

POTENTIAL IMPACTS OF CF₃I ON OZONE AS A REPLACEMENT FOR CF₃Br IN AIRCRAFT APPLICATIONS

Yue Li and Donald J. Wuebbles*
Department of Atmospheric Sciences
University of Illinois, Urbana, IL 61801
Tel: 217-244-1568; wuebbles@atmos.uiuc.edu

Abstract. CF₃I has been considered to be a candidate replacement of CF₃Br 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 current UIUC 2D Chemical Transport Model (CTM). Using the former estimate of aircraft emission profile for tank inerting in military aircraft as used in (1), the resulting equivalent ODPs for CF₃I were in the range of 0.07 to 0.25, above the critical value 0.05, the U.S. EPA for policy consideration. As a sensitivity analysis, we analyzed a case with emissions associated with inerting occurring at lower altitudes. This case resulted in much lower ODPs. Finally, we analyzed the potential effects on ozone resulting from using CF₃I in fire fighting connected with engine nacelle and auxiliary power unit applications. The resulting effects on ozone showed extremely low ODPs ≤ 0.05 . The altitudes where most of aircraft released CF₃I occurs seemed to be a dominant factor in its ozone depletion effects.

INTRODUCTION

CF₃Br has been used for aircraft fire extinguishing systems because of its high fire suppression efficiency, low cost, and low toxicity. However, as a halogen compound, CF₃Br is known as an ozone depletion chemical that could destruct ozone dramatically. For this reason, substitute chemicals must be selected for consideration to replace CF₃Br usage in aircraft engine nacelles. CF₃I, a close chemical cousin of CF₃Br, has been considered to be a potential replacement because its iodine-carbon chemical bond is very weak and it is easily broken by solar radiation even in the troposphere, therefore makes CF₃I's lifetime extremely short. Unfortunately, the ozone depletion effects of CF₃I strongly depend on the altitude where CF₃I emissions occur. With the goal of evaluating this chemical objectively, several estimates of aircraft release of fire extinguishing agents with altitude have been considered. A previous study of surface CF₃I emissions (2), indicated that iodine compounds might not impact ozone significantly. However, as the laboratory results on iodine reactions keep being updated recently and the understanding of chemical processes of iodine chemistry is getting better, reevaluation of CF₃I emissions is a necessity. In addition, emissions from aircraft may have a larger impact than emissions from the Earth surface. Moreover, the role that CF₃I emissions from aircraft play in the ozone depletion is not known and needs to be studied carefully using the newest available chemistry.

UIUC 2D CTM DESCRIPTION AND UPDATES

In the early study, 2002 version UIUC 2D CTM has been employed to evaluate chemical effects of aircraft released CF₃I (1). For the purpose of this project, we have updated our UIUC 2D Chemical Transport Model into a 2004 version with the latest representation of atmospheric chemistry and dynamics.

Table 2 summarizes chemical reactions and rate coefficients related to iodine chemistry in the 2004 version UIUC 2D CTM, by which reactive iodine produced from photodissociation of CF₃I is believed to interact with atmospheric ozone. Recent laboratory studies on iodine chemistry improved the understanding of chemical processes that the iodine species lived through in the atmosphere and have been put into our UIUC 2D CTM. Chemistry updates in the 2D model that could impact effects of CF₃I on stratospheric ozone concentrations include: thermal reaction coefficients of CH₃I + OH = I + H₂O + CH₂O, CF₃I and CH₃I cross sections for photochemical reactions from (3). Since these parameters are directly related to reactive iodine generated from CF₃I emissions, they could impact the model calculations significantly. Other important chemistry updates include reaction coefficient updates for NOx: NO+O₃ from (4); NO₂+O from (5); NO₂+OH from (6). Change in nitrogen radicals affects the partitioning of other radicals significantly. Particularly, at lower stratosphere and higher troposphere, where the most effective iodine ozone depletion cycle is governed by the rate of reaction of HO₂ + IO → HOI + O₂, NOx could also impact the chemical efficiency of iodine compounds through thermal reactions with iodine chemicals.

Updated dynamical processes incorporated in the 2004 version UIUC 2D CTM include diabatic circulation, planetary wave, gravity waves, advection, and eddy turbulent transport. Transport fields in the model are described by the combination of the zonal mean momentum equation, the thermodynamic equation and thermal wind equation. The continuity equation is solved using a variable step, variable order for each individual species with strict error control. Seasonal varying K_{yy} values in the stratosphere are determined by dissipation rate and vorticity of planetary wave number 1 and 2. K_{zz} values are obtained from gravity waves. Boundary conditions for halocarbons are based on (7) WMO(1999) conditions. The net heating rates, including latent heat, are based on National Center for Environmental Prediction (NCEP) analysis, which allows seasonal-dependent climatological temperatures and chemical species distributions. The model includes latest update on the formation of polar stratospheric clouds (PSCs) with a seasonal time-dependent parameterization. As one of the most important driving forces of iodine distribution, dynamics plays an important role in the study, especially the related transport processes which decide the fraction of the emitted iodine reaching the stratosphere. Updates in dynamics in 2004 version could provide more accurate simulation of the atmospheric transport system and therefore better evaluation of potential effects of CF₃I emissions.

Table 1. Major Iodine chemical reactions in the 2004 version UIUC 2D CTM

Thermal Reactions	A	E/R	References
I + O ₃ = IO + O ₂	2.30e-11	870.	(3)
I + HO ₂ = HI + O ₂	1.50e-11	1090.	(3)
I + ClO = IO + Cl	4.40e-11	0.	(8)
I + OClO = IO + ClO	9.70e-12	1190.	(8)
I + BrO = Br + IO	1.45e-11	0.	(9)
I ₂ + O = IO + I	1.40e-10	0.	(10)
I ₂ + OH = HOI + I	1.80e-10	0.	(10)
I ₂ + NO ₃ = I + IONO ₂	1.50e-12	0.	(10)
I ₂ + Cl = I + ICl	2.10e-10	0.	(8)
I ₂ + Br = I + IBr	1.20e-10	0.	(9)

POTENTIAL EFFECTS OF CF₃I ON OZONE

Thermal Reactions	A	E/R	References
IO + O = I + O ₂	1.20e-10	0.	(3)
IO + HO ₂ = HOI + O ₂	8.40e-11	0.	(3)
IO + NO = I + NO ₂	9.10e-12	-240.	(3)
IO + ClO = I + OClO	2.81e-12	-280	(9)
IO + ClO = I + Cl + O ₂	1.28e-12	-280	(9)
IO + ClO = ICl + O ₂	1.02e-12	-280	(9)
IO + Br = I + BrO	2.30e-11	0	(9)
IO + BrO = I + Br + O ₂	8.75e-12	-260	(11)
IO + BrO = IBr + O ₂	1.63e-11	-260	(11)
IO + IO = I ₂ + O ₂	5.00e-12	0	(12)
IO + IO = I + OIO	3.05e-11	0	(12)
IO + IO = 2I + O ₂	6.35e-11	0	(12)
HI + OH = H ₂ O + I	3.00e-11	0.	(3)
INO + INO = I ₂ + 2NO	8.40e-11	2620.	(3)
INO ₂ + INO ₂ = I ₂ + 2NO ₂	2.90e-11	2600.	(3)
CH ₃ I + OH = I + H ₂ O + CH ₂ O	2.90e-12	1100.	(3)

Three body Troe expression	K ₀ (300)	n	K _∞ (300)	f	g	Reference
I + NO = INO	1.80e-32	1.0	1.70e-11	0.0	0.0	(3)
I + NO ₂ = INO ₂	3.00e-31	1.0	6.60e-11	0.0	0.0	(3)
IO + NO ₂ = IONO ₂	5.90e-31	3.5	9.00e-12	1.5	0.0	(3)

Photolysis reactions						
IO + hv = I + O						(10)
HOI + hv = I + OH						(10)
INO + hv = I + NO						(10)
INO ₂ + hv = I + NO ₂						(10)
IONO ₂ + hv = I + NO ₃						(10)
IONO ₂ + hv = IO + NO ₂						(10)
OIO + hv = O + IO						(13)
ICl + hv = I + Cl						(13)
IBr + hv = I + Br						(13)
I ₂ + hv = I + I						(14)
CH ₃ I + hv = CH ₃ + I						(3)
CF ₃ I + hv = CF ₃ + I						(3)

ATMOSPHERIC CHEMISTRY RELATED TO CF₃I

Photodissociation and thermal reactions

CF₃I has been considered one of the leading substitutes for the replacement of halon fire extinguishing agents since the C-I bond in CF₃I is very weak and can be photodissociated rapidly even in the troposphere, which means the impacts of this compound might be trivial. However,

we need to further examine the products of the photodegradation process to evaluate the total impacts of CF₃I release. Previous studies of iodine are quite limited, most of them concentrated on iodine originated from a marine environment where the major natural iodine emissions occur. (15-18). Due to the incomplete understanding of iodine chemistry, the study on impacts of iodine compounds on the atmosphere is still in the initial stage, especially for troposphere. In the UIUC 2D CTM, chemical compounds and free radicals generated from CF₃I emissions are considered to be I, I₂, IO, OIO, HI, HOI, INO, INO₂, IONO₂, ICl, IBr. Among these, I and IO are the reactive iodine radicals that can potentially destroy ozone and HOI, HI, 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. Generally speaking, iodine atoms released from the dissociation of CF₃I act as the starting point of iodine chemistry, which in turn react with oxides (O₃, ClO, BrO) to form IO and with HO₂ to form HI. As a consequence, IO and I are reactants in several catalytic cycles with other species like HO_x, NO_x and halogen. The photolysis happens during the day when there is sufficient sunlight. While during night, I and IO react with HO₂ or NO₂ to form reservoir species, since most reservoir species of iodine are photodissociated quickly 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 1 illustrates the ratio of these reactive species to total iodine species (I_y) with altitude. It is apparent that, no matter what season it is, reactive iodine radicals are a large fraction of the total iodine in the stratosphere, especially the lower and middle stratosphere. In contrast, even the lowest fraction of reactive iodine radicals in the troposphere is comparable to the highest fraction of reactive chlorine radicals in the stratosphere. This shows that iodine compounds are much effective for ozone destruction and the largest impacts may appear in the stratosphere where the fraction of reactive iodine radicals is dramatically high.

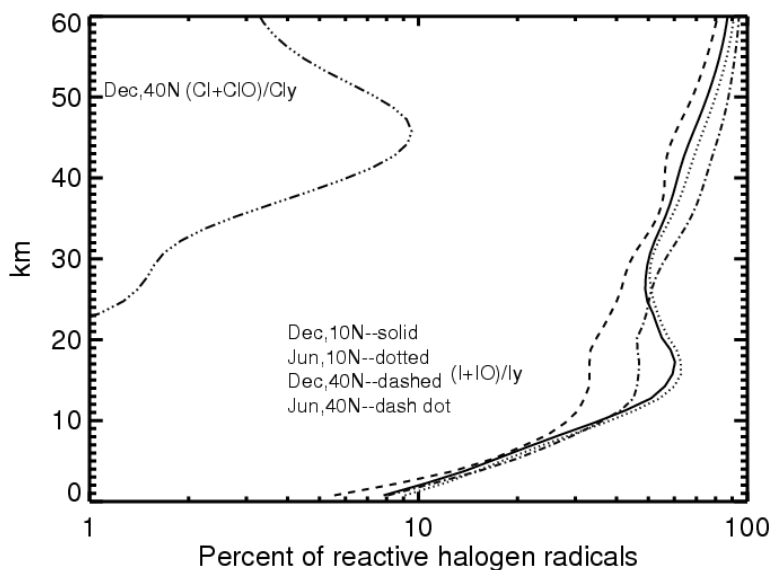


Figure 1. The fraction of reactive free halogen radicals (I+IO/Cl+ClO) among total halogen species (I_y/Cl_y) from the calculation by UIUC 2D CTM for background atmosphere. Results are shown for 10N and 40N for June and December to illustrate the seasonal impacts.

3.2 Iodine catalytic cycles

Similar to chlorine, reactive free iodine radicals destroy ozone mainly through catalytic cycles. Catalytic cycles refer to cycles that have reactive halogen species in the atmosphere act as catalysts in a series of reactions that are closely linked with ozone. The catalytic mechanism

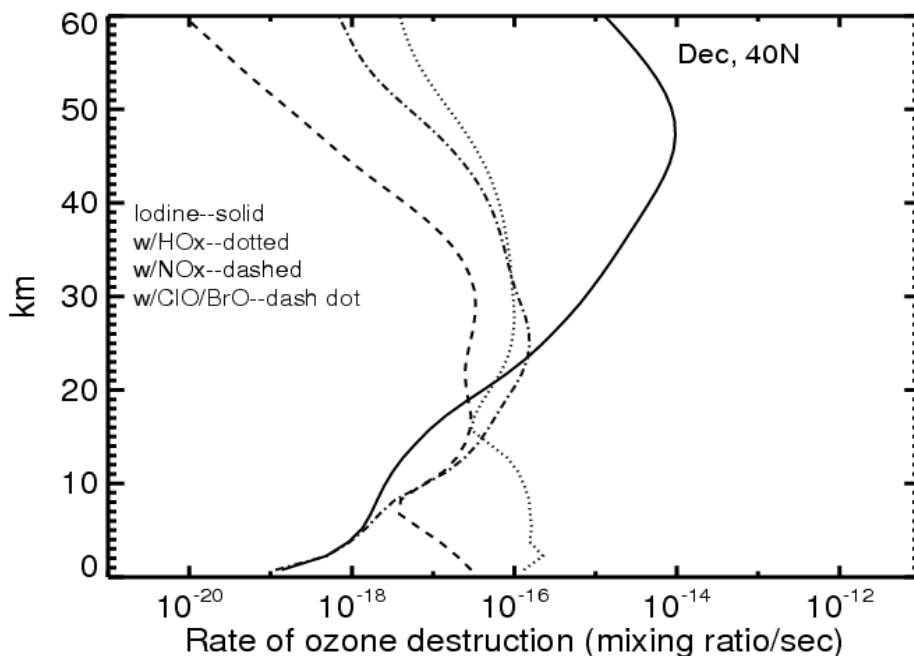


Figure 2. The rates of ozone destruction for iodine catalytic cycles with different chemical processes. In the legend, “Iodine” refers to iodine self-catalytic cycles, “w/HOx” refers to catalytic cycles with HOx, “w/NOx” refers to catalytic cycles with NOx, “w/ClO/BrO” refers to catalytic cycles with ClO and BrO. Results here are calculated by UIUC 2D CTM for 40N for December.

depletes two ozone molecules per cycle. (19) 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 NOx and HOx, as well as halogen. Figure 2 shows the calculated ozone loss rates for 10N and 40N for December by the UIUC 2D CTM. From this analysis we found that the iodine self-catalytic cycles are the dominant cycles in ozone loss from iodine in the middle and upper stratosphere from around 30km to 50km. In contrast, the catalytic cycles with HOx are most important in the troposphere. Catalytic cycles with halogen are relatively weak at latitudes mentioned above but rather important in the upper troposphere and lower stratosphere (UTLS) where the catalytic mechanism is most complicated due to competition between several categories of catalytic cycles. Figure 2 further illustrates the important role of iodine in the stratosphere and the variability with altitude of several catalytic cycles involving iodine. A previous study in (20) suggested iodine catalytic cycles with ClO/BrO were the dominant ozone depletion mechanism of iodine, but the chemical reaction coefficients of ClO+IO and BrO + IO were unavailable and assumed to be $1 \times 10^{-10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. New laboratory results (9,11) showed that the chemical reaction coefficients of these two reactions are

two orders of magnitude smaller than the assumed values in (20). Therefore, discussion about iodine chemistry here should be more justifiable.

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

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 (CFC13) (7, 21-24). To obtain the ODPs of a gas species, 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 favorable 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. Also, chemicals with ODPs of 0.05 or larger should be applied carefully, according to the U.S. EPA.

The potential effects of CF₃I on atmospheric ozone, particularly stratospheric ozone, in terms of ODPs, have been studied in recent years. Assuming CF₃I emissions from the Earth's surface only, early studies obtained extremely small ODPs of CF₃I, which were <0.008 in (20) and 0.006 in (25). Using the 2002 version UIUC 2D CTM, we have determined an ODP for surface emissions of CF₃I that is 0.013, based on the assumption that emissions are evenly spread throughout the Northern Hemisphere. Table 2 summarizes ODP values from several scenarios of surface emissions of CF₃I. In general, ODP values of CF₃I from surface emissions reside in the range of 0.01 to 0.02. The recent model updates including chemical reaction coefficients from (3) and photochemical cross sections of CF₃I and CH₃I do not substantially affect the results discussed here.

Table 2. Surface emissions scenarios for CF₃I and its impacts on ozone with the 2002 version of UIUC 2D CTM

Flux Scenario	$\tau_{\text{CF}_3\text{I}}$ (days)	Percent ozone depletion per mass unit(%/Tg)	ODP
Northern Hemisphere	3.7	0.221	0.013
30°-60°N	3.8	0.142	0.011
5°S-30°N	1.0	0.2973	0.018

However, as a chemical with an extremely short lifetime (on the order of several days), the ODPs for CF₃I are dependent on altitude and latitude. Therefore, emissions of CF₃I from aircraft could have different ODP values from the ones presented here. CF₃I is very reactive in the troposphere and will be quickly decomposed by absorption of solar radiation. Products with iodine will be removed through rainout processes in the lower troposphere. For this reason, only a tiny fraction of CF₃I can reach the stratosphere from the surface emissions. However, when reaching the stratosphere, iodine chemicals could destroy ozone very efficiently through catalytic ozone depletion cycles. Figure 3 shows altitude and latitude dependent annually averaged 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 efficiency of a chemical for ozone destruction. From Figure 3 it is obvious that iodine compounds generated by CF₃I could destruct ozone much more efficiently than chlorine compounds, especially in the

lower and middle stratosphere where most of stratospheric ozone resides. Since chlorine compounds have been considered to be the major driving forces of ozone depletion, chemicals with iodine, such as CF₃I, could have large potential impacts on stratospheric ozone. If released at the Earth's surface, only very small amount of CF₃I will be transported to the stratosphere. Taking the extraordinarily short atmospheric lifetime of CF₃I into account, much of the reactive iodine from the photodissociation reactions of CF₃I will reside at an altitude and latitude near the locations the emissions are released. In the case of CF₃I from aircraft emissions, if emissions were released in the lower stratosphere or higher troposphere above the altitude where they could be rained out, then the reactive iodine could have much stronger effects on ozone than CF₃I released near the surface.

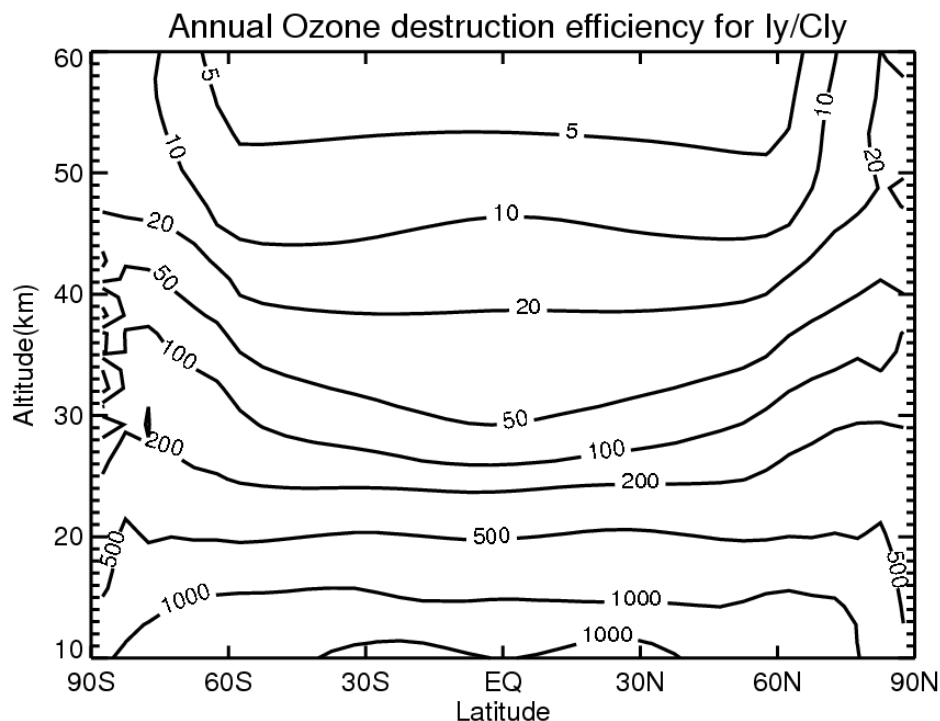


Figure 3. Annually averaged ozone destruction efficiency of iodine chemicals relative to chlorine chemicals with latitude and altitude by 2004 version of UIUC 2D CTM.

COMPATIBILITY OF CF₃I FOR FUEL INERTING IN AIRCRAFT ENGINE NACELLES

As a candidate replacement of CF₃Br, CF₃I released from aircraft for fuel inerting and its related impacts on ozone need to be assessed scientifically. Old estimate of CF₃I emissions of F-16 aircrafts suggested that most of the emissions occur above the altitudes where rain generally happens, which indicated 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 6km-9km), roughly even distributed; and 1% at about 45,000 kft (approximately 13.5km) (1). As a response to the critique of (1) in (26), we further considered a different CF₃I emission profile described in (27), in which most of CF₃I emissions for fuel inerting are released at much lower altitudes, as a sensitivity study. Figure 4 illustrates the difference between these two estimates. Note that most of CF₃I emissions in (1) reside near

the tropopause and therefore have a better opportunity to survive rainout and reach the stratosphere where the reactive iodine radicals fraction is largest, while in (27), a large amount of CF₃I emissions locate in the middle or lower troposphere. To evaluate the effects of CF₃I emissions thoroughly, we have done 3 case studies based on both of the emission profiles above using the 2004 version UIUC 2D CTM. The three cases were designed to simulate flights occurring in three different latitude regions: 0-10°N, 30-40°N, and 55-65°N. All the model runs were scaled to deplete 1% global total ozone from the background atmosphere without CF₃I perturbation, for the purpose of calculating ODPs of CF₃I emissions. Results of these calculations are shown in Table 3 and Table 4.

Table 3. Estimates of ozone depletion effects of CF₃I from aircraft emissions in (1) with the 2004 version of UIUC 2D CTM

Run Description	τ_{CF_3I} (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

Table 4. Estimates of ozone depletion effects of CF₃I from aircraft emissions in (27) with the 2004 version of UIUC 2D CTM

Run Description	τ_{CF_3I} (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 estimate in (1), the resulting ODPs are in the range of 0.07 to 0.25, still above the value of 0.05, to which the U.S. EPA suggests careful consideration be applied. With respect to the estimate in (27), all the calculated ODPs were less than or at most equal to 0.05. Given the fact that aircrafts typically fly at mid-latitudes in North Hemisphere where most of continents reside, CF₃I emissions following this estimate will not have a substantial enough impact on ozone to be a concern. From the comparison of the results from two different estimates, we can see that both the altitude and latitude where the CF₃I emissions from aircraft occur can play a role on the effects of CF₃I on ozone. The altitude factor is more important since it affects the ODE of iodine compounds.

Figure 5 illustrates the ozone concentration changes in the three cases for both estimates of CF₃I emission profile. As we can see, for the estimate in (1), major ozone destruction happens in the lower stratosphere and upper troposphere. For the estimate in (27), the largest amount of ozone concentration decrease takes place at about the same altitudes but with a little lower amount, plus a substantial ozone depletion near the altitudes where most of CF₃I is released. General circulation in the atmosphere moves iodine around the world. This circulation carries iodine species which survive rainout from lower latitudes to higher latitudes in the stratosphere, therefore the largest ozone destruction occurs in polar regions in the stratosphere. Figure 5 also indicates that iodine in the stratosphere has a much longer lifetime than in the troposphere, which is long enough to impact climate on the global scale.

As discussed above, the short atmospheric lifetime of CF₃I in the troposphere allows the reactive iodine from photodissociation to be released at an altitude and latitude close to where the emissions occur. When iodine species reach the stratosphere, they can be transported by the atmospheric circulation effectively and impact stratospheric ozone in the global scale. The higher of the altitudes where most of CF₃I emissions occur, the more likely reactive iodine radicals will achieve the stratosphere and cause ozone depletion. The major difference between estimates in (1) and (27) causes a large disagreement in the ODPs of CF₃I emissions from aircraft. A more reliable estimate is needed in order to assess the effects of CF₃I more accurately. Nonetheless, the ODP calculations based on both estimates showed that the ODP of CF₃I emissions would not exceed the control value of 0.2 in U.S. Clean Air Act, given the fact that most of aircraft flights occur in mid latitudes in Northern Hemisphere

COMPATIBILITY OF CF₃I FOR FIRE EXTINGUISHING SYSTEMS IN AIRCRAFT

Through interactions with the National Institute of Standards and Technology (NIST)(28), 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 5 shows the CF₃I emission profile from NIST in detail. Similarly, we designed three cases (0-10N, 30-40N, 55-65N) for the latitudes where the emissions occur. The calculated results are shown in Table 6. For the tropic case (0-10N), the resulted ODP was 0.084, which just exceeded the suggested value of 0.05 by EPA. 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 U.S. Clean Air Act.

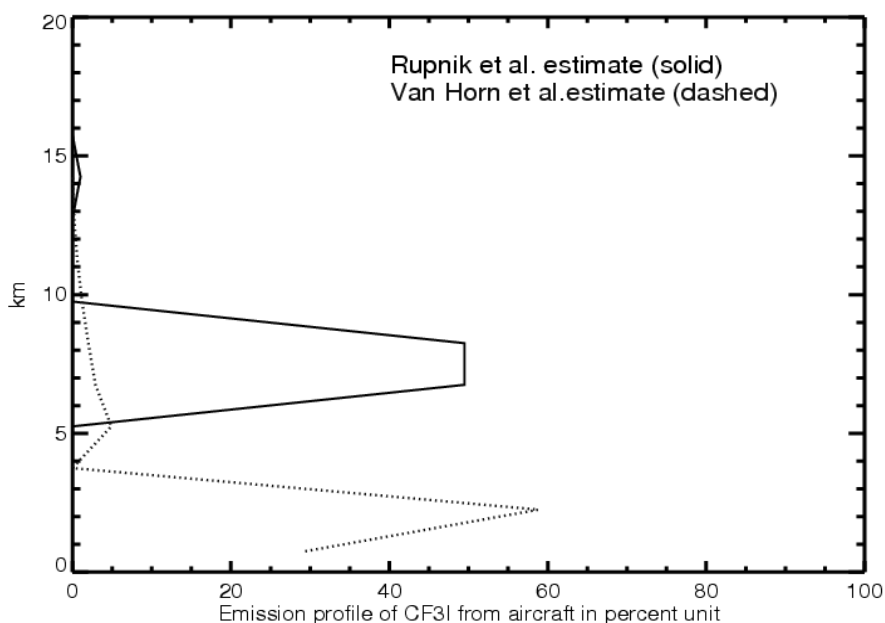


Figure 4. Aircraft emission profile of CF₃I for fuel inerting in military aircraft in (1) Rupnik et al. (2002) and (27) Van Horn et al.(1999). Percent unit is mass-weighted.

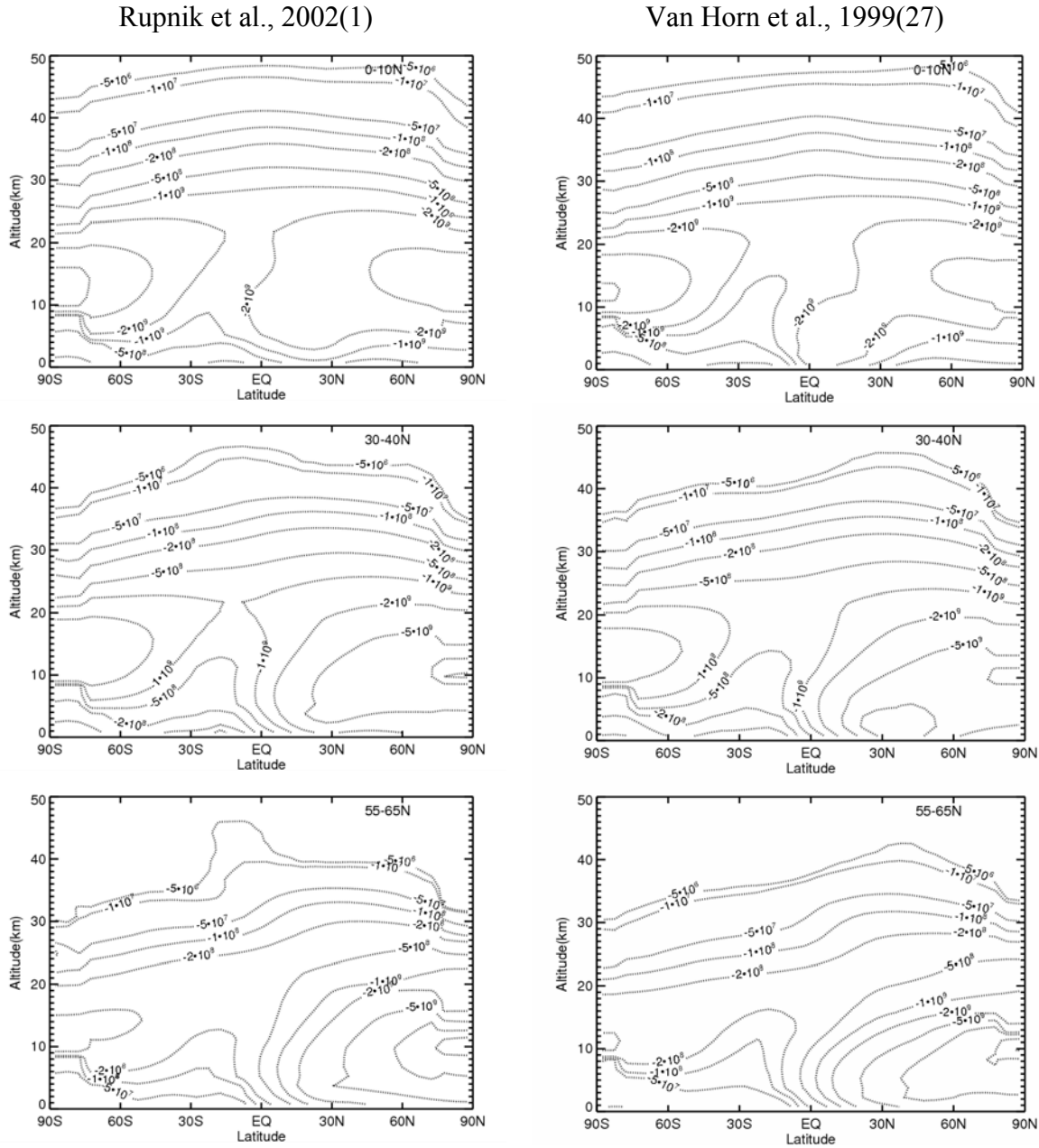


Figure 5. Annually averaged ozone concentration changes in unit of molecule.s-1.cm-3 relative to background atmospheric conditions without CF₃I emissions from aircraft. Results from three cases (0-10N, 30-40N, 55-65N) based on two different estimates (Rupnick et al (1)., left column; Van Horn et al.(27), right column) of CF₃I emission profiles are shown here. All the model runs are scaled to deplete 1% global total ozone from background atmosphere.

Table 5. NIST estimate of emission profile of aircraft emitted CF₃I for fire fighting

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

Table 6. Estimates of ozone depletion effects of CF₃I from aircraft emissions (new estimate, NIST) with 2004 version of UIUC 2D CTM

Run Description	τ_{CF_3I} (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

Though under different assumptions, the discussion of the effects on ozone resulting from aircraft emitted CF₃I for fuel inerting could also apply here. Since most of CF₃I emissions in this estimate occur at lower altitudes, they do not tend to deplete ozone dramatically. Therefore, provided the CF₃I emission profile from NIST is rather representative to the actual release characteristics, CF₃I emissions released from aircraft for fire fighting should have rather low impacts on the ozone layer and could be a qualified substitute of CF₃Br in engine nacelles.

SUMMARY AND CONCLUSION

Compatibility of CF₃I as a replacement of CF₃Br in aircraft engine nacelles for fuel inerting and fire extinguishing has been evaluated by the 2004 version UIUC 2D CTM. Iodine chemistry related to CF₃I emissions have been discussed and iodine self-catalytic cycle dominates the ozone depletion mechanism in the stratosphere. Due to the short lifetime of CF₃I in the troposphere and the high ozone depletion efficiency of iodine species in the stratosphere, altitudes where CF₃I emissions are released will impact the potential effects of iodine species on 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 will not tend to exceed the control value of 0.2 in U.S. Clean Air Act. For the application of CF₃I for fire extinguishing, ODPs of CF₃I emissions indicated the ozone depletion effects will not be significant.

ACKNOWLEDGEMENT

This study was supported in part by the DoD Strategic Environmental Research and Development Program's Next Generation Fire Suppression Technology Program under a contract from the National Institute for Standards and Technology to the University of Illinois.

REFERENCES

1. Rupnik, J., Bowman, R.G., and Berrill, P., eds., "Suitability of CF₃I to Replace Halon 1301 as the Inerting Agent Wing Fuel Tanks on the F-16 Aircraft", HydroGeoLogic, Inc., Herndon, VA, 2002
2. Solomon, S., J.B. Burkholder, A.R. Ravishankara, and R.R. Garcia, Ozone depletion and global warming potentials of CF₃I, *J. Geophys. Res.*, 99, 20929-20935, 1994.
3. Sander, S.P., R.R. Friedl, D.M. Golden, M.J. Kurylo, R.E. Huie, V.L. Orkin, G.K. Moortgat, A.R. Ravishankara, C.E. Kolb, M.J. Molina, B.J. Finlayson-Pitts, Chemical kinetics and photochemical data for use in atmospheric studies, NASA/JPL Publication 02-25, Pasadena, California, 334pp.
4. Moonen, P.C., J.N. Cape, R.L. Storeton-West, and R. McColm, Measurement of the NO+O₃ reaction rate at atmospheric pressure using realistic mixing ratios, *J. Atmos. Chem.*, 29, 299-314, 1998
5. Gierczak, T., J.B. Burkholder, S. Bauerle, and A.R. Ravishankara, Photochemistry of acetone under tropospheric conditions. *Chem. Phys.*, 231, 299-244, 1999.
6. Brown, S.S., R.K. Talukdar, and A.R. Ravishankara, Rate constants for the reaction OH+NO₂+M & HNO₃+M under atmospheric conditions, *Chem. Phys. Lett.*, 299, 277-284, 1999.
7. World Meteorological Organization (WMO), Scientific Assessment of Ozone Depletion: 1998. Global Ozone, Research and Monitoring Project. Report 44, Geneva, 1999.
8. Bedjanian Y, LeBras G, Poulet G, Kinetics and mechanism of the IO+ClO reaction, *J. PHYS. CHEM.*, 101 (22): 4088-4096 MAY 29 1997
9. Bedjanian, Y., LeBras, G., Poulet, G., 1998. Kinetics and mechanism of the IO+BrO reaction. *Journal of Physical Chemistry A* 102, 10501–10511.
10. Atkinson R., Gas-phase tropospheric chemistry of volatile organic compounds, *J. Phys chem ref data*, 26, 1997
11. Gilles, M.K., Turnipseed, A.A., Burkholder, J.B., Ravishankara, A.R., Solomon, S., 1997. Kinetics of the IO radical. 2. Reaction of IO with BrO. *Journal of Physical Chemistry A*, 101, 5526–5534.
12. Harwood, M.H., Burkholder, J.B., Hunter, M., Fox, R.W., Ravishankara, A.R., 1997. Absorption cross sections and self-reaction kinetics of the IO radical. *Journal of Physical Chemistry A* 101, 853–863.

13. DeMore, W.B., Sander, S.P., Golden, D.M., Hampson, R.F., Kurylo, M.J., Howard, C.J., Ravishankara, A.R., Kolb, C.E., Molina, M.J., 1997. Chemical kinetics and photochemical data for use in stratospheric modeling. Evaluation Number 12, Jet Propulsion Laboratory.
14. Tellinghuisen J., Resolution of the visible-infrared absorption spectrum of I₂ into three contributing transitions, *J. Chem. Phys.*, 58 (1973), 2821-2834
15. Chameides, W. L., and D.D. Davis, Iodine: Its possible role in tropospheric photochemistry, *J. Geophys. Res.*, 85, 7383-7398, 1980
16. Chatfield, R.B., and P.J. Crutzen, Are there interactions of iodine and sulfur species in marine air photochemistry?, *J. Geophys. Res.*, 95, 22, 1990
17. Davis, D, Crawford J, Liu S, et al., Potential impact of iodine on tropospheric levels of ozone and other critical oxidants, *J. Geophys. Res.*, 101 (D1), 2135-2147, 1996
18. Aliche B, Hebestreit K, Stutz J, et al., Iodine oxide in the marine boundary layer *Nature*, 397, 572-573, 1999
19. Wayne R.P., Halogen oxides – radicals, sources, and reservoirs in the laboratory and in the atmosphere – preface, *Atmos. Environment*, 29 (20): 2675-2675, 1995
20. Solomon, S, R.R. Garcia, A.R. Ravishankara, On the role of iodine in ozone depletion, *J. Geophys. Res.*, 99 (D10), 20491-20499 OCT 20 1994
21. Wuebbles D, Weighing functions for ozone depletion and greenhouse gas effects on climate, *Annual review of energy and environment*, 20, 45-70, 1995
22. Wuebbles, D. J., K. O. Patten, M. T. Johnson, and R. Kotamarthi, The new methodology for Ozone Depletion Potentials of short-lived compounds: n-propyl bromide as an example. *J. Geophys. Res.*, 106, 14551-14571, 2001.
23. Solomon, S., and D. L. Albritton, Time-dependent Ozone Depletion Potentials for short- and long-term forecasts, *Nature*, 357, 33-37, 7 May, 1992.
24. World Meteorological Organization (WMO), Scientific Assessment of Ozone Depletion: 1994. Global Ozone, Research and Monitoring Project. Report 37, Geneva, 1995.
25. Connell, P.S.; Kinnison, D.E.; Bergmann, D.J.; Patten, K.O.; Wuebbles, D.J.; Daniel, R.G.; Williamson, C.K.; Miziolek, A.W.; Huie, R.E.; “Environmental Aspects of Halon Replacements: Considerations for Advanced Agents and the Ozone Depletion Potential of CF₃I,” presented May 7-9, 1996 at the Halon Options Technical Working Conference (HOTWC), Albuquerque, NM.
26. Banister, W. et al., Critique of the Report Suitability of CF₃I to Replace Halon 1301 as the Inerting Agent in Wing Fuel Tanks on the F-16 Aircraft, Performed by Hydro Geologics, Inc., Contract Number DACA39-99-C-0002 for the Director of Defense Research and Engineering, September 20, 2002
27. Van Horn, S.R., Juan Vitali, Capt. James Tucker, Max Delgado, Betty Rodriguez, “CF₃I Agent for Fire Extinguishment in Unoccupied Areas – Aircraft Fuel Tank Inerting Application,” Technology Transition Briefing, AFRL# 99P10VA, ASC Program #292, ASC Validated Technology # 131, June 8, 1999.
28. Data from Donald Bein of the Naval Air Systems Command by private communication, 2005.