions indicated the ozone depletion effects depend on latitude and altitude of emissions, but assuming the NIST altitude distribution is correct, ODPs should be less than 0.08.

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