



*Supplement of*

## **Influence of total ozone column (TOC) on the occurrence of tropospheric ozone depletion events (ODEs) in the Antarctic**

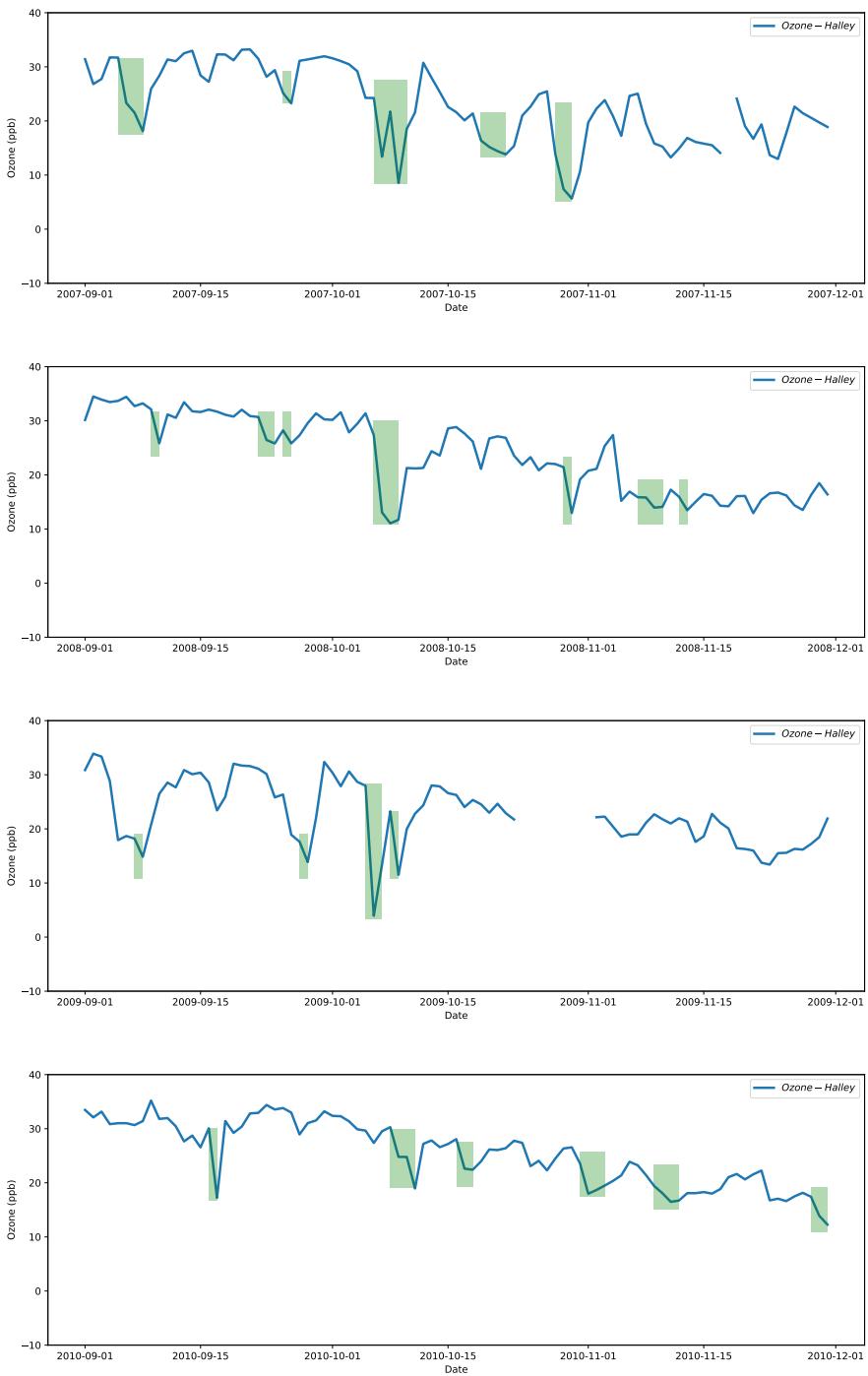
Le Cao et al.

*Correspondence to:* Le Cao (le.cao@nuist.edu.cn)

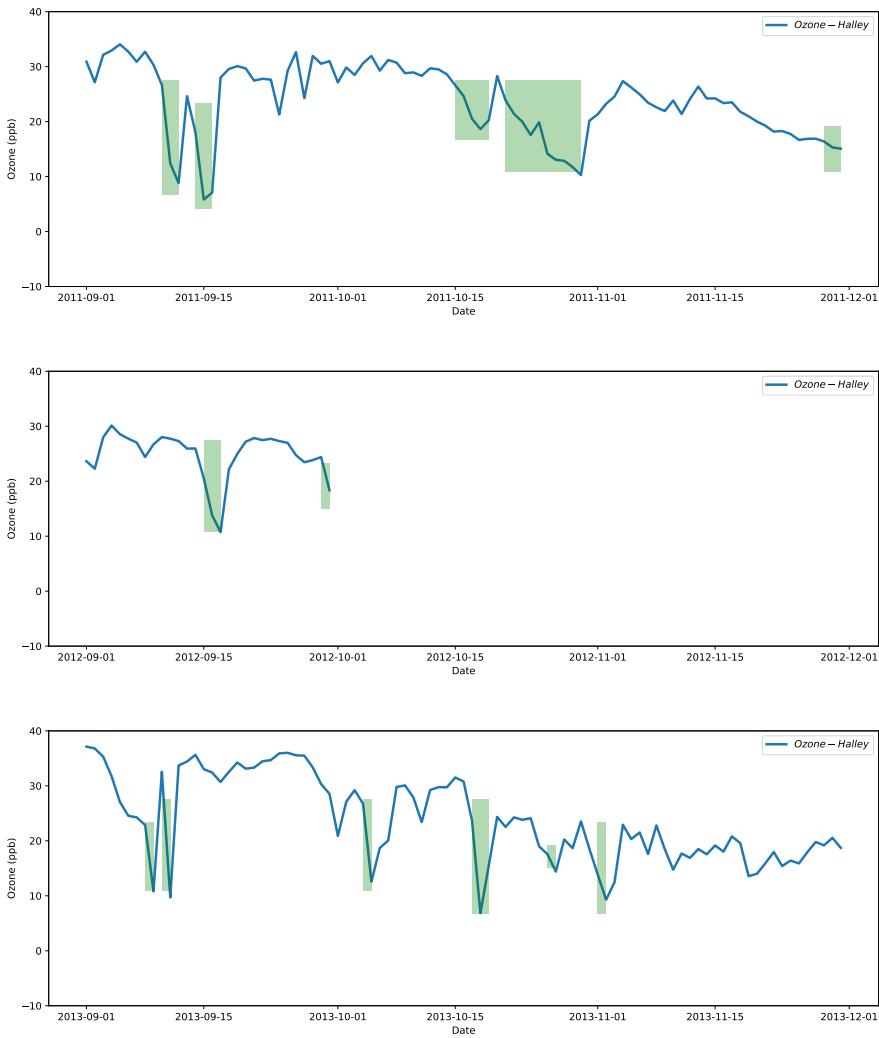
The copyright of individual parts of the supplement might differ from the article licence.

**Table S1.** Correlation coefficients between the daily TOCs belonging to different stations in the Antarctic.

Year	2007	2008	2009	2010	2011	2012	2013
Halley vs. Belgrano II	0.92	0.85	0.92	0.82	0.92	0.96	0.99
Faraday-Vernadsky vs. Marambio	0.94	0.91	0.95	0.95	0.89	0.92	0.96
Halley vs. Faraday-Vernadsky	0.62	0.35	0.13	0.39	0.41	0.47	0.72



**Figure S1.** (Continued...)



**Figure S1.** Time series of the surface ozone detected at the Halley station during the springtime of years 2007-2013. The green-shaded areas in the figure indicate the periods identified as the occurrence of ODEs in the present study. Note that the observational data of the surface ozone for October and November in the year 2012 are missing.

**Table S2.** Input parameters of the TUV model.

Parameter	Option	Value	Unit
Wavelength	Start	280	nm
	End	420	nm
	Increments	140	
Latitude		-65.25	degrees
Longitude		-64.27	degrees
Date		vary with time	
Time		12 PM	
TOC		vary with time	DU
Surface albedo		0.85	
Ground elevation		0.01	km
Measurement altitude		0.21	km
Clouds	Optical depth	0.00	km
	Base	4.00	km
	Top	5.00	km
Aerosols	Optical depth	0.235	km
	Single scattering albedo	0.990	
	Angstrom exponent	1.000	
Sunlight	Direct beam	1.0	
	Diffuse down	1.0	
	Diffuse up	1.0	

**Table S3.** The complete chemical reaction mechanism with an implementation of a constant temperature  $T = 258$  K, and the rate of third-body reactions is estimated as  $k = k_\infty \times \frac{k_0/k_\infty}{(1+k_0/k_\infty)} \times F_c^{\frac{1}{1+(\log_{10}(k_0/k_\infty))^2}}$  (Atkinson et al., 2006).

Reaction Number	Reaction	$k$ [(molec. cm <sup>-3</sup> ) <sup>1-n</sup> s <sup>-1</sup> ]	Order $n$	Reference
(SR1)	$O_3 + h\nu \rightarrow O(^1D) + O_2$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR2)	$O(^1D) + O_2 \rightarrow O_3$	$3.20 \times 10^{-11} \exp(67/T)$	2	Atkinson et al. (2006)
(SR3)	$O(^1D) + N_2 \rightarrow O_3 + N_2$	$1.80 \times 10^{-11} \exp(107/T)$	2	Atkinson et al. (2006)
(SR4)	$O(^1D) + H_2O \rightarrow 2OH$	$2.20 \times 10^{-10}$	2	Atkinson et al. (2006)
(SR5)	$Br + O_3 \rightarrow BrO + O_2$	$1.70 \times 10^{-11} \exp(-800/T)$	2	Atkinson et al. (2006)
(SR6)	$Br_2 + h\nu \rightarrow 2Br$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR7)	$BrO + h\nu \xrightarrow{O_2} Br + O_3$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR8)	$BrO + BrO \rightarrow 2Br + O_2$	$2.70 \times 10^{-12}$	2	Atkinson et al. (2006)
(SR9)	$BrO + BrO \rightarrow Br_2 + O_2$	$2.90 \times 10^{-14} \exp(840/T)$	2	Atkinson et al. (2006)
(SR10)	$BrO + HO_2 \rightarrow HOBr + O_2$	$4.5 \times 10^{-12} \exp(500/T)$	2	Atkinson et al. (2006)
(SR11)	$HOBr + h\nu \rightarrow Br + OH$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR12)	$CO + OH(+M) \xrightarrow{O_2} HO_2 + CO_2(+M)$	$1.44 \times 10^{-13} (1 + \frac{[N_2]}{4 \times 10^{19}})$	2	Atkinson et al. (2006)
(SR13)	$Br + HO_2 \rightarrow HBr + O_2$	$7.70 \times 10^{-12} \exp(-450/T)$	2	Atkinson et al. (2006)
(SR14)	$HOBr + HBr \xrightarrow{aerosol} Br_2 + H_2O$	$(\frac{r}{D_g} + \frac{4}{v_{therm}\gamma})^{-1} \alpha_{eff,aerosol}$		Cao et al. (2014)
(SR15)	$HOBr + H^+ + Br^- \xrightarrow{ice} Br_2 + H_2O$	$(r_a + r_b + r_c)^{-1} \alpha_{eff,ice}$		Cao et al. (2014)
(SR16)	$Br + HCHO \xrightarrow{O_2} HBr + CO + HO_2$	$7.70 \times 10^{-12} \exp(-580/T)$	2	Atkinson et al. (2006)
(SR17)	$Br + CH_3CHO \xrightarrow{O_2} HBr + CH_3CO_3$	$1.80 \times 10^{-11} \exp(-460/T)$	2	Atkinson et al. (2006)
(SR18)	$Br_2 + OH \rightarrow HOBr + Br$	$2.0 \times 10^{-11} \exp(240/T)$	2	Atkinson et al. (2006)
(SR19)	$HBr + OH \rightarrow H_2O + Br$	$5.50 \times 10^{-12} \exp(205/T)$	2	Atkinson et al. (2006)
(SR20)	$Br + C_2H_2 \xrightarrow{3O_2} 2CO + 2HO_2 + Br$	$4.20 \times 10^{-14}$	2	Borken (1996)
(SR21)	$Br + C_2H_2 \xrightarrow{2O_2} 2CO + HO_2 + HBr$	$8.92 \times 10^{-14}$	2	Borken (1996)
(SR22)	$Br + C_2H_4 \xrightarrow{3.5O_2} 2CO + 2HO_2 + Br + H_2O$	$2.52 \times 10^{-13}$	2	Barnes et al. (1993)
(SR23)	$Br + C_2H_4 \xrightarrow{2.5O_2} 2CO + HO_2 + HBr + H_2O$	$5.34 \times 10^{-13}$	2	Barnes et al. (1993)
(SR24)	$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O$	$1.85 \times 10^{-12} \exp(-1690/T)$	2	Atkinson et al. (2006)
(SR25)	$BrO + CH_3O_2 \rightarrow Br + HCHO + HO_2$	$1.60 \times 10^{-12}$	2	Aranda et al. (1997)
(SR26)	$BrO + CH_3O_2 \rightarrow HOBr + HCHO + 0.5O_2$	$4.10 \times 10^{-12}$	2	Aranda et al. (1997)
(SR27)	$OH + O_3 \rightarrow HO_2 + O_2$	$1.70 \times 10^{-12} \exp(-940/T)$	2	Atkinson et al. (2006)
(SR28)	$OH + HO_2 \rightarrow H_2O + O_2$	$4.80 \times 10^{-11} \exp(250/T)$	2	Atkinson et al. (2006)
(SR29)	$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$2.90 \times 10^{-12} \exp(-160/T)$	2	Atkinson et al. (2006)
(SR30)	$OH + OH \xrightarrow{O_2} H_2O + O_3$	$6.20 \times 10^{-14} (T/298)^{2.6} \exp(945/T)$	2	Atkinson et al. (2006)
(SR31)	$HO_2 + O_3 \rightarrow OH + 2O_2$	$2.03 \times 10^{-16} (T/300)^{4.57} \exp(693/T)$	2	Atkinson et al. (2006)
(SR32)	$HO_2 + HO_2 \rightarrow O_2 + H_2O_2$	$2.20 \times 10^{-13} \exp(600/T)$	2	Atkinson et al. (2006)
(SR33)	$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$	$6.90 \times 10^{-12} \exp(-1000/T)$	2	Atkinson et al. (2006)
(SR34)	$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$	$3.80 \times 10^{-15}$	2	Atkinson et al. (2006)

**Table S3.** (continued).

Reaction Number	Reaction	$k$ [(molec. cm <sup>-3</sup> ) <sup>1-n</sup> s <sup>-1</sup> ]	Order $n$	Reference
(SR35)	$\text{C}_2\text{H}_5 + \text{O}_2(+\text{M}) \rightarrow \text{C}_2\text{H}_5\text{O}_2(+\text{M})$	$k_0 = 5.90 \times 10^{-29} (T/300)^{-3.8} [\text{N}_2]$ $k_\infty = 7.80 \times 10^{-12}$ $F_c = 0.58 \exp(-T/1250)$ $+ 0.42 \exp(-T/183)$	2	Atkinson et al. (2006)
(SR36)	$\text{C}_2\text{H}_4 + \text{OH}(+\text{M}) \xrightarrow{1.5\text{O}_2} \text{CH}_3\text{O}_2 + \text{CO} + \text{H}_2\text{O}(+\text{M})$	$k_0 = 8.60 \times 10^{-29} (T/300)^{-3.1} [\text{N}_2]$ $k_\infty = 9.00 \times 10^{-12} (T/300)^{-0.85}$ $F_c = 0.48$	2	Atkinson et al. (2006)
(SR37)	$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{HCHO} + \text{CO} + \text{H}_2\text{O}$	$4.33 \times 10^{-19}$	2	Sander et al. (1997)
(SR38)	$\text{C}_2\text{H}_2 + \text{OH}(+\text{M}) \xrightarrow{1.5\text{O}_2} \text{HCHO} + \text{CO} + \text{HO}_2(+\text{M})$	$k_0 = 5.00 \times 10^{-30} (T/300)^{-1.5} [\text{N}_2]$ $k_\infty = 1.00 \times 10^{-12}$ $F_c = 0.37$	2	Atkinson et al. (2006)
(SR39)	$\text{C}_3\text{H}_8 + \text{OH} \xrightarrow{2\text{O}_2} \text{C}_2\text{H}_5\text{O}_2 + \text{CO} + 2\text{H}_2\text{O}$	$7.60 \times 10^{-12} \exp(-585/T)$	2	Atkinson et al. (2006)
(SR40)	$\text{HCHO} + \text{OH} \xrightarrow{\text{O}_2} \text{CO} + \text{H}_2\text{O} + \text{HO}_2$	$5.40 \times 10^{-12} \exp(135/T)$	2	Atkinson et al. (2006)
(SR41)	$\text{CH}_3\text{CHO} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_3\text{CO}_3 + \text{H}_2\text{O}$	$4.40 \times 10^{-12} \exp(365/T)$	2	Atkinson et al. (2006)
(SR42)	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2$	$3.42 \times 10^{-13} \exp(780/T)$	2	Atkinson et al. (2006)
(SR43)	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O} + \text{O}_2$	$3.79 \times 10^{-14} \exp(780/T)$	2	Atkinson et al. (2006)
(SR44)	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	$1.00 \times 10^{-12} \exp(190/T)$	2	Atkinson et al. (2006)
(SR45)	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{HCHO} + \text{OH} + \text{H}_2\text{O}$	$1.90 \times 10^{-12} \exp(190/T)$	2	Atkinson et al. (2006)
(SR46)	$\text{CH}_3\text{OOH} + \text{Br} \rightarrow \text{CH}_3\text{O}_2 + \text{HBr}$	$2.66 \times 10^{-12} \exp(-1610/T)$	2	Mallard et al. (1993)
(SR47)	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2$	$6.29 \times 10^{-14} \exp(365/T)$	2	Atkinson et al. (2006)
(SR48)	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \xrightarrow{\text{O}_2} 2\text{HCHO} + 2\text{HO}_2$	$3.71 \times 10^{-14} \exp(365/T)$	2	Atkinson et al. (2006)
(SR49)	$\text{CH}_3\text{OH} + \text{OH} \xrightarrow{\text{O}_2} \text{HCHO} + \text{HO}_2 + \text{H}_2\text{O}$	$2.42 \times 10^{-12} \exp(-345/T)$	2	Atkinson et al. (2006)
(SR50)	$\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O} + \text{C}_2\text{H}_5\text{O} + \text{O}_2$	$6.40 \times 10^{-14}$	2	Atkinson et al. (2006)
(SR51)	$\text{C}_2\text{H}_5\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	$7.44 \times 10^{-15}$	2	Sander et al. (1997)
(SR52)	$\text{C}_2\text{H}_5\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{O}_2 + \text{HCHO}$	$7.51 \times 10^{-17}$	2	Sander et al. (1997)
(SR53)	$\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_5\text{OOH} + \text{O}_2$	$3.80 \times 10^{-13} \exp(900/T)$	2	Atkinson et al. (2006)
(SR54)	$\text{C}_2\text{H}_5\text{OOH} + \text{OH} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{H}_2\text{O}$	$8.21 \times 10^{-12}$	2	Sander et al. (1997)
(SR55)	$\text{C}_2\text{H}_5\text{OOH} + \text{Br} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{HBr}$	$5.19 \times 10^{-15}$	2	Sander et al. (1997)
(SR56)	$\text{OH} + \text{OH}(+\text{M}) \rightarrow \text{H}_2\text{O}_2(+\text{M})$	$k_0 = 6.90 \times 10^{-31} (T/300)^{-0.8} [\text{N}_2]$ $k_\infty = 2.60 \times 10^{-11}$ $F_c = 0.50$	2	Atkinson et al. (2006)
(SR57)	$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR58)	$\text{HCHO} + h\nu \xrightarrow{2\text{O}_2} 2\text{HO}_2 + \text{CO}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR59)	$\text{HCHO} + h\nu \rightarrow \text{H}_2 + \text{CO}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR60)	$\text{C}_2\text{H}_4\text{O} + h\nu \rightarrow \text{CH}_3\text{O}_2 + \text{CO} + \text{HO}_2$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)

**Table S3.** (continued).

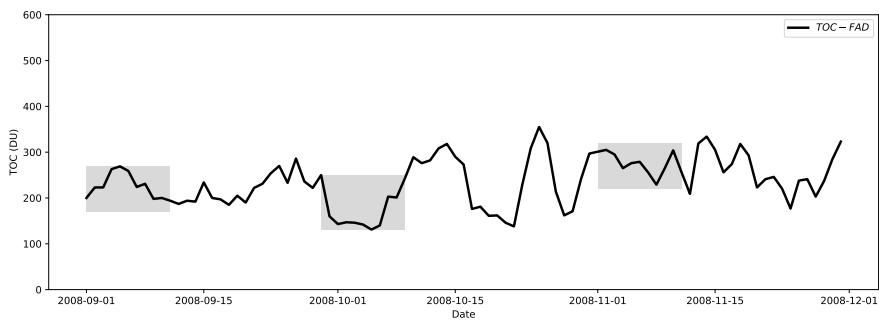
Reaction Number	Reaction	$k$ [(molec. cm <sup>-3</sup> ) <sup>1-n</sup> s <sup>-1</sup> ]	Order $n$	Reference
(SR61)	$\text{CH}_3\text{O}_2\text{H} + h\nu \rightarrow \text{OH} + \text{HCHO} + \text{HO}_2$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR62)	$\text{C}_2\text{H}_5\text{O}_2\text{H} + h\nu \rightarrow \text{C}_2\text{H}_5\text{O} + \text{OH}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR63)	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$1.40 \times 10^{-12} \exp(-1310/T)$	2	Atkinson et al. (2006)
(SR64)	$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	$3.60 \times 10^{-12} \exp(270/T)$	2	Atkinson et al. (2006)
(SR65)	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$1.40 \times 10^{-13} \exp(-2470/T)$	2	Atkinson et al. (2006)
(SR66)	$\text{NO}_2 + \text{OH}(+\text{M}) \rightarrow \text{HNO}_3(+\text{M})$	$k_0 = 3.30 \times 10^{-30} (T/300)^{-3.0} [\text{N}_2]$ $k_\infty = 4.10 \times 10^{-11}$ $F_c = 0.40$	2	Atkinson et al. (2006)
(SR67)	$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	$1.80 \times 10^{-11} \exp(110/T)$	2	Atkinson et al. (2006)
(SR68)	$\text{HONO} + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	$2.50 \times 10^{-12} \exp(260/T)$	2	Atkinson et al. (2006)
(SR69)	$\text{HO}_2 + \text{NO}_2(+\text{M}) \rightarrow \text{HNO}_4(+\text{M})$	$k_0 = 1.80 \times 10^{-31} (T/300)^{-3.2} [\text{N}_2]$ $k_\infty = 4.70 \times 10^{-12}$ $F_c = 0.60$	2	Atkinson et al. (2006)
(SR70)	$\text{HNO}_4(+\text{M}) \rightarrow \text{NO}_2 + \text{HO}_2(+\text{M})$	$k_0 = 4.10 \times 10^{-5} \exp(-10650/T) [\text{N}_2]$ $k_\infty = 4.80 \times 10^{15} \exp(-11170/T)$ $F_c = 0.60$	1	Atkinson et al. (2006)
(SR71)	$\text{HNO}_4 + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{O}_2$	$3.20 \times 10^{-13} \exp(690/T)$	2	Atkinson et al. (2006)
(SR72)	$\text{NO} + \text{OH}(+\text{M}) \rightarrow \text{HONO}(+\text{M})$	$k_0 = 7.40 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2]$ $k_\infty = 3.30 \times 10^{-11} (T/300)^{-0.3}$ $F_c = 0.81$	2	Atkinson et al. (2006)
(SR73)	$\text{OH} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{HO}_2$	$2.00 \times 10^{-11}$	2	Atkinson et al. (2006)
(SR74)	$\text{HNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR75)	$\text{NO}_2 + h\nu \xrightarrow{\text{O}_2} \text{NO} + \text{O}_3$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR76)	$\text{NO}_3 + h\nu \xrightarrow{\text{O}_2} \text{NO}_2 + \text{O}_3$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR77)	$\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR78)	$\text{NO} + \text{CH}_3\text{O}_2 \xrightarrow{\text{O}_2} \text{HCHO} + \text{HO}_2 + \text{NO}_2$	$2.30 \times 10^{-12} \exp(360/T)$	2	Atkinson et al. (2006)
(SR79)	$\text{NO}_3 + \text{CH}_3\text{OH} \xrightarrow{\text{O}_2} \text{HCHO} + \text{HO}_2 + \text{HNO}_3$	$9.40 \times 10^{-13} \exp(-2650/T)$	2	Atkinson et al. (2006)
(SR80)	$\text{NO}_3 + \text{HCHO} \xrightarrow{\text{O}_2} \text{CO} + \text{HO}_2 + \text{HNO}_3$	$5.60 \times 10^{-16}$	2	Atkinson et al. (2006)
(SR81)	$\text{NO} + \text{C}_2\text{H}_5\text{O}_2 \xrightarrow{\text{O}_2} \text{CH}_3\text{CHO} + \text{NO}_2 + \text{HO}_2$	$2.60 \times 10^{-12} \exp(380/T)$	2	Atkinson et al. (2006)
(SR82)	$\text{NO} + \text{CH}_3\text{CO}_3 \xrightarrow{\text{O}_2} \text{CH}_3\text{O}_2 + \text{NO}_2 + \text{CO}_2$	$7.50 \times 10^{-12} \exp(290/T)$	2	Atkinson et al. (2006)
(SR83)	$\text{NO}_2 + \text{CH}_3\text{CO}_3(+\text{M}) \rightarrow \text{PAN}(+\text{M})$	$k_0 = 2.70 \times 10^{-28} (T/300)^{-7.1} [\text{N}_2]$ $k_\infty = 1.20 \times 10^{-11} (T/300)^{-0.9}$ $F_c = 0.30$	2	Atkinson et al. (2006)
(SR84)	$\text{Br} + \text{NO}_2(+\text{M}) \rightarrow \text{BrNO}_2(+\text{M})$	$k_0 = 4.20 \times 10^{-31} (T/300)^{-2.4} [\text{N}_2]$ $k_\infty = 2.70 \times 10^{-11}$ $F_c = 0.55$	2	Atkinson et al. (2006)
(SR85)	$\text{Br} + \text{NO}_3 \rightarrow \text{BrO} + \text{NO}_2$	$1.60 \times 10^{-11}$	2	Atkinson et al. (2006)

**Table S3.** (continued).

Reaction Number	Reaction	$k$ [(molec. cm <sup>-3</sup> ) <sup>1-n</sup> s <sup>-1</sup> ]	Order $n$	Reference
(SR86)	$\text{BrO} + \text{NO}_2(+\text{M}) \rightarrow \text{BrONO}_2(+\text{M})$	$k_0 = 4.70 \times 10^{-31} (T/300)^{-3.1} [\text{N}_2]$ $k_\infty = 1.80 \times 10^{-11}$ $F_c = 0.40$	2	Atkinson et al. (2006)
(SR87)	$\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$	$8.70 \times 10^{-12} \exp(260/T)$	2	Atkinson et al. (2006)
(SR88)	$\text{BrONO}_2 + h\nu \rightarrow \text{NO}_2 + \text{BrO}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR89)	$\text{BrNO}_2 + h\nu \rightarrow \text{NO}_2 + \text{Br}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR90)	$\text{BrONO}_2 + \text{H}_2\text{O} \xrightarrow{\text{aerosol}} \text{HOBr} + \text{HNO}_3$	$(\frac{r}{D_g} + \frac{4}{v_{\text{therm}} \gamma})^{-1} \alpha_{\text{eff,aerosol}}$		Cao et al. (2014)
(SR91)	$\text{PAN} + h\nu \rightarrow \text{NO}_2 + \text{CH}_3\text{CO}_3$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR92)	$\text{BrONO}_2 + \text{H}_2\text{O} \xrightarrow{\text{ice}} \text{HOBr} + \text{HNO}_3$	$(r_a + r_b + r_c)^{-1} \alpha_{\text{eff,ice}}$		Cao et al. (2014)
(SR93)	$\text{CH}_3\text{O}_2\text{H} + \text{Cl} \rightarrow \text{CH}_3\text{O}_2 + \text{HCl}$	$5.90 \times 10^{-11}$	2	Atkinson et al. (2006)
(SR94)	$\text{C}_2\text{H}_5\text{O}_2\text{H} + \text{Cl} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{HCl}$	$5.70 \times 10^{-11}$	2	Sander et al. (1997)
(SR95)	$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	$3.61 \times 10^{-11}$	2	Atkinson et al. (2006)
(SR96)	$\text{Cl} + \text{HO}_2 \rightarrow \text{ClO} + \text{HO}$	$6.30 \times 10^{-11} \exp(-570/T)$	2	Atkinson et al. (2006)
(SR97)	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$1.10 \times 10^{-11} \exp(-980/T)$	2	Atkinson et al. (2006)
(SR98)	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.80 \times 10^{-11} \exp(-250/T)$	2	Atkinson et al. (2006)
(SR99)	$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3\text{O}_2$	$6.60 \times 10^{-12} \exp(-1240/T)$	2	Atkinson et al. (2006)
(SR100)	$\text{Cl} + \text{C}_2\text{H}_2 \rightarrow 2\text{CO} + 2\text{HO}_2 + \text{Cl}$	$2.00 \times 10^{-11}$	2	Borken (1996)
(SR101)	$\text{Cl} + \text{C}_2\text{H}_2 \rightarrow 2\text{CO} + \text{HO}_2 + \text{HCl}$	$4.24 \times 10^{-11}$	2	Borken (1996)
(SR102)	$\text{Cl} + \text{C}_2\text{H}_4(+\text{M}) \rightarrow 2\text{CO} + 2\text{HO}_2 + \text{Cl} + \text{H}_2\text{O}(+\text{M})$	$k_0 = 0.59 \times 10^{-29} (T/300)^{-3.3} [\text{air}]$ $k_\infty = 6.00 \times 10^{-10}$ $F_c = 0.40$	2	Atkinson et al. (2006)
(SR103)	$\text{Cl} + \text{C}_2\text{H}_4(+\text{M}) \rightarrow 2\text{CO} + \text{HO}_2 + \text{HCl} + \text{H}_2\text{O}(+\text{M})$	$k_0 = 1.26 \times 10^{-29} (T/300)^{-3.3} [\text{air}]$ $k_\infty = 6.00 \times 10^{-10}$ $F_c = 0.40$	2	Atkinson et al. (2006)
(SR104)	$\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HCl}$	$8.30 \times 10^{-11} \exp(-100/T)$	2	Atkinson et al. (2006)
(SR105)	$\text{Cl} + \text{C}_3\text{H}_8 \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{HCl} + \text{H}_2\text{O} + \text{CO}_2$	$1.40 \times 10^{-10}$	2	Atkinson et al. (2006)
(SR106)	$\text{Cl} + \text{HCHO} \rightarrow \text{HCl} + \text{CO} + \text{HO}_2$	$8.10 \times 10^{-11} \exp(-34/T)$	2	Atkinson et al. (2006)
(SR107)	$\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO}_3 + \text{HCl}$	$8.00 \times 10^{-11}$	2	Atkinson et al. (2006)
(SR108)	$\text{OH} + \text{Cl}_2 \rightarrow \text{HOCl} + \text{Cl}$	$3.60 \times 10^{-12} \exp(-1200/T)$	2	Atkinson et al. (2006)
(SR109)	$\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$	$1.80 \times 10^{-12} \exp(-240/T)$	2	Atkinson et al. (2006)
(SR110)	$\text{OH} + \text{HOCl} \rightarrow \text{ClO} + \text{H}_2\text{O}$	$5.00 \times 10^{-13}$	2	Atkinson et al. (2006)
(SR111)	$\text{OH} + \text{ClO} \rightarrow \text{Cl} + \text{HO}_2$	$6.86 \times 10^{-12} \exp(300/T)$	2	Atkinson et al. (2006)
(SR112)	$\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$	$4.37 \times 10^{-13} \exp(300/T)$	2	Atkinson et al. (2006)
(SR113)	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$1.00 \times 10^{-12} \exp(-1590/T)$	2	Atkinson et al. (2006)
(SR114)	$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	$3.00 \times 10^{-11} \exp(-2450/T)$	2	Atkinson et al. (2006)
(SR115)	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	$3.50 \times 10^{-13} \exp(-1370/T)$	2	Atkinson et al. (2006)

**Table S3.** (continued).

Reaction Number	Reaction	$k$ [(molec. cm <sup>-3</sup> ) <sup>1-n</sup> s <sup>-1</sup> ]	Order $n$	Reference
(SR116)	$\text{ClO} + \text{ClO}(+\text{M}) \rightarrow \text{Cl}_2\text{O}_2(+\text{M})$	$k_0 = 2.00 \times 10^{-32} (T/300)^{-4} [\text{N}_2]$ $k_\infty = 1.00 \times 10^{-11}$ $F_c = 0.45$	2	Atkinson et al. (2006)
(SR117)	$\text{Cl}_2\text{O}_2(+\text{M}) \rightarrow 2\text{ClO}(+\text{M})$	$k_0 = 3.70 \times 10^{-7} \exp(-7690/T) [\text{N}_2]$ $k_\infty = 1.80 \times 10^{14} \exp(-7690/T)$ $F_c = 0.45$	1	Atkinson et al. (2006)
(SR118)	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$2.20 \times 10^{-12} \exp(340/T)$	2	Atkinson et al. (2006)
(SR119)	$\text{ClO} + \text{CH}_3\text{O}_2 \rightarrow \text{Cl} + \text{CH}_2\text{O} + \text{HO}_2$	$2.40 \times 10^{-12} \exp(-20/T)$	2	Atkinson et al. (2006)
(SR120)	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$6.20 \times 10^{-12} \exp(295/T)$	2	Atkinson et al. (2006)
(SR121)	$\text{ClO} + \text{NO}_2(+\text{M}) \rightarrow \text{ClONO}_2(+\text{M})$	$k_0 = 1.60 \times 10^{-31} (T/300)^{-3.4} [\text{N}_2]$ $k_\infty = 7.00 \times 10^{-11}$ $F_c = 0.40$	2	Atkinson et al. (2006)
(SR122)	$\text{Cl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{NO}_3$	$6.20 \times 10^{-12} \exp(145/T)$	2	Atkinson et al. (2006)
(SR123)	$\text{OCIO} + \text{NO} \rightarrow \text{NO}_2 + \text{ClO}$	$1.10 \times 10^{-13} \exp(350/T)$	2	Atkinson et al. (2006)
(SR124)	$\text{OH} + \text{ClONO}_2 \rightarrow \text{HOCl} + \text{NO}_3$	$1.20 \times 10^{-12} \exp(-330/T)$	2	Atkinson et al. (2006)
(SR125)	$\text{ClO} + \text{BrO} \rightarrow \text{Br} + \text{OCIO}$	$1.60 \times 10^{-12} \exp(430/T)$	2	Atkinson et al. (2006)
(SR126)	$\text{ClO} + \text{BrO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$	$2.90 \times 10^{-12} \exp(220/T)$	2	Atkinson et al. (2006)
(SR127)	$\text{ClO} + \text{BrO} \rightarrow \text{BrCl} + \text{O}_2$	$5.80 \times 10^{-13} \exp(170/T)$	2	Atkinson et al. (2006)
(SR128)	$\text{Br} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO}$	$2.70 \times 10^{-11} \exp(-1300/T)$	2	Atkinson et al. (2006)
(SR129)	$\text{Br} + \text{Cl}_2\text{O}_2 \rightarrow \text{BrCl} + \text{ClOO}$	$3.00 \times 10^{-12}$	2	Atkinson et al. (2006)
(SR130)	$\text{Br}_2 + \text{Cl} \rightarrow \text{BrCl} + \text{Br}$	$1.20 \times 10^{-10}$	2	Sander and Crutzen (1996)
(SR131)	$\text{BrCl} + \text{Br} \rightarrow \text{Br}_2 + \text{Cl}$	$3.30 \times 10^{-15}$	2	Sander and Crutzen (1996)
(SR132)	$\text{Br} + \text{Cl}_2 \rightarrow \text{BrCl} + \text{Cl}$	$1.10 \times 10^{-15}$	2	Sander and Crutzen (1996)
(SR133)	$\text{BrCl} + \text{Cl} \rightarrow \text{Br} + \text{Cl}_2$	$1.50 \times 10^{-11}$	2	Sander and Crutzen (1996)
(SR134)	$\text{HOBr} + \text{H}^+ + \text{Cl}^- \xrightarrow{\text{ice}} \text{BrCl} + \text{H}_2\text{O}$	$3.03 \times 10^{-5}$ $(r_a + r_b + r_c)^{-1} \alpha_{\text{eff,ice}}$		Cao et al. (2014)
(SR135)	$\text{BrCl} + h\nu \rightarrow \text{Br} + \text{Cl}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR136)	$\text{Cl}_2 + h\nu \rightarrow \text{Cl}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR137)	$\text{ClO} + h\nu \rightarrow \text{Cl} + \text{O}_3$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR138)	$\text{HOCl} + h\nu \rightarrow \text{HO} + \text{Cl}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR139)	$\text{ClONO}_2 + h\nu \rightarrow \text{NO}_3 + \text{Cl}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR140)	$\text{OCIO} + h\nu \rightarrow \text{O}_3 + \text{ClO}$	calculated by TUV model	1	Madronich and Flocke (1997, 1999)
(SR141)	$\text{HOBr} + \text{HCl} \xrightarrow{\text{aerosol}} \text{BrCl} + \text{H}_2\text{O}$	$(\frac{r}{D_g} + \frac{4}{v_{\text{therm}} \gamma})^{-1} \alpha_{\text{eff,aerosol}}$		Cao et al. (2014)



**Figure S2.** Time series of the total ozone column (TOC) detected at the Faraday-Vernadsky (FAD) station during the springtime of the year 2008. The gray-shaded areas in the figure indicate the periods investigated in the sensitivity tests of the present study.

## References

- Aranda, A., Le Bras, G., La Verdet, G., and Poulet, G.: The BrO + Ch<sub>3</sub>O<sub>2</sub> reaction: Kinetics and role in the atmospheric ozone budget, Geophys. Res. Lett., 24, 2745–2748, <https://doi.org/10.1029/97GL02686>, 1997.
- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Kerr, J. A., Rossi, M., and Troe, J.: 5 Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, Tech. rep., 2006.
- Barnes, I., Becker, K., and Overath, R.: Oxidation of organic sulfur compounds, in: The Tropospheric Chemistry of Ozone in the Polar Regions, edited by Niki, H. and Becker, K., vol. 7, pp. 371–383, Springer Berlin Heidelberg, [https://doi.org/10.1007/978-3-642-78211-4\\_27](https://doi.org/10.1007/978-3-642-78211-4_27), 1993.
- Borken, J.: Ozonabbau durch Halogene in der arktischen Grenzschicht, Ph.D. thesis, Heidelberg University, 1996.
- 10 Cao, L., Sihler, H., Platt, U., and Gutheil, E.: Numerical analysis of the chemical kinetic mechanisms of ozone depletion and halogen release in the polar troposphere, Atmos. Chem. Phys., 14, 3771–3787, <https://doi.org/10.5194/acp-14-3771-2014>, 2014.
- Madronich, S. and Flocke, S.: Theoretical Estimation of Biologically Effective UV Radiation at the Earth's Surface, in: Solar Ultraviolet Radiation, edited by Zerefos, C. S. and Bais, A. F., pp. 23–48, Springer Berlin Heidelberg, Berlin, Heidelberg, 1997.
- 15 Madronich, S. and Flocke, S.: The Role of Solar Radiation in Atmospheric Chemistry, pp. 1–26, Springer Berlin Heidelberg, Berlin, Heidelberg, [https://doi.org/10.1007/978-3-540-69044-3\\_1](https://doi.org/10.1007/978-3-540-69044-3_1), 1999.
- Mallard, W. G., Westley, F., Herron, J. T., Hampson, R. F., and Frizzel, D. H.: NIST chemical kinetics database: version 5.0, Tech. rep., Gaithersburg, 1993.
- Sander, R. and Crutzen, P. J.: Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea, J. Geophys. Res. Atmos., 101, 9121–9138, <https://doi.org/10.1029/95JD03793>, <http://dx.doi.org/10.1029/95JD03793>, 1996.
- 20 Sander, R., Vogt, R., Harris, G. W., and Crutzen, P. J.: Modelling the chemistry of ozone, halogen compounds, and hydrocarbons in the arctic troposphere during spring, Tellus B, 49, 522–532, <https://doi.org/10.1034/j.1600-0889.49.issue5.8.x>, 1997.