Supplement to "Air-snowpack exchange of bromine, ozone and mercury in the springtime Arctic simulated by the 1-D model PHANTAS – Part 1: In-snow bromine activation and its impact on ozone"

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S1 Full list of reactions in PHANTAS

Table S1. Species in gas- and aqueous-phases

Table S2. Gas-phase reactions

Table S3. Photolysis reactions in gas- and aqueous-phases and their calculated 24-h mean J-values at the top of snowpack

Table S4. Reactive uptake of gaseous species represented by heterogeneous reactions and their reactive uptake coefficients (γ)

Table S5. Henry's law constants (K_{H}) and mass accommodation coefficients (α) for species transferred across gas-aqueous interface

Table S6. Aqueous-phase equilibrium constants (K_{eq}) for acids, bases, hydrates, and other species that undergo ion dissociation in water

Table S7. Other aqueous-phase reactions and their rate constants

Table S1. List of species in gas- and aqueous-phases.

	Gas-phase species
O	$O(^3P)$, $O(^1D)$, O_2, O_3
H	H_2, OH, HO_2, H_2O_2, H_2O
N	NO, NO_3, N_2O_5, HO_2NO_2, HONO, NO_2, HNO_3, $CH_3CO_3NO_2$ (PAN), $HCOCO_3NO_2$ (GLYPAN), NH_3, N_2
C	CH_4, C_2H_6, C_2H_2, CO, HCHO, $HOCH_2OO$, $CH_2(OH)_2$, $HOCH_2OOH$, CH_3OO, CH_3OH, CH_3OOH, HCOOH, C_2H_5OO, C_2H_5OH, C_2H_5OOH, CH_3CHO, CH_3CO_3, CH_3COOH, CH_3CO_3H, HCOCHO, $HCOCO_3$, HCOCOOH, $HCOCO_3H$, CH_2OO^*, CH_2OO, CO_2
Cl	Cl, ClO, OClO, Cl_2O_2, HOCl, HCl, $ClNO_2$, $ClONO_2$, Cl_2, HCOCl, CH_3OCl
Br	Br, BrO, Br_2, HOBr, HBr, $BrNO_2$, $BrONO_2$, BrCl, $CHBr_3$, HCOBr, CBr_2O
S	SO_2, SO_3, H_2SO_4
Hg	Hg, $Hg(OH)_2$, $HgCl_2$, HgBr, $HgBr_2$, Hg(OH)Cl, Hg(OH)Br, Hg(O)Br, Hg(OBr)Br, HgClBr
	Aqueous-phase species
O	$O(^3P)$, O_3, O_2
H	H_2O, H^+, OH^-, OH, HO_2, O_2^-, H_2O_2, HO_2^-
N	NH_3, NH_4^+, NO, NO_2, H_2ONO^+, HONO, NO_2^-, HNO_3, NO_3^-, HO_2NO_2, NO_4^-, NO_3, N_2O_5
C	CH_3OH, CH_3OO, CH_3OOH, CH_3CO_3H, $CH_3CO_3^-$, HCHO, $CH_2(OH)_2$, HCOOH, $HCOO^-$, CH_3CHO, $CH_3CH(OH)_2$, CH_3COOH, CH_3COO^-, HCOCOOH, $HCOCOO^-$, CO_2, HCO_3^-, CO_3^-
Na	Na^+
Cl	HCl, Cl^-, Cl, Cl_2^-, Cl_3^-, HOCl, ClO^-, CH_3OCl, $ClOH^-$, Cl_2, $ClNO_2$, $ClONO_2$
Br	HBr, Br^-, Br, Br_2^-, Br_3^-, HOBr, BrO^-, $BrOH^-$, Br_2, BrCl, Br_2Cl^-, $BrCl_2^-$, $BrNO_2$, $BrONO_2$
S	SO_2, HSO_3^-, SO_3^{2-}, $HOCH_2SO_3^-$ ($HMSA^-$), HSO_4^-, SO_4^{2-}, HSO_5^-, SO_5^{2-}, SO_3^-, SO_4^-, SO_5^-
Hg	Hg, Hg^+, HgO, Hg^{2+}, $HgOH^+$, $Hg(OH)_2$, $HgCl^+$, $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$, $HgBr^+$, $HgBr_2$, $HgBr_3^-$, $HgBr_4^{2-}$, Hg(OH)Cl, Hg(OH)Br, Hg(O)Br, Hg(OBr)Br, HgClBr, $HgCl_2Br^-$, $HgClBr_2^-$, $HgCl_3Br^{2-}$, $HgCl_2Br_2^{2-}$, $HgClBr_3^{2-}$

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Table S2. Gas-phase reactions (see note[a, b, c]).

No.	Reaction	Rate Constant	Reference
G1	$O(^3P) + O_2 \overset{M}{\rightarrow} O_3$	$k_0 = 6.00 \times 10^{-34}\,(T/300)^{-2.4}$	1
G2	$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	$1.80 \times 10^{-11} \exp(110/T)$	2
G3	$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	$3.20 \times 10^{-11} \exp(70/T)$	2
G4	$O(^3P) + O_3 \rightarrow 2\,O_2$	$8.00 \times 10^{-12} \exp(-2060/T)$	2
G5	$O(^1D) + O_3 \rightarrow 2\,O(^3P) + O_2$	1.20×10^{-10}	2
G6	$O(^1D) + O_3 \rightarrow 2\,O_2$	1.20×10^{-10}	2
G7	$O(^1D) + H_2O \rightarrow 2\,OH$	2.20×10^{-10}	1
G8	$O(^1D) + H_2 \overset{O_2}{\rightarrow} OH + HO_2$	1.10×10^{-10}	2
G9	$O(^3P) + OH \overset{O_2}{\rightarrow} HO_2 + O_2$	$2.20 \times 10^{-11} \exp(120/T)$	2
G10	$O(^3P) + HO_2 \rightarrow OH + O_2$	$3.00 \times 10^{-11} \exp(200/T)$	1
G11	$O(^3P) + H_2O_2 \rightarrow OH + HO_2$	$1.40 \times 10^{-12} \exp(-2000/T)$	2
G12	$OH + O_3 \rightarrow HO_2 + O_2$	$1.50 \times 10^{-12} \exp(-880/T)$	1
G13	$HO_2 + O_3 \rightarrow OH + 2\,O_2$	$2.00 \times 10^{-14} \exp(-680/T)$	1
G14	$OH + HO_2 \rightarrow H_2O + O_2$	$4.80 \times 10^{-11} \exp(250/T)$	1
G15	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$2.90 \times 10^{-12} \exp(-160/T)$	2
G16	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$2.3 \times 10^{-13} \exp(600/T) \times f(H_2O)$	2
G17	$HO_2 + HO_2 \overset{M}{\rightarrow} H_2O_2 + O_2$	$k_0 = 1.9 \times 10^{-33} \exp(980/T) \times f(H_2O)$ $f(H_2O) = 1 + 1.4 \times 10^{-21}\,[H_2O]\,\exp(2200/T)$	3
G18	$OH + H_2 \overset{O_2}{\rightarrow} H_2O + HO_2$	$5.50 \times 10^{-12} \exp(-2000/T)$	2
G19	$OH + OH \rightarrow H_2O + O(^3P)$	$4.20 \times 10^{-12} \exp(-240/T)$	2
G20	$OH + OH \overset{M}{\rightarrow} H_2O_2$	$F_c = 0.5,\ k_0 = 6.90 \times 10^{-31}(T/300)^{-0.8},\ k_\infty = 2.6 \times 10^{-11}$	3
G21	$O(^3P) + NO_2 \rightarrow NO + O_2$	$5.60 \times 10^{-12} \exp(180/T)$	1
G22	$O(^3P) + NO_3 \rightarrow NO_2 + O_2$	1.00×10^{-11}	2
G23	$O(^3P) + NO \overset{M}{\rightarrow} NO_2$	$F_c = 0.6,\ k_0 = 9.0 \times 10^{-32}(T/300)^{-1.5},\ k_\infty = 3.0 \times 10^{-11}$	1
G24	$O(^3P) + NO_2 \overset{M}{\rightarrow} NO_3$	$F_c = \exp(-T/1300),\ k_0 = 9.0 \times 10^{-32}(T/300)^{-2.0},\ k_\infty = 2.2 \times 10^{-11}$	3
G25	$NO + O_3 \rightarrow NO_2 + O_2$	$3.00 \times 10^{-12} \exp(-1500/T)$	1
G26	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$1.20 \times 10^{-13} \exp(-2450/T)$	2
G27	$HO_2 + NO \rightarrow OH + NO_2$	$3.50 \times 10^{-12} \exp(250/T)$	2
G28	$NO + NO_3 \rightarrow 2\,NO_2$	$1.50 \times 10^{-11} \exp(170/T)$	2
G29	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	$4.50 \times 10^{-14} \exp(-1260/T)$	2
G30	$NO_2 + NO_3 \overset{M}{\rightarrow} N_2O_5$	$F_c = 0.33,\ k_0 = 2.7 \times 10^{-30}(T/300)^{-3.4},\ k_\infty = 2.0 \times 10^{-12}(T/300)^{0.2}$	3
G31	$N_2O_5 \overset{M}{\rightarrow} NO_2 + NO_3$	$F_c = 0.33,\ k_0 = 1.0 \times 10^{-3}(T/300)^{-3.5}\exp(-11000/T),\ k_\infty = 9.7 \times 10^{14}(T/300)^{0.1}\exp(-11080/T)$	3
G32	$OH + NO_3 \rightarrow HO_2 + NO_2$	2.20×10^{-11}	2
G33	$HO_2 + NO_3 \rightarrow OH + NO_2 + O_2$	3.50×10^{-12}	2
G34	$OH + NO_2 \overset{M}{\rightarrow} HNO_3$	$F_c = 0.6,\ k_0 = 2.4 \times 10^{-30}(T/300)^{-3.1},\ k_\infty = 1.7 \times 10^{-11}(T/300)^{-2.1}$	1
G35	$OH + HNO_3 \rightarrow H_2O + NO_3$	$k = k_0 + k_3[M]/(1 + k_3[M]/k_2)$ $k_0 = 2.4 \times 10^{-14}\exp(460/T),\ k_2 = 2.7 \times 10^{-17}\exp(2199/T),\ k_3 = 6.5 \times 10^{-34}\exp(1335/T)$	1
G36	$OH + NO \overset{M}{\rightarrow} HONO$	$F_c = 0.9,\ k_0 = 7.4 \times 10^{-31}(T/300)^{-2.4},\ k_\infty = 4.50 \times 10^{-11}$	2
G37	$OH + HONO \rightarrow H_2O + NO_2$	$1.80 \times 10^{-11} \exp(-390/T)$	2
G38	$HO_2 + NO_2 \overset{M}{\rightarrow} HO_2NO_2$	$F_c = 0.6,\ k_0 = 1.8 \times 10^{-31}(T/300)^{-3.2},\ k_\infty = 4.7 \times 10^{-12}$	3

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Table S2. (Continued.)

No.	Reaction	Rate Constant	Reference
G39	$HO_2NO_2 \xrightarrow{M} HO_2 + NO_2$	$F_c = 0.6,\ k_0 = 5.0 \times 10^{-6} \exp(-10000/T),\ k_\infty = 2.6 \times 10^{15} \exp(-10900/T)$	3
G40	$OH + HO_2NO_2 \rightarrow H_2O + NO_2 + O_2$	$1.30 \times 10^{-12} \exp(380/T)$	2
G41	$OH + CO \xrightarrow{O_2} HO_2 + CO_2$	$1.50 \times 10^{-13} (1 + P_{atm})$	2
G42	$O(^1D) + CH_4 \xrightarrow{O_2} OH + CH_3OO$	1.50×10^{-10}	2
G43	$OH + CH_4 \xrightarrow{O_2} H_2O + CH_3OO$	$2.45 \times 10^{-12} \exp(-1775/T)$	2
G44	$Cl + CH_4 \xrightarrow{O_2} HCl + CH_3OO$	$9.60 \times 10^{-12} \exp(-1360/T)$	1
G45	$HO_2 + CH_3OO \rightarrow CH_3OOH + O_2$	$3.80 \times 10^{-13} \exp(800/T)$	2
G46	$CH_3OO + CH_3OO \rightarrow CH_3OH + HCHO + O_2$	$1.50 \times 10^{-13} \exp(190/T)$	2
G47	$CH_3OO + CH_3OO \xrightarrow{O_2} 2\,HCHO + 2\,HO_2 + O_2$	$1.00 \times 10^{-13} \exp(190/T)$	2
G48	$CH_3OO + NO \xrightarrow{O_2} NO_2 + HCHO + HO_2$	$3.00 \times 10^{-12} \exp(280/T)$	2
G49	$CH_3OO + NO_3 \xrightarrow{O_2} HCHO + HO_2 + NO_2 + O_2$	1.30×10^{-12}	4
G50	$O(^3P) + HCHO \xrightarrow{O_2} OH + CO + HO_2$	$3.40 \times 10^{-11} \exp(-1600/T)$	2
G51	$NO_3 + HCHO \xrightarrow{O_2} HNO_3 + CO + HO_2$	5.80×10^{-16}	2
G52	$OH + HCHO \xrightarrow{O_2} H_2O + CO + HO_2$	1.00×10^{-11}	2
G53	$Br + HCHO \xrightarrow{O_2} HBr + CO + HO_2$	$1.70 \times 10^{-11} \exp(-800/T)$	4
G54	$Cl + HCHO \xrightarrow{O_2} HCl + CO + HO_2$	$8.20 \times 10^{-11} \exp(-34/T)$	4
G55	$OH + CH_3OH \xrightarrow{O_2} H_2O + HCHO + HO_2$	$3.10 \times 10^{-12} \exp(-360/T)$	4
G56	$Cl + CH_3OH \xrightarrow{O_2} HCl + HCHO + HO_2$	5.50×10^{-11}	4
G57	$OH + CH_3OOH \rightarrow H_2O + CH_3OO$	$1.90 \times 10^{-12} \exp(190/T)$	4
G58	$OH + CH_3OOH \rightarrow H_2O + HCHO + OH$	$1.00 \times 10^{-12} \exp(190/T)$	4
G59	$Br + CH_3OOH \rightarrow HBr + CH_3OO$	$2.63 \times 10^{-12} \exp(-1610/T)$	5
G60	$Cl + CH_3OOH \rightarrow HCl + HCHO + OH$	5.90×10^{-11}	4
G61	$HO_2 + HCHO \rightarrow HOCH_2OO$	$9.70 \times 10^{-15} \exp(625/T)$	4
G62	$HOCH_2OO \xrightarrow{M} HO_2 + HCHO$	$k_{uni} = 2.4 \times 10^{12} \exp(-7000/T)$	4
G63	$HOCH_2OO + NO \xrightarrow{O_2} HCOOH + HO_2 + NO_2$	5.60×10^{-12}	6
G64	$HOCH_2OO + NO_3 \xrightarrow{O_2} HCOOH + HO_2 + NO_2 + O_2$	2.50×10^{-12}	7
G65	$HOCH_2OO + HO_2 \rightarrow HOCH_2OOH + O_2$	$3.36 \times 10^{-15} \exp(2300/T)$	4
G66	$HOCH_2OO + HO_2 \rightarrow HCOOH + H_2O + O_2$	$2.24 \times 10^{-15} \exp(2300/T)$	4
G67	$HOCH_2OO + CH_3OO \xrightarrow{O_2} HCOOH + HCHO + 2\,HO_2 + O_2$	1.20×10^{-12}	8
G68	$HOCH_2OO + CH_3OO \rightarrow HCOOH + CH_3OH + O_2$	4.00×10^{-13}	8
G69	$HOCH_2OO + CH_3OO \rightarrow CH_2(OH)_2 + HCHO + O_2$	4.00×10^{-13}	8
G70	$HOCH_2OO + HOCH_2OO \rightarrow HCOOH + CH_2(OH)_2 + O_2$	$5.70 \times 10^{-14} \exp(750/T)$	4
G71	$HOCH_2OO + HOCH_2OO \xrightarrow{O_2} 2\,HCOOH + 2\,HO_2 + O_2$	5.50×10^{-12}	4
G72	$OH + CH_2(OH)_2 \xrightarrow{O_2} H_2O + HCOOH + HO_2$	1.17×10^{-11}	9
G73	$OH + HOCH_2OOH \rightarrow HOCH_2OO$	$1.90 \times 10^{-12} \exp(190/T)$	9
G74	$OH + HOCH_2OOH \rightarrow H_2O + HCOOH + OH$	4.26×10^{-11}	9
G75	$OH + HCOOH \xrightarrow{O_2} H_2O + HO_2 + CO_2$	4.00×10^{-13}	2
G76	$Br + O_3 \rightarrow BrO + O_2$	$1.70 \times 10^{-11} \exp(-800/T)$	2
G77	$Br + HO_2 \rightarrow HBr + O_2$	$1.40 \times 10^{-11} \exp(-590/T)$	10
G78	$Br + NO_2 \xrightarrow{M} BrNO_2$	$F_c = 0.6,\ k_0 = 4.2 \times 10^{-31} (T/300)^{-2.4},\ k_\infty = 2.7 \times 10^{-11}$	11
G79	$Br + NO_3 \rightarrow BrO + NO_2$	1.60×10^{-11}	2
G80	$BrO + O(^3P) \rightarrow Br + O_2$	$1.90 \times 10^{-11} \exp(230/T)$	2
G81	$BrO + HO_2 \rightarrow HOBr + O_2$	$3.70 \times 10^{-12} \exp(545/T)$	10
G82	$BrO + NO \rightarrow Br + NO_2$	$8.70 \times 10^{-12} \exp(260/T)$	10

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Table S2. (Continued.)

No.	Reaction	Rate Constant	Reference
G83	$BrO + NO_2 \xrightarrow{M} BrONO_2$		
		$F_c = \exp(-T/327),\ k_0 = 4.7 \times 10^{-31}(T/300)^{-3.1},\ k_\infty = 1.4 \times 10^{-11}(T/300)^{-1.2}$	10
G84	$BrONO_2 \xrightarrow{M} BrO + NO_2$	$k_{uni} = 2.79 \times 10^{13} \exp(-12360/T)$	12
G85	$Br + BrONO_2 \rightarrow Br_2 + NO_3$	4.90×10^{-11}	12
G86	$BrO + CH_3OO \xrightarrow{M} Br + HO_2 + HCHO$	4.10×10^{-12}	13, 14
G87	$BrO + CH_3OO \xrightarrow{O_2} Br + HCHO + HO_2 + O_2$	1.60×10^{-12}	13
G88	$BrO + BrO \rightarrow 2\,Br + O_2$	2.70×10^{-12}	10
G89	$BrO + BrO \rightarrow Br_2 + O_2$	$2.90 \times 10^{-14} \exp(840/T)$	10
G90	$BrO + ClO \rightarrow Br + OClO$	$9.50 \times 10^{-13} \exp(550/T)$	1
G91	$BrO + ClO \rightarrow Br + Cl + O_2$	$2.30 \times 10^{-12} \exp(260/T)$	1
G92	$BrO + ClO \rightarrow BrCl + O_2$	$4.10 \times 10^{-13} \exp(290/T)$	1
G93	$Br_2 + Cl \rightarrow BrCl + Br$	1.66×10^{-10}	15
G94	$BrCl + Br \rightarrow Br_2 + Cl$	3.32×10^{-15}	15
G95	$Br + Cl_2 \rightarrow BrCl + Cl$	1.10×10^{-15}	16
G96	$BrCl + Cl \rightarrow Br + Cl_2$	1.45×10^{-11}	17
G97	$O(^3P) + HBr \rightarrow OH + Br$	$5.80 \times 10^{-12} \exp(-1500/T)$	2
G98	$O(^1D) + HBr \rightarrow OH + Br$	1.50×10^{-10}	2
G99	$OH + HBr \rightarrow H_2O + Br$	1.10×10^{-11}	2
G100	$Cl + CH_3OO \rightarrow HCl + CH_2OO^*$	8.00×10^{-11}	2
G101	$Cl + CH_3OO \xrightarrow{O_2} ClO + HCHO + HO_2$	8.00×10^{-11}	2
G102	$Cl + CH_3OCl \xrightarrow{O_2} Cl_2 + HCHO + HO_2$	4.87×10^{-11}	18
G103	$Cl + CH_3OCl \xrightarrow{O_2} HCl + HCOCl + HO_2$	1.22×10^{-11}	18
G104	$Cl + O_3 \rightarrow ClO + O_2$	$2.30 \times 10^{-11} \exp(-200/T)$	1
G105	$ClO + ClO \rightarrow Cl_2 + O_2$	$1.00 \times 10^{-12} \exp(-1590/T)$	2
G106	$ClO + ClO \rightarrow 2\,Cl + O_2$	$3.00 \times 10^{-11} \exp(-2450/T)$	2
G107	$ClO + ClO \rightarrow OClO + Cl$	$3.50 \times 10^{-13} \exp(-1370/T)$	2
G108	$ClO + ClO \xrightarrow{M} Cl_2O_2$		
		$F_c = 0.6,\ k_0 = 1.7 \times 10^{-32}(T/300)^{-4},\ k_\infty = 5.4 \times 10^{-12}$	10
G109	$Cl_2O_2 \xrightarrow{M} ClO + ClO$		
		$F_c = 0.6,\ k_0 = 1.0 \times 10^{-6} \exp(-8000/T),\ k_\infty = 4.8 \times 10^{15} \exp(-8820/T)$	10
G110	$ClO + OH \rightarrow Cl + HO_2$	$7.40 \times 10^{-12} \exp(270/T)$	1
G111	$ClO + OH \rightarrow HCl + O_2$	$3.20 \times 10^{-13} \exp(320/T)$	1
G112	$ClO + HO_2 \rightarrow HOCl + O_2$	$4.80 \times 10^{-13} \exp(700/T)$	2
G113	$ClO + CH_3OO \xrightarrow{O_2} Cl + HCHO + HO_2$	$4.90 \times 10^{-12} \exp(-330/T)$	3
G114	$ClO + CH_3OO \rightarrow CH_3OCl + O_2$	$2.60 \times 10^{-13} \exp(260/T)$	3
G115	$ClO + NO \rightarrow Cl + NO_2$	$6.40 \times 10^{-12} \exp(290/T)$	2
G116	$ClO + NO_2 \xrightarrow{M} ClONO_2$		10
		$F_c = \exp(-T/430),\ k_0 = 1.6 \times 10^{-31}(T/300)^{-3.4},\ k_\infty = 1.5 \times 10^{-11}$	10
G117	$ClONO_2 \xrightarrow{M} ClO + NO_2$	$k_{uni} = 6.92 \times 10^{-7}\,[M] \exp(-10908/T)$	19
G118	$NO + OClO \rightarrow NO_2 + ClO$	$2.50 \times 10^{-12} \exp(-600/T)$	2
G119	$OH + OClO \rightarrow HOCl + O_2$	$4.50 \times 10^{-13} \exp(800/T)$	2
G120	$OH + HCl \rightarrow H_2O + Cl$	$2.60 \times 10^{-12} \exp(-350/T)$	1
G121	$OH + HOCl \rightarrow H_2O + ClO$	$3.00 \times 10^{-12} \exp(-500/T)$	2
G122	$OH + CH_3OCl \xrightarrow{O_2} HCOCl + HO_2 + H_2O$	$2.40 \times 10^{-12} \exp(-360/T)$	2
G123	$OH + C_2H_6 \xrightarrow{O_2} H_2O + C_2H_5OO$	$8.70 \times 10^{-12} \exp(-1070/T)$	2
G124	$Cl + C_2H_6 \xrightarrow{O_2} HCl + C_2H_5OO$	$7.70 \times 10^{-11} \exp(-90/T)$	2
G125	$C_2H_5OO + NO \xrightarrow{O_2} CH_3CHO + HO_2 + NO_2$	$2.50 \times 10^{-12} \exp(380/T)$	4
G126	$C_2H_5OO + HO_2 \rightarrow C_2H_5OOH + O_2$	$3.80 \times 10^{-13} \exp(900/T)$	4

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Table S2. (Continued.)

No.	Reaction	Rate Constant	Reference
G127	$C_2H_5OO + NO_3 \overset{O_2}{\rightarrow} CH_3CHO + HO_2 + NO_2 + O_2$	2.30×10^{-12}	4
G128	$C_2H_5OO + CH_3OO \overset{O_2}{\rightarrow} CH_3CHO + HCHO + 2\,HO_2 + O_2$	1.21×10^{-13}	20
G129	$C_2H_5OO + CH_3OO \rightarrow CH_3CHO + CH_3OH + O_2$	4.00×10^{-14}	20
G130	$C_2H_5OO + CH_3OO \rightarrow C_2H_5OH + HCHO + O_2$	4.00×10^{-14}	20
G131	$C_2H_5OO + C_2H_5OO \overset{O_2}{\rightarrow}$ $1.24 \times (CH_3CHO + HO_2) + 0.38 \times (CH_3CHO + C_2H_5OH) + O_2$	6.40×10^{-14}	3
G132	$C_2H_5OO + Cl \overset{O_2}{\rightarrow} CH_3CHO + HO_2 + ClO$	7.40×10^{-11}	2
G133	$C_2H_5OO + Cl \rightarrow HCl$ + products	7.70×10^{-11}	2
G134	$CH_3CHO + OH \overset{O_2}{\rightarrow} CH_3C(O)OO + H_2O$	$5.60 \times 10^{-12} \exp(310/T)$	4
G135	$CH_3CHO + NO_3 \overset{O_2}{\rightarrow} CH_3C(O)OO + HNO_3$	$1.40 \times 10^{-12} \exp(-1860/T)$	4
G136	$CH_3CHO + Cl \overset{O_2}{\rightarrow} CH_3C(O)OO + HCl$	7.20×10^{-11}	4
G137	$CH_3CHO + Br \overset{O_2}{\rightarrow} CH_3C(O)OO + HBr$	$1.30 \times 10^{-11} \exp(-360/T)$	4
G138	$C_2H_5OH + OH \overset{O_2}{\rightarrow} CH_3CHO + HO_2 + H_2O$	$4.10 \times 10^{-12} \exp(-70/T)$	4
G139	$C_2H_5OH + Cl \overset{O_2}{\rightarrow} CH_3CHO + HO_2 + HCl$	9.00×10^{-11}	4
G140	$C_2H_5OOH + OH \rightarrow H_2O + C_2H_5OO$	$1.90 \times 10^{-12} \exp(190/T)$	7
G141	$C_2H_5OOH + OH \rightarrow H_2O + CH_3CHO + OH$	8.01×10^{-12}	7
G142	$C_2H_5OOH + Cl \rightarrow HCl + CH_3CHO + OH$	1.07×10^{-10}	21
G143	$CH_3C(O)OO + HO_2 \rightarrow CH_3C(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	4, 7
G144	$CH_3C(O)OO + HO_2 \rightarrow CH_3COOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	4, 7
G145	$CH_3C(O)OO + CH_3OO \overset{O_2}{\rightarrow} CH_3OO + CO_2 + HCHO + HO_2 + O_2$	$1.26 \times 10^{-12} \exp(500/T)$	4, 8
G146	$CH_3C(O)OO + CH_3OO \rightarrow CH_3COOH + HCHO + O_2$	$5.40 \times 10^{-13} \exp(500/T)$	4, 8
G147	$CH_3C(O)OO + CH_3C(O)OO \rightarrow 2\,CH_3OO + 2\,CO_2 + O_2$	$2.90 \times 10^{-12} \exp(500/T)$	4
G148	$CH_3C(O)OO + C_2H_5OO \overset{O_2}{\rightarrow} CH_3OO + CO_2 + CH_3CHO + HO_2 + O_2$	7.00×10^{-12}	4, 8
G149	$CH_3C(O)OO + C_2H_5OO \rightarrow CH_3COOH + CH_3CHO + O_2$	3.00×10^{-12}	4, 8
G150	$CH_3C(O)OO + NO \overset{O_2}{\rightarrow} CH_3OO + CO_2 + NO_2$	$7.80 \times 10^{-12} \exp(300/T)$	4
G151	$CH_3C(O)OO + NO_3 \overset{O_2}{\rightarrow} CH_3OO + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G152	$CH_3COOH + OH \overset{O_2}{\rightarrow} CH_3OO + CO_2 + H_2O$	8.00×10^{-13}	4
G153	$CH_3C(O)OOH + OH \rightarrow CH_3C(O)OO + H_2O$	3.70×10^{-12}	7
G154	$CH_3C(O)OO + NO_2 \overset{M}{\rightarrow} PAN$	$F_c = 0.3,\ k_0 = 2.7 \times 10^{-28}(T/300)^{-7.1},\ k_\infty = 1.2 \times 10^{-11}(T/300)^{0.9}$	4
G155	$PAN \overset{M}{\rightarrow} CH_3C(O)OO + NO_2$	$F_c = 0.3,\ k_0 = 4.9 \times 10^{-3} \exp(-12100/T),\ k_\infty = 5.4 \times 10^{16} \exp(-13830/T)$	4
G156	$HCOCHO + OH \overset{O_2}{\rightarrow} 2\,CO + HO_2 + H_2O$	6.60×10^{-12}	4, 7
G157	$HCOCHO + OH \overset{O_2}{\rightarrow} HCOC(O)OO + H_2O$	4.40×10^{-12}	4, 7
G158	$HCOCHO + Cl \overset{O_2}{\rightarrow} 2\,CO + HO_2 + HCl$	2.28×10^{-11}	22
G159	$HCOCHO + Cl \overset{O_2}{\rightarrow} HCOC(O)OO + HCl$	1.52×10^{-11}	22
G160	$HCOCHO + Br \overset{O_2}{\rightarrow} 2\,CO + HO_2 + HBr$	8.40×10^{-14}	23
G161	$HCOCHO + Br \overset{O_2}{\rightarrow} HCOC(O)OO + HBr$	5.60×10^{-14}	23
G162	$HCOC(O)OO + NO \overset{O_2}{\rightarrow} CO + HO_2 + NO_2 + CO_2$	$8.10 \times 10^{-12} \exp(270/T)$	7
G163	$HCOC(O)OO + NO_3 \overset{O_2}{\rightarrow} CO + HO_2 + CO_2 + NO_2 + O_2$	4.00×10^{-12}	7
G164	$HCOC(O)OO + HO_2 \rightarrow HCOC(O)OOH + O_2$	$3.05 \times 10^{-13} \exp(1040/T)$	8
G165	$HCOC(O)OO + HO_2 \rightarrow HCOCOOH + O_3$	$1.25 \times 10^{-13} \exp(1040/T)$	8
G166	$HCOC(O)OO + CH_3OO \overset{O_2}{\rightarrow} CO + HCHO + 2\,HO_2 + CO_2 + O_2$	7.00×10^{-12}	7
G167	$HCOC(O)OO + CH_3OO \rightarrow HCOCOOH + HCHO + O_2$	3.00×10^{-12}	7
G168	$HCOCOOH + OH \overset{O_2}{\rightarrow} CO + HO_2 + CO_2 + H_2O$	1.23×10^{-11}	7

(continued on the next page)

Table S2. (Continued.)

No.	Reaction	Rate Constant	Reference
G169	$HCOC(O)OOH + OH \rightarrow HCOC(O)OO + H_2O$	1.58×10^{-11}	7
G170	$HCOC(O)OO + NO_2 \overset{M}{\rightarrow}$ GLYPAN		$= k_{G154}$
G171	GLYPAN $\overset{M}{\rightarrow} HCOC(O)OO + NO_2$		$= k_{G155}$
G172	$CH_2OO^* \overset{M}{\rightarrow} CH_2OO$	$k_{uni} = 3.7 \times 10^5$	4
G173	$CH_2OO^* \rightarrow CO_2 + H_2$	$k_{uni} = 1.3 \times 10^5$	4
G174	$CH_2OO^* \rightarrow CO + H_2O$	$k_{uni} = 3.8 \times 10^5$	4
G175	$CH_2OO^* \overset{O_2}{\rightarrow} OH + CO + HO_2$	$k_{uni} = 1.2 \times 10^5$	4
G176	$CH_2OO + H_2O \rightarrow HCOOH + H_2O$	4.00×10^{-18}	24
G177	$OH + C_2H_2 \overset{M,O_2}{\rightarrow} 0.364 \times (HCOOH + CO + HO_2) + 0.636 \times (HCOCHO + OH)$	$F_c = 0.62,\ k_0 = 5.0 \times 10^{-30}(T/300)^{-1.5},\ k_\infty = 9.0 \times 10^{-13}(T/300)^{2.0}$	3
G178	$Cl + C_2H_2 \overset{M,O_2}{\rightarrow} 0.26 \times (HCOCl + CO + HO_2) + 0.21 \times (HCOCHO + Cl) + 0.53 \times (HCl + 2\,CO + HO_2)$	$F_c = 0.6,\ k_0 = 6.1 \times 10^{-30}(T/300)^{-3.0},\ k_\infty = 2.0 \times 10^{-10}$	4, 25
G179	$Br + C_2H_2 \overset{M,O_2}{\rightarrow} 0.17 \times (HCOBr + CO + HO_2) + 0.09 \times (HCOCHO + Br) + 0.74 \times (HBr + 2\,CO + HO_2)$	$9.39 \times 10^{-15} \exp(341/T)$	23, 25
G180	$HCOCl + OH \rightarrow CO + Cl + H_2O$	$3.67 \times 10^{-11} \exp(-1419/T)$	26
G181	$HCOCl + Cl \rightarrow CO + Cl + HCl$	$1.20 \times 10^{-11} \exp(-815/T)$	3
G182	$HCOCl + Br \rightarrow CO + Cl + HBr$	4.00×10^{-14}	$= k_{G185}$
G183	$HCOBr + OH \rightarrow CO + Br + H_2O$	$3.67 \times 10^{-11} \exp(-1419/T)$	$= k_{G180}$
G184	$HCOBr + Cl \rightarrow CO + Br + HCl$	$1.20 \times 10^{-11} \exp(-815/T)$	$= k_{G181}$
G185	$HCOBr + Br \rightarrow CO + Br + HBr$	4.00×10^{-14}	25
G186	$CHBr_3 + OH \overset{O_2}{\rightarrow} \cdots \rightarrow Br + CBr_2O + H_2O$	$1.60 \times 10^{-12} \exp(-710/T)$	2, 27
G187	$CHBr_3 + Cl \overset{O_2}{\rightarrow} \cdots \rightarrow Br + CBr_2O + HCl$	$4.00 \times 10^{-12} \exp(-809/T)$	27, 28
G188	$OH + SO_2 \overset{M,O_2}{\rightarrow} SO_3 + HO_2$	$F_c = 0.45,\ k_0 = 4.0 \times 10^{-31}(T/300)^{-3.33},\ k_\infty = 2.0 \times 10^{-12}$	3
G189	$SO_3 + H_2O \overset{M}{\rightarrow} H_2SO_4$	2.40×10^{-15}	29
G190	$Hg + Br \overset{M}{\rightarrow} HgBr$	$k_0 = 1.44 \times 10^{-32}(T/300)^{-1.86}$	30
G191	$HgBr + M \rightarrow Hg + Br + M$	$k = 2.49 \times 10^{-9} \exp(-7670/T)$	31
G192	$HgBr + Br \rightarrow HgBr_2$	$k = 2.98 \times 10^{-11}$	32
G193	$HgBr + Br \rightarrow Hg + Br_2$	$k = 3.89 \times 10^{-11}$	32
G194	$HgBr + BrO \rightarrow Hg(OBr)Br$	$k = 2.98 \times 10^{-11}$	$= k_{G192}$
G195	$Hg(O)Br + HO_2 \rightarrow Hg(OH)Br + O_2$	$k = 2.2 \times 10^{-11}$	33

References:
1. Sander et al. (2000); 2. DeMore et al. (1997); 3. Atkinson et al. (1997); 4. Atkinson et al. (1999); 5. Kondo and Benson (1984); 6. Veyret et al. (1982); 7. Saunders et al. (2003); 8. Jenkin et al. (1997); 9. Toyota et al. (2004); 10. Atkinson et al. (2000); 11. Sander et al. (2006); 12. Orlando and Tyndall (1996); 13. Aranda et al. (1997); 14. Guha and Francisco (2003); 15. Baulch et al. (1981); 16. Dolson and Leone (1987); 17. Clyne and Cruse (1972); 18. Carl et al. (1996); 19. Anderson and Fahey (1990); 20. Villenave and Lesclaux (1996); 21. Wallington et al. (1989a); 22. Niki et al. (1985); 23. Ramacher et al. (2001); 24. Atkinson (1990); 25. Yarwood et al. (1991); 26. Francisco (1992); 27. McGivern et al. (2002); 28. Kambanis et al. (1997); 29. DeMore et al. (1994); 30. Donohoue et al. (2006); 31. Shepler et al. (2007); 32. Balabanov et al. (2005); 33. Calvert and Lindberg (2004).

Note:
[a] Units of bimolecular reaction rate constants are cm^3 molecule^{-1} s^{-1}.
[b] Units of termolecular reaction rate constants (k_0) are cm^6 molecule^{-2} s^{-1}. Where a pressure fall-off correction is necessary, an additional entry (k_∞) gives the limiting high-pressure rate constant. In this case, the following formula is used to obtain an effective second-order rate constant (k):

$$k = \frac{k_0[M]}{1 + (k_0[M]/k_\infty)} F_c^{\{1+[\log_{10}(k_0[M]/k_\infty)/(0.75-1.27\log_{10}F_c)]^2\}^{-1}}$$

In some cases, effective second-order rate constants at ∼1 atm of air are directly taken from the literature.
[c] Rate laws for some of the thermal decomposition reactions are given by a first-order loss rate constant (k_{uni}) in s^{-1}, whereas for others by a second-order loss rate constant (k) in cm^3 molecule^{-1} s^{-1}.

Table S3. Photolysis reactions in gas- and aqueous-phases and their calculated 24-h mean J-values at the top of snowpack (see note[a,b]).

No.	Phase	Reaction	J, s^{-1}	Reference
P1	gas	$O_3 \rightarrow O(^1D) + O_2$	1.63×10^{-6}	1, 2, 3
P2	gas	$O_3 \rightarrow O(^3P) + O_2$	2.06×10^{-4}	1, 2, 3
P3	aq	$O_3 \overset{H_2O}{\rightarrow} H_2O_2 + O_2$	5.05×10^{-6}	4
P4	gas	$H_2O_2 \rightarrow 2\,OH$	1.80×10^{-6}	5
P5	aq	$H_2O_2 \rightarrow 2\,OH$	2.17×10^{-7}	6
P6	gas	$NO_2 \rightarrow NO + O(^3P)$	3.32×10^{-3}	5
P7	gas	$NO_3 \rightarrow NO + O_2$	1.23×10^{-2}	7
P8	gas	$NO_3 \rightarrow NO_2 + O(^3P)$	9.46×10^{-2}	5
P9	gas	$N_2O_5 \rightarrow NO_3 + NO_2$	6.85×10^{-6}	5
P10	gas	$HONO \rightarrow OH + NO$	7.00×10^{-4}	5
P11	aq	$H_2ONO^+ \rightarrow NO + OH + H^+$	8.83×10^{-6}	8
P12	aq	$HONO \rightarrow NO + OH$	5.96×10^{-5}	8
P13	aq	$NO_2^- \overset{H_2O}{\rightarrow} NO + OH + OH^-$	3.25×10^{-6}	9
P14	gas	$HNO_3 \rightarrow OH + NO_2$	6.96×10^{-8}	5
P15	aq	$NO_3^- \overset{H_2O}{\rightarrow} NO_2 + OH + OH^-$	1.46×10^{-8}	10
P16	aq	$NO_3^- \rightarrow NO_2^- + O(^3P)$	5.85×10^{-9}	10, 11
P17	gas	$HO_2NO_2 \rightarrow 0.33 \times (OH + NO_3) + 0.67 \times (HO_2 + NO_2)$	6.00×10^{-7}	5
P18	gas	$OClO \rightarrow ClO + O(^3P)$	3.18×10^{-2}	12
P19	gas	$Cl_2O_2 \rightarrow 2\,Cl + O_2$	4.20×10^{-4}	5
P20	gas	$HOCl \rightarrow Cl + OH$	8.85×10^{-5}	13
P21	aq	$HOCl \rightarrow Cl + OH$	8.85×10^{-5}	$= J_{P20} \times \beta_{pef}$
P22	gas	$CH_3OCl \overset{O_2}{\rightarrow} HCHO + HO_2 + Cl$	2.95×10^{-5}	5
P23	aq	$CH_3OCl \overset{O_2}{\rightarrow} HCHO + HO_2 + Cl$	2.95×10^{-5}	$= J_{P22} \times \beta_{pef}$
P24	gas	$ClNO_2 \rightarrow Cl + NO_2$	1.03×10^{-4}	5
P25	gas	$ClONO_2 \rightarrow Cl + NO_3$	1.17×10^{-5}	5
P26	gas	$ClONO_2 \rightarrow ClO + NO_2$	1.47×10^{-6}	5
P27	gas	$Cl_2 \rightarrow 2\,Cl$	8.20×10^{-4}	5
P28	aq	$Cl_2 \rightarrow 2\,Cl$	8.20×10^{-4}	$= J_{P27} \times \beta_{pef}$
P29	gas	$BrO \rightarrow Br + O(^3P)$	1.23×10^{-2}	5
P30	gas	$HOBr \rightarrow Br + OH$	8.65×10^{-4}	13
P31	aq	$HOBr \rightarrow Br + OH$	8.65×10^{-4}	$= J_{P30} \times \beta_{pef}$
P32	gas	$BrNO_2 \rightarrow Br + NO_2$	7.38×10^{-4}	see note[c]
P33	gas	$BrONO_2 \rightarrow Br + NO_3$	4.77×10^{-4}	5
P34	gas	$Br_2 \rightarrow 2\,Br$	1.46×10^{-2}	14
P35	aq	$Br_2 \rightarrow 2\,Br$	1.46×10^{-2}	$= J_{P34} \times \beta_{pef}$
P36	gas	$BrCl \rightarrow Br + Cl$	4.52×10^{-3}	5
P37	aq	$BrCl \rightarrow Br + Cl$	4.52×10^{-3}	$= J_{P36} \times \beta_{pef}$
P38	gas	$CHBr_3 \rightarrow 2\,Br + HBr$ + products	1.03×10^{-7}	5, 15, 16
P39	gas	$HCHO \overset{O_2}{\rightarrow} CO + 2\,HO_2$	6.31×10^{-6}	5
P40	gas	$HCHO \rightarrow H_2 + CO$	1.44×10^{-5}	5
P41	gas	$CH_3OOH \overset{O_2}{\rightarrow} HCHO + HO_2 + OH$	1.36×10^{-6}	5
P42	gas	$CH_3CHO \overset{O_2}{\rightarrow} CH_3OO + HO_2 + CO$	5.34×10^{-7}	17
P43	gas	$HCOCHO \overset{O_2}{\rightarrow} 2\,CO + 2\,HO_2$	2.01×10^{-5}	18
P44	gas	$HCOCOOH \overset{O_2}{\rightarrow} CO + 2\,HO_2 + CO_2$	3.38×10^{-5}	see note[d]
P45	gas	$HCOCO_3H \overset{O_2}{\rightarrow} CO + HO_2 + OH + CO_2$	1.36×10^{-6}	$= J_{P41}$
P46	gas	$HCOCO_3H \overset{O_2}{\rightarrow} CO + HO_2 + OH + CO_2$	3.38×10^{-5}	see note[d]
P47	gas	$HCOCl \overset{O_2}{\rightarrow} HO_2 + CO + Cl$	1.46×10^{-8}	18

(continued on the next page)

Table S3. (Continued.)

No.	Phase	Reaction	J, s^{-1}	Reference
P48	gas	$HCOBr \xrightarrow{O_2} HO_2 + CO + Br$	1.18×10^{-6}	19
P49	gas	$CBr_2O \rightarrow CO + 2\,Br$	1.88×10^{-7}	19
P50	gas	$HOCH_2OOH \xrightarrow{O_2} HCOOH + HO_2 + OH$	1.35×10^{-6}	20
P51	gas	$C_2H_5OOH \xrightarrow{O_2} CH_3CHO + HO_2 + OH$	1.36×10^{-6}	$= J_{P41}$
P52	gas	$CH_3CO_3H \xrightarrow{O_2} CH_3OO + OH + CO_2$	1.36×10^{-6}	$= J_{P41}$
P53	gas	$PAN \rightarrow CH_3C(O)OO + NO_2$	9.58×10^{-8}	18
P54	gas	$GLYPAN \xrightarrow{O_2} 2\,CO + HO_2 + O_2 + NO_2$	9.58×10^{-8}	$= J_{P53}$
P55	gas	$Hg(OBr)Br \rightarrow Hg(O)Br + Br$	8.65×10^{-4}	$= J_{P30}$, see note[e]
P56	aq	$Hg(OBr)Br \rightarrow Hg(O)Br + Br$	8.65×10^{-4}	$= J_{P31}$, see note[e]
P57	aq	$Hg^{2+} \xrightarrow{2\,e^-} Hg$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P58	aq	$HgOH^+ \xrightarrow{2\,e^-} Hg + OH^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P59	aq	$Hg(OH)_2 \xrightarrow{2\,e^-} Hg + 2\,OH^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P60	aq	$HgCl^+ \xrightarrow{2\,e^-} Hg + Cl^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P61	aq	$HgCl_2 \xrightarrow{2\,e^-} Hg + 2\,Cl^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P62	aq	$HgCl_3^- \xrightarrow{2\,e^-} Hg + 3\,Cl^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P63	aq	$HgCl_4^{2-} \xrightarrow{2\,e^-} Hg + 4\,Cl^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P64	aq	$HgBr^+ \xrightarrow{2\,e^-} Hg + Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P65	aq	$HgBr_2 \xrightarrow{2\,e^-} Hg + 2\,Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P66	aq	$HgBr_3^- \xrightarrow{2\,e^-} Hg + 3\,Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P67	aq	$HgBr_4^{2-} \xrightarrow{2\,e^-} Hg + 4\,Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P68	aq	$Hg(OH)Cl \xrightarrow{2\,e^-} Hg + OH^- + Cl^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P69	aq	$Hg(OH)Br \xrightarrow{2\,e^-} Hg + OH^- + Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P70	aq	$HgClBr \xrightarrow{2\,e^-} Hg + Cl^- + Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P71	aq	$HgCl_2Br^- \xrightarrow{2\,e^-} Hg + 2\,Cl^- + Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P72	aq	$HgClBr_2^- \xrightarrow{2\,e^-} Hg + Cl^- + 2\,Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P73	aq	$HgCl_3Br^{2-} \xrightarrow{2\,e^-} Hg + 3\,Cl^- + Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P74	aq	$HgCl_2Br_2^{2-} \xrightarrow{2\,e^-} Hg + 2\,Cl^- + 2\,Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]
P75	aq	$HgClBr_3^{2-} \xrightarrow{2\,e^-} Hg + Cl^- + 3\,Br^-$	5.78×10^{-7}	$= \alpha_{PRHg} \times J_{P1}$, see note[e]

References for absorption cross sections and product/quantum yields:
1. WMO (1986); 2. Molina and Molina (1986); 3. Matsumi et al. (2002); 4. Graedel and Weschler (1981); 5. DeMore et al. (1997); 6. Chu and Anastasio (2005); 7. Wayne et al. (1991); 8. Anastasio and Chu (2009); 9. Chu and Anastasio (2007); 10. Chu and Anastasio (2003); 11. Dubowski et al. (2002); 12. Wahner et al. (1987); 13. Sander et al. (2000); 14. Hubinger and Nee (1995); 15. Weller et al. (1992); 16. McGivern et al. (2000); 17. Atkinson et al. (1997); 18. Atkinson et al. (1999); 19. Libuda (1992); 20. Bauerle and Moortgat (1999).

Note:

[a] 24-h average at the top of the snowpack on March 30 at the latitude of 71° with total column ozone of 400 Dobson units and at $T = 253$ K.

[b] Actinic flux inside aerosol particles is assumed to be a factor of two ($\beta_{bef} = 2$) greater than that in the gas phase (Ruggaber et al., 1997). In the snowpack, actinic flux is assumed to be identical between snowpack interstitial air (SIA) and liquid-like layer (LLL), viz. $\beta_{bef} = 1$, while both attenuating with depth at the same exponential factor.

[c] Absorption cross sections are assumed to be red-shifted by 50 nm relative to $ClNO_2$.

[d] Absorption cross sections are assumed to identical to those for methyl glyoxal (CH_3COCHO) and taken from Atkinson et al. (1999).

[e] Photolysis of Hg(OBr)Br (P55–P56) is assumed to occur in both of the gas- and aqueous-phases in ambient air as well as in snowpack, whereas photo-reduction of Hg(II) (P57–P75) is assumed to occur only in the LLL of the snowpack; all parameters such as α_{PRHg} ($= 0.354$, in our baseline scenario) for P57–P75 are estimated empirically (Toyota et al., 2013).

Table S4. Reactive uptake of gaseous species represented by heterogeneous reactions and their reactive uptake coefficients (γ).

No.	Reaction	γ	Reference
H1	$N_2O_5(g) \rightarrow N_2O_5(aq) \xrightarrow{H_2O,\,Cl^-,\,Br^-}$ products (A189–A191, Table S7)	0.032	Behnke et al. (1997), see note[a]
H2	$ClONO_2(g) \rightarrow ClONO_2(aq) \xrightarrow{H_2O,\,Cl^-,\,Br^-}$ products (A192–A194, Table S7)	0.1	Koch and Rossi (1998), see note[a]
H3	$BrONO_2(g) \rightarrow BrONO_2(aq) \xrightarrow{H_2O,\,Cl^-,\,Br^-}$ products (A195–A197, Table S7)	0.8	Hanson et al. (1996), see note[a]
H4	$H_2SO_4(g) \rightarrow SO_4^{2-} + 2\,H^+$	0.65	Pöschl et al. (1998)
H5	$CH_3C(O)OO(g) \xrightarrow{H_2O} CH_3COOH(aq) + HO_2(aq)$	0.001	DeMore et al. (1997)
H6	$HCOCl(g) \rightarrow CO(g) + HCl(aq)$	0.1	Sander et al. (1997), see note[b]
H7	$HCOBr(g) \rightarrow CO(g) + HBr(aq)$	0.1	Sander et al. (1997), see note[b]

Note:
[a] Products assigned for these heterogeneous reactions, viz. $N_2O_5(aq)$, $ClONO_2(aq)$, and $BrONO_2(aq)$, react instantaneously with H_2O and halide ions on aqueous surface; in PHANTAS, these subsequent reactions are handled as aqueous-phase reactions (Table S7) where relative reactivities towards H_2O, Cl^-, and Br^- are assumed to be 3.3×10^{-6}, 1.7×10^{-3}, and 1, respectively, according to Sander et al. (1999).
[b] In their modeling study Sander et al. (1997) tentatively assigned this value for reactive uptake of formyl halides, which appears quite reasonable considering the rapid non-hydrolytic decay of HCOCl to give CO + HCl that occurs in aqueous solution (Dowideit et al., 1996). The latter authors also found that hydrolysis of HCOCl to give HCOOH + HCl occurs negligibly slowly as compared with the non-hydrolytic decay.

Table S5. Henry's law constants (K_H) and mass accommodation coefficients (α) for species transferred across gas-aqueous interface (see note[a,b]).

Species	$K_H^\ominus$, M atm^{-1}	$-\Delta H_{soln}/R$, K	Reference	$\alpha^\ominus$	$-\Delta H^{\#}_{obs}/R$, K	Reference
O_2	1.70×10^{-3}	1500	1	0.01		2
O_3	1.20×10^{-2}	2560	3	0.002		4
OH	2.50×10^{1}		5	0.2		6
HO_2	9.00×10^{3}		7	0.2		6
H_2O_2	9.90×10^{4}	6300	8	0.115	2769	9
NO	1.90×10^{-3}	1400	1	0.0015		$= \alpha(NO_2)$
NO_2	7.00×10^{-3}		10	0.0015		11
NO_3	1.80×10^{0}		12	0.002		12
HONO	4.90×10^{1}	4780	13	0.05		14
HNO_3	2.10×10^{5}	8700	5	0.06	3323	9
HO_2NO_2	1.26×10^{4}	6868	15	0.115	2769	$= \alpha(H_2O_2)$
NH_3	5.80×10^{1}	4085	3	0.097		6
CH_3OH	2.20×10^{2}	5200	16	0.017	4028	9
CH_3OO	6.00×10^{0}	5586	17	0.01		2
CH_3OOH	3.00×10^{2}	5300	8	0.0046	3273	18
HCHO	3.00×10^{3}	7193	19, see note[c]	0.04		6
CH_3CHO	6.70×10^{0}	6267	19, see note[d]	0.03		20
HCOOH	8.90×10^{3}	6100	21	0.014	3977	9
CH_3COOH	4.10×10^{3}	6300	21	0.02	4078	9
CH_3CO_3H	6.70×10^{2}	5900	8	0.0046	3273	$= \alpha(CH_3COOH)$
HCOCOOH	9.00×10^{3}		22	0.02	4078	$= \alpha(CH_3COOH)$
CO_2	3.10×10^{-2}	2423	3	0.01		2
HCl	1.10×10^{0}	2023	23	0.066	3625	24

(continued on the next page)

Table S5. (Continued.)

Species	$K_{\mathrm{H}}^{\ominus}$, M atm^{-1}	$-\Delta H_{\mathrm{soln}}/R$, K	Reference	$\alpha^{\ominus}$	$-\Delta H^{\#}_{\mathrm{obs}}/R$, K	Reference
HOCl	6.60×10^{2}	5900	25	0.066	3625	$= \alpha(\mathrm{HCl})$
CH_3OCl	6.60×10^{1}	5900	$= K_{\mathrm{H}}(\mathrm{HOCl}) \times 0.1$	0.066	3625	$= \alpha(\mathrm{HCl})$
Cl_2	9.40×10^{-2}	2109	1	0.038	6545	26
$ClNO_2$	4.60×10^{-2}		27	0.009		28
Br	3.40×10^{-2}	1800	29	0.1		(estimated)
HBr	1.30×10^{0}	10239	30, 31	0.018	5035	24
HOBr	6.10×10^{3}		27	0.6		32
Br_2	7.70×10^{-1}	229	33	0.038	6545	26
BrCl	9.40×10^{-1}	5629	33	0.33		34
$BrNO_2$	3.00×10^{-1}		27	0.009		$= \alpha(\mathrm{ClNO_2})$
SO_2	1.20×10^{0}	3120	3	0.11		6
Hg	1.28×10^{-1}	2482	35	0.1		(estimated)
$Hg(OH)_2$	1.28×10^{4}	3901	36	0.1		(estimated)
$HgCl_2$	1.00×10^{6}	8060	37	0.1		(estimated)
$HgBr_2$	1.17×10^{5}	8912	38	0.1		(estimated)
Hg(OH)Cl	1.00×10^{6}	8060	$= K_{\mathrm{H}}(\mathrm{HgCl_2})$	0.1		(estimated)
HgClBr	1.00×10^{6}	8060	$= K_{\mathrm{H}}(\mathrm{HgCl_2})$	0.1		(estimated)
Hg(OH)Br	1.17×10^{5}	8912	$= K_{\mathrm{H}}(\mathrm{HgBr_2})$	0.1		(estimated)
Hg(OBr)Br	1.17×10^{5}	8912	$= K_{\mathrm{H}}(\mathrm{HgBr_2})$	0.1		(estimated)

References:
1. Lide (1999); 2. Sander and Crutzen (1996); 3. Chameides (1984); 4. Utter et al. (1992); 5. Lelieveld and Crutzen (1991); 6. DeMore et al. (1997); 7. Weinstein-Lloyd and Schwartz (1991); 8. Lind and Kok (1994); 9. Jayne et al. (1991); 10. Lee and Schwartz (1981); 11. Ponche et al. (1993); 12. Thomas et al. (1998); 13. Schwartz and White (1981); 14. Bongartz et al. (1994); 15. Régimbal and Mozurkewich (1997); 16. Snider and Dawson (1985); 17. Seinfeld and Pandis (1998); 18. Magi et al. (1997); 19. Betterton and Hoffmann (1988b); 20. Jayne et al. (1992); 21. Johnson et al. (1996); 22. Saxena and Hildemann (1996); 23. Marsh and McElroy (1985); 24. Schweitzer et al. (2000); 25. Huthwelker et al. (1995); 26. Hu et al. (1995); 27. Frenzel et al. (1998); 28. Fickert et al. (1998); 29. Berdnikov and Bazhin (1970); 30. Brimblecombe and Clegg (1988); 31. Brimblecombe and Clegg (1989); 32. Wachsmuth et al. (2002); 33. Bartlett and Margerum (1999); 34. Katrib et al. (2001); 35. Sanemasa (1975); 36. Iverfeldt and Lindqvist (1980); 37. Sommar et al. (2000); 38. Hepler and Olofsson (1975).

Note:
[a] Temperature dependence of Henry's law constants is given by $K_{\mathrm{H}} = K_{\mathrm{H}}^{\ominus} \times \exp[-\Delta H_{\mathrm{soln}}/R \times (1/T - 1/T^{\ominus})]$, where $K_{\mathrm{H}}^{\ominus}$ is K_{H} at $T^{\ominus}$, $T^{\ominus}$ = 298.15 K, ΔH_{soln} is the enthalpy of solution and R is gas constant.
[b] Temperature dependence of mass accommodation coefficients is given by $\mathrm{d}\ln[\alpha/(1-\alpha)]/\mathrm{d}(1/T) = -\Delta H^{\#}_{\mathrm{obs}}/R$, where $\Delta H^{\#}_{\mathrm{obs}}$ is the enthalpy of transition state between the gas and solvated states and R is gas constant.
[c] Effective Henry's law constant that takes into account the hydrolysis of HCHO in the aqueous phase, as reported by Betterton and Hoffmann (1988b): $K_{\mathrm{H}} = ([\mathrm{HCHO}]_{\mathrm{aq}} + [\mathrm{CH_2(OH)_2}])/p(\mathrm{HCHO})$. Considering a fact that formaldehyde in the aqueous phase predominantly exists as its hydrated form ($[\mathrm{HCHO}]_{\mathrm{aq}} \ll [\mathrm{CH_2(OH)_2}]$; see Table S6), $K_{\mathrm{H}} = [\mathrm{CH_2(OH)_2}]/p(\mathrm{HCHO})$ is assumed to hold at equilibrium of $\mathrm{HCHO(gas)} \rightleftharpoons \mathrm{CH_2(OH)_2}$.
[d] Effective Henry's law constant that takes into account the hydrolysis of CH_3CHO in the aqueous phase as reported by Betterton and Hoffmann (1988b) is corrected using a hydrolysis constant given in Table S6; $K_{\mathrm{H}} = [\mathrm{CH_3CH(OH)_2}]/p(\mathrm{CH_3CHO})$ at equilibrium of $\mathrm{CH_3CHO(gas)} \rightleftharpoons \mathrm{CH_3CH(OH)_2}$.

Table S6. Aqueous-phase equilibrium constants (K_{eq}) for acids, bases, hydrates, and other species that undergo ion dissociation in water (see note[a]).

No.	Reaction	$K_{eq}^{\ominus}$, M	$-\Delta H/R$, K	Reference
E1	$H_2O \rightleftharpoons H^+ + OH^-$	1.00×10^{-14}	-6716	1
E2	$HO_2 \rightleftharpoons H^+ + O_2^-$	1.60×10^{-5}		2
E3	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	2.20×10^{-12}	-3730	3
E4	$NH_3 + H_2O \rightleftharpoons OH^- + NH_4^+$	1.70×10^{-5}	-4325	4
E5	$HONO \rightleftharpoons H^+ + NO_2^-$	5.10×10^{-4}	-1260	5
E6	$H_2ONO^+ \rightleftharpoons H^+ + HONO$	3.16×10^{-2}		6
E7	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	1.50×10^{1}		7
E8	$HO_2NO_2 \rightleftharpoons H^+ + NO_4^-$	1.41×10^{-6}		8
E9	$HCHO + H_2O \rightleftharpoons CH_2(OH)_2$	2.45×10^{3}	4000	9
E10	$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2$	1.43×10^{0}	2518	10, 11
E11	$HCOOH \rightleftharpoons H^+ + HCOO^-$	1.80×10^{-4}		12
E12	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.76×10^{-5}		12
E13	$HCOCOOH \rightleftharpoons H^+ + HCOCOO^-$	1.48×10^{-4}		see note[b]
E14	$CH_3CO_3H \rightleftharpoons H^+ + CH_3CO_3^-$	6.31×10^{-9}		13
E15	$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$	4.30×10^{-7}	-913	4
E16	$HCl \rightleftharpoons H^+ + Cl^-$	1.70×10^{6}	6896	14
E17	$Cl_2^- \rightleftharpoons Cl + Cl^-$	5.20×10^{-6}		15
E18	$Cl_3^- \rightleftharpoons Cl_2 + Cl^-$	5.56×10^{0}		16
E19	$HOCl \rightleftharpoons H^+ + ClO^-$	3.20×10^{-8}		17
E20	$HBr \rightleftharpoons H^+ + Br^-$	1.00×10^{9}		17
E21	$Br_2^- \rightleftharpoons Br + Br^-$	1.53×10^{-6}		18
E22	$HOBr \rightleftharpoons H^+ + BrO^-$	2.30×10^{-9}	-3091	19
E23	$Br_3^- \rightleftharpoons Br^- + Br_2$	6.21×10^{-2}		16
E24	$BrCl_2^- \rightleftharpoons Br^- + Cl_2$	2.38×10^{-7}		20
E25	$BrCl_2^- \rightleftharpoons BrCl + Cl^-$	2.63×10^{-1}		20
E26	$Br_2Cl^- \rightleftharpoons Br^- + BrCl$	5.56×10^{-5}	-7500	16, 21
E27	$Br_2Cl^- \rightleftharpoons Cl^- + Br_2$	7.69×10^{-1}		16
E28	$SO_2 + H_2O \rightleftharpoons H^+ + HSO_3^-$	1.70×10^{-2}	2090	4
E29	$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	6.00×10^{-8}	1120	4
E30	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.02×10^{-2}	2720	3
E31	$HSO_5^- \rightleftharpoons H^+ + SO_5^{2-}$	3.98×10^{-10}		13
E32	$Hg^{2+} + OH^- \rightleftarrows HgOH^+$	2.62×10^{10}	2966	22, 23
E33	$HgOH^+ + OH^- \rightleftarrows Hg(OH)_2$	2.70×10^{11}	5449	22, 23
E34	$Hg^{2+} + Cl^- \rightleftarrows HgCl^+$	5.50×10^{6}	2730	22, 23
E35	$HgCl^+ + Cl^- \rightleftarrows HgCl_2$	2.55×10^{6}	3637	22, 23
E36	$HgCl_2 + Cl^- \rightleftarrows HgCl_3^-$	6.86×10^{0}	630	22, 23
E37	$HgCl_3^- + Cl^- \rightleftarrows HgCl_4^{2-}$	1.31×10^{1}	-223	22, 23
E38	$Hg^{2+} + Br^- \rightleftarrows HgBr^+$	1.07×10^{9}	5196	22, 23
E39	$HgBr^+ + Br^- \rightleftarrows HgBr_2$	2.50×10^{8}	5454	22, 23
E40	$HgBr_2 + Br^- \rightleftarrows HgBr_3^-$	1.45×10^{2}	1329	22, 23
E41	$HgBr_3^- + Br^- \rightleftarrows HgBr_4^{2-}$	2.27×10^{1}	1942	22, 23
E42	$HgOH^+ + Cl^- \rightleftarrows Hg(OH)Cl$	6.70×10^{6}	4455	22, 23
E43	$HgOH^+ + Br^- \rightleftarrows Hg(OH)Br$	1.25×10^{9}	4455	22, 23, see note[c]
E44	$HgCl^+ + OH^- \rightleftarrows Hg(OH)Cl$	3.19×10^{10}	4691	22, 23
E45	$HgBr^+ + OH^- \rightleftarrows Hg(OH)Br$	3.06×10^{10}	4691	22, 23, see note[c]
E46	$HgCl_2 + Br^- \rightleftarrows HgClBr + Cl^-$	3.37×10^{2}	2200	22, 23, 24
E47	$HgClBr + Br^- \rightleftarrows HgBr_2 + Cl^-$	5.67×10^{1}	2083	22, 23, 24
E48	$HgCl_3^- + Br^- \rightleftarrows HgCl_2Br^- + Cl^-$	3.05×10^{2}	1755	22, 23, 24
E49	$HgCl_2Br^- + Br^- \rightleftarrows HgClBr_2^- + Cl^-$	7.38×10^{1}	1661	22, 23, 24
E50	$HgClBr_2^- + Br^- \rightleftarrows HgBr_3^- + Cl^-$	1.80×10^{1}	1566	22, 23, 24
E51	$HgCl_4^{2-} + Br^- \rightleftarrows HgCl_3Br^{2-} + Cl^-$	1.87×10^{2}	1929	22, 23, 24

(continued on the next page)

Table S6. (Continued.)

No.	Reaction	$K^{\ominus}_{eq}$, M	$-\Delta H/R$, K	Reference
E52	$HgCl_3Br^{2-} + Br^- \rightleftarrows HgCl_2Br_2^{2-} + Cl^-$	5.07×10^1	1834	22, 23, 24
E53	$HgCl_2Br_2^{2-} + Br^- \rightleftarrows HgClBr_3^{2-} + Cl^-$	1.64×10^1	1740	22, 23, 24
E54	$HgClBr_3^{2-} + Br^- \rightleftarrows HgBr_4^{2-} + Cl^-$	4.50×10^0	1645	22, 23, 24

References:
1. National Bureau of Standards (1965); 2. Weinstein-Lloyd and Schwartz (1991); 3. Smith and Martell (1976); 4. Chameides (1984); 5. Schwartz and White (1981); 6. Riordan et al. (2005); 7. Lelieveld and Crutzen (1991); 8. Løgager and Sehested (1993); 9. Warneck (1998) and references therein; 10. Bell (1966); 11. Bell and Evans (1966); 12. Lide (1999); 13. Fortnum et al. (1960); 14. Marsh and McElroy (1985); 15. Jayson et al. (1973); 16. Wang et al. (1994); 17. Lax (1969); 18. Merényi and Lind (1994); 19. Kelly and Tartar (1956); 20. Liu and Margerum (2001); 21. Sander et al. (2006); 22. Hepler and Olofsson (1975); 23. Wagman et al. (1982); 24. Marcus and Eliezer (1962).

Note:
[a] Temperature dependence of equilibrium constants is given by $K_{eq} = K^{\ominus}_{eq} \times \exp[-\Delta H/R \times (1/T - 1/T^{\ominus})]$, where ΔH is reaction enthalpy, R is gas constant and $T^{\ominus}$ = 298.15 K.
[b] Equilibrium constant is assumed to be identical to that for the ionic dissociation of glycolic acid ($HOCH_2COOH \rightleftharpoons H^+ + HOCH_2COO^-$) and taken from Lide (1999).
[c] Temperature dependence is taken from K_{eq} for Hg(OH)Cl.

Table S7. Other aqueous-phase reactions and their rate constants (see note[a]).

No.	Reaction (of Order n)	n	$k^{\ominus}$, $M^{1-n}\,s^{-1}$	$-E_a/R$, K	Reference
A1	$O_3 + O_2^- \xrightarrow{H_2O} OH + OH^- + 2\,O_2$	2	1.50×10^{9}		1
A2	$O_3 + OH \rightarrow HO_2 + O_2$	2	1.10×10^{8}		2
A3	$OH + OH \rightarrow H_2O_2$	2	5.50×10^{9}		3
A4	$OH + HO_2 \rightarrow H_2O + O_2$	2	7.10×10^{9}		4
A5	$OH + O_2^- \rightarrow OH^- + O_2$	2	1.00×10^{10}		4
A6	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	2	2.70×10^{7}		5
A7	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	2	9.70×10^{5}	-2500	6
A8	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$	2	1.00×10^{8}	-900	6
A9	$O_2 + O(^3P) \rightarrow O_3$	2	4.00×10^{9}		7
A10	$H_2O_2 + O(^3P) \rightarrow OH + HO_2$	2	1.60×10^{9}		8
A11	$HO_2^- + O(^3P) \rightarrow OH + O_2^-$	2	5.30×10^{9}		8
A12	$OH^- + O(^3P) \rightarrow HO_2^-$	2	4.20×10^{8}		8
A13	$NO + NO_2 \xrightarrow{H_2O} 2\,NO_2^- + 2\,H^+$	2	2.00×10^{8}		9
A14	$NO + OH \rightarrow NO_2^- + H^+$	2	2.00×10^{10}		10
A15	$NO_2 + NO_2 \xrightarrow{H_2O} NO_2^- + NO_3^- + 2\,H^+$	2	6.50×10^{7}		11
A16	$NO_2 + OH \rightarrow NO_3^- + H^+$	2	1.30×10^{9}		12
A17	$NO_2 + O_2^- \rightarrow NO_2^- + O_2$	2	4.50×10^{9}		13
A18	$NO_2 + HO_2 \rightarrow HO_2NO_2$	2	1.80×10^{9}	-2778	13
A19	$HO_2NO_2 + HONO \rightarrow 2\,NO_3^- + 2\,H^+$	2	1.20×10^{1}		13
A20	$HO_2NO_2 \rightarrow HONO + O_2$	1	7.00×10^{-4}		13
A21	$HO_2NO_2 \rightarrow HO_2 + NO_2$	1	2.60×10^{-2}	-13242	14
A22	$NO_4^- \rightarrow NO_2^- + O_2$	1	1.00×10^{0}		13
A23	$HONO + OH \rightarrow NO_2 + H_2O$	2	1.00×10^{9}	-1500	15
A24	$HONO + NO_3 \rightarrow NO_2 + NO_3^- + H^+$	2	8.00×10^{6}		16
A25	$HONO + H_2O_2 + H^+ \rightarrow NO_3^- + 2\,H^+ + H_2O$	3	6.30×10^{3}	-6700	17
A26	$NO_2^- + OH \rightarrow NO_2 + OH^-$	2	8.00×10^{9}		18
A27	$NO_2^- + Cl_2^- \rightarrow NO_2 + 2\,Cl^-$	2	2.50×10^{8}		19
A28	$NO_2^- + Br_2^- \rightarrow NO_2 + 2\,Br^-$	2	2.00×10^{7}		20
A29	$NO_2^- + NO_3 \rightarrow NO_2 + NO_3^-$	2	1.20×10^{9}		21
A30	$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	2	3.30×10^{5}		22
A31	$NO_3^- + O(^3P) \rightarrow NO_2^- + O_2$	2	2.24×10^{8}		23
A32	$NO_2^- + O(^3P) \rightarrow NO_3^-$	2	1.48×10^{9}		23
A33	$NO_3 + HO_2 \rightarrow NO_3^- + H^+ + O_2$	2	4.50×10^{9}	-1500	24
A34	$NO_3 + O_2^- \rightarrow NO_3^- + O_2$	2	1.00×10^{9}	-1500	24
A35	$NO_3 + H_2O_2 \rightarrow NO_3^- + HO_2 + H^+$	2	7.10×10^{6}	-241	25
A36	$NO_3 + OH^- \rightarrow NO_3^- + OH$	2	8.20×10^{7}	-2700	26
A37	$CH_3OO + HO_2 \rightarrow CH_3OOH + O_2$	2	4.30×10^{5}		24
A38	$CH_3OO + O_2^- \xrightarrow{H_2O} CH_3OOH + OH^- + O_2$	2	5.00×10^{7}		24
A39	$CH_3OOH + OH \rightarrow CH_3OO + H_2O$	2	2.70×10^{7}	-1700	24
A40	$CH_3OOH + OH \rightarrow HCHO + OH + H_2O$	2	1.90×10^{7}	-1800	24
A41	$CH_3OH + OH \xrightarrow{O_2} HCHO + HO_2 + H_2O$	2	9.70×10^{8}		3
A42	$CH_3OH + SO_4^- \xrightarrow{O_2} HCHO + HO_2 + SO_4^{2-} + H^+$	2	9.00×10^{6}	-2190	27
A43	$CH_3OH + NO_3 \xrightarrow{O_2} HCHO + HO_2 + NO_3^- + H^+$	2	5.40×10^{5}	-4300	28
A44	$CH_3OH + Cl_2^- \xrightarrow{O_2} HCHO + HO_2 + 2\,Cl^- + H^+$	2	1.00×10^{3}	-5500	29
A45	$CH_3OH + Br_2^- \xrightarrow{O_2} HCHO + HO_2 + 2\,Br^- + H^+$	2	4.40×10^{3}		30
A46	$CH_3OH + CO_3^- \xrightarrow{O_2} HCHO + HO_2 + HCO_3^-$	2	2.60×10^{3}		29
A47	$CH_2(OH)_2 + OH \xrightarrow{O_2} HCOOH + HO_2 + H_2O$	2	2.00×10^{9}	-1500	31
A48	$CH_2(OH)_2 + SO_4^- \xrightarrow{O_2} HCOOH + HO_2 + SO_4^{2-} + H^+$	2	1.40×10^{7}	-1300	32

(continued on the next page)

Table S7. (Continued.)

No.	Reaction (of Order n)	n	$k^{\ominus}$, $M^{1-n}\,s^{-1}$	$-E_a/R$, K	Reference
A49	$CH_2(OH)_2 + NO_3 \overset{O_2}{\rightarrow} HCOOH + HO_2 + NO_3^- + H^+$	2	1.00×10^6	-4500	33
A50	$CH_2(OH)_2 + Cl_2^- \overset{O_2}{\rightarrow} HCOOH + HO_2 + 2\,Cl^- + H^+$	2	3.10×10^4	-4400	29
A51	$CH_2(OH)_2 + Br_2^- \overset{O_2}{\rightarrow} HCOOH + HO_2 + 2\,Br^- + H^+$	2	3.00×10^3		34
A52	$CH_2(OH)_2 + CO_3^- \overset{O_2}{\rightarrow} HCOOH + HO_2 + HCO_3^-$	2	1.30×10^4		29
A53	$CH_3CH(OH)_2 + OH \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + H_2O$	2	1.20×10^9		35
A54	$CH_3CHO + OH \overset{H_2O,O_2}{\rightarrow} CH_3COOH + HO_2 + H_2O$	2	3.60×10^9		35
A55	$CH_3CH(OH)_2 + SO_4^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + SO_4^{2-} + H^+$	2	1.00×10^7		34
A56	$CH_3CH(OH)_2 + NO_3 \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + NO_3^- + H^+$	2	1.90×10^6		29
A57	$CH_3CH(OH)_2 + Cl_2^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + 2\,Cl^- + H^+$	2	4.00×10^4		36
A58	$CH_3CH(OH)_2 + Br_2^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + 2\,Br^- + H^+$	2	4.00×10^4		34
A59	$CH_3CH(OH)_2 + CO_3^- \overset{O_2}{\rightarrow} CH_3COOH + HO_2 + HCO_3^-$	2	1.00×10^4		34
A60	$HCOOH + OH \overset{O_2}{\rightarrow} HO_2 + CO_2 + H_2O$	2	1.10×10^8	-991	37
A61	$HCOO^- + OH \overset{O_2}{\rightarrow} OH^- + HO_2 + CO_2$	2	3.10×10^9	-1240	37
A62	$HCOOH + SO_4^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + SO_4^{2-} + H^+$	2	2.50×10^6		38
A63	$HCOO^- + SO_4^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + SO_4^{2-}$	2	2.10×10^7		38
A64	$HCOOH + NO_3 \overset{O_2}{\rightarrow} HO_2 + CO_2 + NO_3^- + H^+$	2	3.80×10^5	-3400	39
A65	$HCOO^- + NO_3 \overset{O_2}{\rightarrow} HO_2 + CO_2 + NO_3^-$	2	5.10×10^7	-2200	39
A66	$HCOOH + Cl_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Cl^- + H^+$	2	5.50×10^3	-4500	40
A67	$HCOO^- + Cl_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Cl^-$	2	1.90×10^6		19
A68	$HCOOH + Br_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Br^- + H^+$	2	4.00×10^3		41
A69	$HCOO^- + Br_2^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + 2\,Br^-$	2	4.90×10^3		36
A70	$HCOO^- + CO_3^- \overset{O_2}{\rightarrow} HO_2 + CO_2 + HCO_3^- + OH^-$	2	1.40×10^5	-3300	29
A71	$HCO_3^- + OH \rightarrow H_2O + CO_3^-$	2	8.50×10^6		3
A72	$CO_3^- + O_2^- \overset{H_2O}{\rightarrow} HCO_3^- + OH^- + O_2$	2	6.50×10^8		42
A73	$CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2$	2	4.30×10^5		43
A74	$CO_3^- + HCOO^- \overset{H_2O,O_2}{\rightarrow} 2\,HCO_3^- + HO_2$	2	1.50×10^5		43
A75	$Cl^- + OH \rightarrow ClOH^-$	2	4.30×10^9		44
A76	$Cl^- + NO_3 \rightarrow Cl + NO_3^-$	2	1.00×10^7	-4300	26
A77	$Cl + H_2O \rightarrow ClOH^- + H^+$	1	1.30×10^3		45
A78	$ClOH^- \rightarrow Cl^- + OH$	1	6.10×10^9		44
A79	$ClOH^- + H^+ \rightarrow Cl + H_2O$	2	2.10×10^{10}		44
A80	$Cl_2^- + Cl_2^- \rightarrow Cl_3^- + Cl^-$	2	7.00×10^8		45
A81	$Cl_2^- + OH \rightarrow HOCl + Cl^-$	2	1.00×10^9		46
A82	$Cl_2^- + HO_2 \rightarrow 2\,Cl^- + H^+ + O_2$	2	4.50×10^9		47
A83	$Cl_2^- + O_2^- \rightarrow 2\,Cl^- + O_2$	2	1.00×10^9		48
A84	$Cl_2^- + H_2O_2 \rightarrow 2\,Cl^- + HO_2 + H^+$	2	1.40×10^5		19
A85	$Cl^- + HOCl + H^+ \rightarrow Cl_2 + H_2O$	3	2.20×10^4	-3508	49
A86	$Cl^- + CH_3OCl + H^+ \rightarrow Cl_2 + CH_3OH$	3	2.20×10^4	-3508	$= k_{A85}$
A87	$Cl_2 + H_2O \rightarrow Cl^- + HOCl + H^+$	1	2.20×10^1	-8012	49
A88	$Cl^- + HOCl + HSO_4^- \rightarrow Cl_2 + SO_4^{2-} + H_2O$	3	2.80×10^3		49
A89	$Cl^- + CH_3OCl + HSO_4^- \rightarrow Cl_2 + SO_4^{2-} + CH_3OH$	3	2.80×10^3		$= k_{A88}$
A90	$Cl_2 + SO_4^{2-} \overset{H_2O}{\rightarrow} Cl^- + HOCl + HSO_4^-$	2	3.20×10^1		49
A91	$Cl^- + HOCl + HCOOH \rightarrow Cl_2 + HCOO^- + H_2O$	3	1.20×10^{-1}		49
A92	$Cl^- + CH_3OCl + HCOOH \rightarrow Cl_2 + HCOO^- + CH_3OH$	3	1.20×10^{-1}		$= k_{A91}$
A93	$Cl_2 + HCOO^- \overset{H_2O}{\rightarrow} Cl^- + HOCl + HCOOH$	2	1.20×10^2		49

(continued on the next page)

Table S7. (Continued.)

No.	Reaction (of Order n)	n	$k^{\ominus}$, $M^{1-n}\,s^{-1}$	$-E_a/R$, K	Reference
A94	$Br^- + OH \rightarrow BrOH^-$	2	1.10×10^{10}		50
A95	$Br^- + NO_3 \rightarrow Br + NO_3^-$	2	4.00×10^{9}		51
A96	$Br + OH^- \rightarrow BrOH^-$	2	1.30×10^{10}		50
A97	$BrOH^- \rightarrow Br^- + OH$	1	3.30×10^{7}		50
A98	$BrOH^- \rightarrow Br + OH^-$	1	4.20×10^{6}		50
A99	$BrOH^- + H^+ \rightarrow Br + H_2O$	2	4.40×10^{10}		50
A100	$BrOH^- + Br^- \rightarrow Br_2^- + OH^-$	2	2.00×10^{8}		52
A101	$Br_2^- + Br_2^- \rightarrow Br^- + Br_3^-$	2	1.90×10^{9}		53
A102	$Br_2^- + HO_2 \rightarrow Br_2 + HO_2^-$	2	4.40×10^{9}		54
A103	$Br_2^- + HO_2 \rightarrow 2\,Br^- + H^+ + O_2$	2	0.00×10^{0}		54
A104	$Br_2^- + O_2^- \rightarrow 2\,Br^- + O_2$	2	1.70×10^{8}		55
A105	$Br_2^- + H_2O_2 \rightarrow 2\,Br^- + H^+ + HO_2$	2	5.00×10^{2}		56
A106	$HOBr + O_2^- \rightarrow Br + OH^- + O_2$	2	3.50×10^{9}		57
A107	$HOBr + H_2O_2 \rightarrow Br^- + H^+ + O_2 + H_2O$	2	3.40×10^{6}		58
A108	$Br_2 + O_2^- \rightarrow Br_2^- + O_2$	2	5.00×10^{9}		57
A109	$Br_2 + HO_2 \rightarrow Br_2^- + O_2 + H^+$	2	1.30×10^{8}		57
A110	$Br_3^- + O_2^- \rightarrow Br^- + Br_2^- + O_2$	2	1.50×10^{9}		57
A111	$Cl^- + HOBr \rightarrow Br^- + HOCl$	2	1.01×10^{-2}		59, 60
A112	$Br^- + HOCl \rightarrow Cl^- + HOBr$	2	1.55×10^{3}		60
A113	$Br^- + CH_3OCl \xrightarrow{H_2O} Cl^- + HOBr + CH_3OH$	2	1.55×10^{3}		$= k_{A112}$
A114	$Br^- + HOCl + H^+ \rightarrow BrCl + H_2O$	3	1.32×10^{6}		59
A115	$Br^- + CH_3OCl + H^+ \rightarrow BrCl + CH_3OH$	3	1.32×10^{6}		$= k_{A114}$
A116	$BrCl + H_2O \rightarrow Br^- + HOCl + H^+$	1	1.15×10^{-3}		61
A117	$Cl^- + HOBr + H^+ \rightarrow BrCl + H_2O$	3	2.31×10^{10}		61
A118	$BrCl + H_2O \rightarrow Cl^- + HOBr + H^+$	1	3.00×10^{6}		61
A119	$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	3	1.60×10^{10}		62
A120	$Br_2 + H_2O \rightarrow Br^- + HOBr + H^+$	1	9.70×10^{1}		62
A121	$Br^- + HOBr + HSO_4^- \rightarrow Br_2 + SO_4^{2-} + H_2O$	3	3.70×10^{9}		62
A122	$Br_2 + SO_4^{2-} \xrightarrow{H_2O} Br^- + HOBr + HSO_4^-$	2	4.10×10^{2}		62
A123	$BrNO_2 + Br^- \rightarrow Br_2 + NO_2^-$	2	7.11×10^{5}		63
A124	$Br_2 + NO_2^- \rightarrow BrNO_2 + Br^-$	2	1.85×10^{6}		63
A125	$BrNO_2 + NO_2^- \xrightarrow{H_2O} Br^- + NO_3^- + NO_2^- + 2\,H^+$	2	1.27×10^{4}		63
A126	$ClNO_2 + Br^- \rightarrow BrNO_2 + Cl^-$	2	1.18×10^{6}		63
A127	$BrNO_2 + Cl^- \rightarrow ClNO_2 + Br^-$	2	3.00×10^{2}		63
A128	$ClNO_2 + Cl^- \rightarrow Cl_2 + NO_2^-$	2	0.00×10^{0}		63
A129	$Cl_2 + NO_2^- + ClNO_2 + Cl^-$	2	2.50×10^{6}		63
A130	$ClNO_2 + NO_2^- \xrightarrow{H_2O} Cl^- + NO_3^- + NO_2^- + 2\,H^+$	2	7.98×10^{3}		63
A131	$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2$	2	3.70×10^{5}	-5500	64
A132	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	2	1.50×10^{9}	-5300	64
A133	$HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O$	2	see note[b]	-3650	65
A134	$HSO_3^- + CH_3OOH + H^+ \rightarrow SO_4^{2-} + CH_3OH + 2\,H^+$	3	1.60×10^{7}	-3800	66
A135	$SO_3^{2-} + CH_3OOH + H^+ \rightarrow SO_4^{2-} + CH_3OH + H^+$	3	1.60×10^{7}	-3800	66
A136	$HSO_3^- + CH_3CO_3H + H^+ \rightarrow SO_4^{2-} + CH_3COOH + 2\,H^+$	3	4.83×10^{7}	-3993	66
A137	$HSO_3^- + CH_3CO_3H \rightarrow SO_4^{2-} + CH_3COOH + H^+$	3	8.42×10^{2}	-3993	66
A138	$HSO_3^- + OH \rightarrow SO_3^- + H_2O$	2	2.70×10^{9}		67
A139	$SO_3^{2-} + OH \rightarrow SO_3^- + OH^-$	2	4.60×10^{9}		67
A140	$HSO_3^- + HO_2 \rightarrow SO_3^- + H_2O_2$	2	3.00×10^{4}		68
A141	$HSO_3^- + O_2^- \rightarrow SO_3^- + HO_2^-$	2	3.00×10^{4}		68
A142	$HSO_3^- + NO_3 \rightarrow SO_3^- + NO_3^- + H^+$	2	1.40×10^{9}	-2000	26
A143	$SO_3^{2-} + NO_3 \rightarrow SO_3^- + NO_3^-$	2	2.00×10^{9}		51
A144	$HSO_3^- + Cl_2^- \rightarrow SO_3^- + 2\,Cl^- + H^+$	2	4.80×10^{8}	-1079	69

(continued on the next page)

Table S7. (Continued.)

No.	Reaction (of Order n)	n	$k^{\ominus}$, $M^{1-n}\,s^{-1}$	$-E_a/R$, K	Reference
A145	$SO_3^{2-} + Cl_2^- \rightarrow SO_3^- + 2\,Cl^-$	2	6.20×10^7		70
A146	$HSO_3^- + Br_2^- \rightarrow SO_3^- + 2\,Br^- + H^+$	2	6.40×10^7	-779	69
A147	$SO_3^{2-} + Br_2^- \rightarrow SO_3^- + 2\,Br^-$	2	2.20×10^8	-647	69
A148	$HSO_3^- + HCHO \rightarrow HMS^-$	2	4.50×10^2	-2660	71
A149	$SO_3^{2-} + HCHO \overset{H_2O}{\rightarrow} HMS^- + OH^-$	2	5.40×10^6	-2530	71
A150	$HMS^- + OH^- \rightarrow SO_3^{2-} + CH_2(OH)_2$	2	4.60×10^3	-4880	71
A151	$HMS^- + OH \overset{H_2O, O_2}{\rightarrow} HSO_3^- + HCOOH + HO_2 + H_2O$	2	3.00×10^8		72
A152	$HMS^- + SO_4^- \rightarrow SO_4^{2-} + H^+ + HCHO + SO_3^-$	2	2.80×10^6		72
A153	$HMS^- + NO_3 \rightarrow NO_3^- + H^+ + HCHO + SO_3^-$	2	4.20×10^6		28
A154	$HMS^- + Cl_2^- \rightarrow 2\,Cl^- + H^+ + HCHO + SO_3^-$	2	5.00×10^5		36
A155	$HMS^- + Br_2^- \rightarrow 2\,Br^- + H^+ + HCHO + SO_3^-$	2	5.00×10^4		34
A156	$HSO_3^- + HSO_5^- + H^+ \rightarrow 2\,SO_4^{2-} + 3\,H^+$	3	7.10×10^6		73
A157	$HSO_3^- + SO_4^- \rightarrow SO_3^- + SO_4^{2-} + H^+$	2	6.80×10^8		67
A158	$SO_3^{2-} + SO_4^- \rightarrow SO_3^- + SO_4^{2-}$	2	3.10×10^8		67
A159	$HSO_3^- + SO_5^- \rightarrow SO_4^- + SO_4^{2-} + H^+$	2	3.60×10^2		67
A160	$SO_3^{2-} + SO_5^- \rightarrow SO_4^- + SO_4^{2-}$	2	5.50×10^5		67
A161	$HSO_3^- + SO_5^- \rightarrow SO_3^- + HSO_5^-$	2	8.60×10^3		67
A162	$SO_3^{2-} + SO_5^- \overset{H^+}{\rightarrow} SO_3^- + HSO_5^-$	2	2.10×10^5		67
A163	$SO_3^- + O_2 \rightarrow SO_5^-$	2	2.50×10^9		67
A164	$SO_4^- + O_2^- \rightarrow SO_4^{2-} + O_2$	2	4.00×10^9		67
A165	$SO_4^- + NO_3^- \rightarrow SO_4^{2-} + NO_3$	2	2.30×10^5		74
A166	$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl$	2	2.70×10^8		45
A167	$SO_4^- + Br^- \rightarrow SO_4^{2-} + Br$	2	3.50×10^9		75
A168	$SO_4^- + SO_4^- \rightarrow (S_2O_8^{2-})$	2	4.50×10^8		67
A169	$SO_5^- + O_2^- \overset{H^+}{\rightarrow} HSO_5^- + O_2$	2	2.34×10^8		67
A170	$SO_5^- + HO_2 \rightarrow HSO_5^- + O_2$	2	5.00×10^7		76
A171	$SO_5^- + SO_5^- \rightarrow SO_4^- + SO_4^- + O_2$	2	2.20×10^8		67
A172	$SO_5^- + SO_5^- \rightarrow O_2\ (+\,S_2O_8^{2-})$	2	4.80×10^7		67
A173	$BrO^- + SO_3^{2-} \rightarrow Br^- + SO_4^{2-}$	2	1.00×10^8		77
A174	$HOBr + SO_3^{2-} \rightarrow Br^- + SO_4^{2-} + H^+$	2	5.00×10^9		77
A175	$HOBr + HSO_3^- \rightarrow Br^- + SO_4^{2-} + 2\,H^+$	2	5.00×10^9		$= k_{A174}$
A176	$HOCl + SO_3^{2-} \rightarrow Cl^- + SO_4^{2-} + H^+$	2	7.60×10^8		78
A177	$CH_3OCl + SO_3^{2-} \overset{H_2O}{\rightarrow} Cl^- + SO_4^{2-} + CH_3OH + H^+$	2	7.60×10^8		$= k_{A176}$
A178	$HOCl + HSO_3^- \rightarrow Cl^- + SO_4^{2-} + 2\,H^+$	2	7.60×10^8		$= k_{A176}$
A179	$CH_3OCl + HSO_3^- \overset{H_2O}{\rightarrow} Cl^- + SO_4^{2-} + CH_3OH + 2\,H^+$	2	7.60×10^8		$= k_{A176}$
A180	$HO_2NO_2 + HSO_3^- \rightarrow SO_4^{2-} + NO_3^- + 2\,H^+$	2	3.30×10^5		79
A181	$Br^- + HSO_5^- \rightarrow HOBr + SO_4^{2-}$	2	1.04×10^0	-5338	80
A182	$Cl^- + HSO_5^- \rightarrow HOCl + SO_4^{2-}$	2	1.80×10^{-3}	-7352	80
A183	$Br^- + CH_3CO_3H \rightarrow HOBr + CH_3COO^-$	2	2.58×10^{-1}	-6897	80
A184	$Cl^- + CH_3CO_3H \rightarrow HOCl + CH_3COO^-$	2	4.47×10^{-4}	-8911	$= k_{A183} \times k_{A182}/k_{A181}$
A185	$Br^- + HO_2NO_2 \rightarrow HOBr + NO_3^-$	2	5.44×10^{-1}		81
A186	$Cl^- + HO_2NO_2 \rightarrow HOCl + NO_3^-$	2	1.40×10^{-3}	-7216	81
A187	$Br^- + O_3 \rightarrow BrO^- + O_2$	2	2.10×10^2	-4450	82
A188	$BrO^- + O_3 \rightarrow Br^- + 2\,O_2$	2	3.30×10^2		82
A189	$N_2O_5 + H_2O \rightarrow 2\,NO_3^- + 2\,H^+$	1	5.56×10^5		see note[c]
A190	$N_2O_5 + Cl^- \rightarrow ClNO_2 + NO_3^-$	2	5.00×10^6		see note[c]
A191	$N_2O_5 + Br^- \rightarrow BrNO_2 + NO_3^-$	2	3.00×10^9		see note[c]
A192	$ClONO_2 + H_2O \rightarrow HOCl + NO_3^- + H^+$	1	5.56×10^5		see note[c]
A193	$ClONO_2 + Cl^- \rightarrow Cl_2 + NO_3^-$	2	5.00×10^6		see note[c]
A194	$ClONO_2 + Br^- \rightarrow BrCl + NO_3^-$	2	3.00×10^9		see note[c]

(continued on the next page)

Table S7. (Continued.)

No.	Reaction (of Order n)	n	$k^{\ominus}$, $\mathrm{M^{1-n}\,s^{-1}}$	$-E_a/R$, K	Reference
A195	$BrONO_2 + H_2O \rightarrow HOBr + NO_3^- + H^+$	1	5.56×10^5		see note[c]
A196	$BrONO_2 + Cl^- \rightarrow BrCl + NO_3^-$	2	5.00×10^6		see note[c]
A197	$BrONO_2 + Br^- \rightarrow Br_2 + NO_3^-$	2	3.00×10^9		see note[c]
A198	$Hg + O_3 \rightarrow HgO + O_2$	2	4.70×10^7		83
A199	$HgO + H^+ \rightarrow Hg^{2+} + OH^-$	2	1.00×10^{10}		84
A200	$Hg + OH \rightarrow Hg^+ + OH^-$	2	2.40×10^9		85
A201	$Hg^+ + O_2 \rightarrow Hg^{2+} + O_2^-$	2	1.00×10^9		86
A202	$Hg^+ + OH \rightarrow Hg^{2+} + OH^-$	2	1.00×10^{10}		86
A203	$Hg + HOCl \rightarrow Hg^{2+} + Cl^- + OH^-$	2	2.09×10^6		87
A204	$Hg + ClO^- \rightarrow Hg^{2+} + Cl^- + 2\,OH^-$	2	1.99×10^6		87
A205	$Hg + HOBr \rightarrow Hg^{2+} + Br^- + OH^-$	2	2.79×10^{-1}		88
A206	$Hg + BrO^- \rightarrow Hg^{2+} + Br^- + 2\,OH^-$	2	2.73×10^{-1}		88
A207	$Hg + Br_2 \rightarrow Hg^{2+} + 2\,Br^-$	2	1.96×10^{-1}		88
A208	$Hg^{2+} + O_2^- \rightarrow Hg^+ + O_2$	2	5.00×10^3		89
A209	$Hg^{2+} + HO_2 \rightarrow Hg^+ + O_2 + H+$	2	5.00×10^3		$= k_{A208}$
A210	$Hg^+ + O_2^- \rightarrow Hg + O_2$	2	1.00×10^{10}		see note[d]
A211	$Hg^+ + HO_2 \rightarrow Hg + O_2 + H+$	2	1.00×10^{10}		see note[d]
A212	$Hg(O)Br + HO_2 \rightarrow Hg(OH)Br + O_2$	2	1.00×10^{10}		see note[e]
A213	$Hg(O)Br + O_2^- \rightarrow Hg(OH)Br + O_2 + OH^-$	2	1.00×10^{10}		see note[e]

References:
1. Sehested et al. (1983); 2. Sehested et al. (1984); 3. Buxton et al. (1988); 4. Sehested et al. (1968); 5. Christensen et al. (1982); 6. Christensen and Sehested (1988); 7. Kläning et al. (1984); 8. Sauer et al. (1984); 9. Park and Lee (1988); 10. Strehlow and Wagner (1982); 11. Grätzel et al. (1969); 12. Grätzel et al. (1970); 13. Løgager and Sehested (1993); 14. Régimbal and Mozurkewich (1997); 15. Rettich (1978); 16. Katsumura et al. (1991); 17. Lee and Rind (1986); 18. Buxton (1969); 19. Hasegawa and Neta (1978); 20. Huie and Neta (1986); 21. Daniels (1969); 22. Garland et al. (1980); 23. Warneck and Wurzinger (1988); 24. Jacob (1986); 25. Herrmann et al. (1994); 26. Exner et al. (1992); 27. Clifton and Huie (1989); 28. Herrmann and Zellner (1998); 29. Zellner et al. (1996); 30. Fel'dman et al. (1986); 31. Bothe and Schulte-Frohlinde (1980); 32. Buxton et al. (1990); 33. Exner et al. (1993); 34. Herrmann et al. (2000); 35. Schuchmann and von Sonntag (1988); 36. Jacobi (1996); 37. Chin and Wine (1994); 38. Resse (1997); 39. Exner et al. (1994); 40. Jacobi et al. (1999); 41. Resse et al. (1999); 42. Eriksen et al. (1985); 43. Draganic et al. (1991); 44. Jayson et al. (1973); 45. McElroy (1990); 46. Wagner et al. (1986); 47. Gilbert et al. (1977); 48. Lelieveld and Crutzen (1991); 49. Wang and Margerum (1994); 50. Kläning and Wolff (1985); 51. Neta and Huie (1986); 52. Mamou et al. (1977); 53. D'Angelantonio et al. (1988); 54. Matthew et al. (2003); 55. Wagner and Strehlow (1987); 56. Chameides and Stelson (1992); 57. Schwarz and Bielski (1986); 58. Edwards (1952); 59. Bard et al. (1985); 60. Kumar and Margerum (1987); 61. Liu and Margerum (2001); 62. Beckwith et al. (1996); 63. Frenzel et al. (1998); 64. Hoffmann (1986); 65. Martin and Damschen (1981); 66. Lind et al. (1987); 67. Buxton et al. (1996); 68. Weinstein-Lloyd and Schwartz (1991); 69. Shoute et al. (1991); 70. Herrmann et al. (1996); 71. Warneck (1998) and references therein; 72. Buxton (1994); 73. Betterton and Hoffmann (1988a); 74. Buxton et al. (1993); 75. Redpath and Willson (1975); 76. Yermakov et al. (1995); 77. Troy and Margerum (1991); 78. Fogelman et al. (1989); 79. Amels et al. (1996); 80. Fortnum et al. (1960); 81. Régimbal and Mozurkewich (2000); 82. Haag and Hoigné (1983); 83. Munthe and McElroy (1992); 84. Pleijel and Munthe (1995); 85. Gårdfeldt et al. (2001); 86. Nazhat and Asmus (1973); 87. Lin and Pehkonen (1998); 88. Wang and Pehkonen (2004); 89. Gårdfeldt and Jonsson (2003).

Note:

[a] Temperature dependence of rate constants is given by $k = k^{\ominus} \times \exp[-E_a/R \times (1/T - 1/T^{\ominus})]$, where E_a is activation energy, R is gas constant and $T^{\ominus}$ = 298.15 K.

[b] The rate constant depends on pH: $k^{\ominus} = 5.2 \times 10^6 \times [H^+]/([H^+] + 0.1M)$.

[c] Rate constants for these reactions are chosen arbitrarily so that relative reactivities of $N_2O_5(aq)$, $ClONO_2(aq)$, and $BrONO_2(aq)$ (taken up from the gas phase, see Table S4) towards H_2O, Cl^-, and Br^- become 3.3×10^{-6}, 1.7×10^{-3}, and 1, respectively, according to Sander et al. (1999).

[d] Assumed to be very fast.

[e] Analogically expanded from gas-phase reactions.

S2 Impacts of using alternative stability functions on the diagnosed profiles of vertical diffusivity in the ABL

For diagnosing the vertical profiles of vertical diffusivity, $K(z)$, in the statically stable atmospheric boundary layer (ABL) (see Sect. 2.7 in the main paper), we adopted surface-layer stability functions proposed by Cheng and Brutsaert (2005):

$$\Phi_{\mathrm{M}} = 1 + a\left(\frac{\zeta + \zeta^b(1+\zeta^b)^{\frac{1-b}{b}}}{\zeta + (1+\zeta^b)^{\frac{1}{b}}}\right) \tag{S1}$$

$$\Phi_{\mathrm{H}} = 1 + c\left(\frac{\zeta + \zeta^d(1+\zeta^d)^{\frac{1-d}{d}}}{\zeta + (1+\zeta^d)^{\frac{1}{d}}}\right) \tag{S2}$$

where $a = 0.7$, $b = 0.75$, $c = 5$ and $d = 0.35$ for the stated applicability range of $0 \leq \zeta \leq 5$. For diagnosing the turbulence properties at the lowest discretized layer of the ABL, we also used integral forms of the stability functions taken from Cheng and Brutsaert (2005):

$$\Psi_{\mathrm{M}}(\zeta) = \int_0^{\zeta} \frac{1-\Phi_{\mathrm{M}}(\xi)}{\xi}\,\mathrm{d}\xi = -a\,\ln\{\zeta + [1+\zeta^b]^{(1/b)}\} \tag{S3}$$

$$\Psi_{\mathrm{H}}(\zeta) = \int_0^{\zeta} \frac{1-\Phi_{\mathrm{H}}(\xi)}{\xi}\,\mathrm{d}\xi = -c\,\ln\{\zeta + [1+\zeta^d]^{(1/d)}\}. \tag{S4}$$

To examine how sensitive the diagnosed profiles of $K(z)$ are to the choice of the surface-layer stability functions, we tested two more sets of stability functions other than those proposed by Cheng and Brutsaert (2005). The first alternative set was adopted from Holtslag and de Bruin (1988):

$$\Phi_{\mathrm{H}}(=\Phi_{\mathrm{M}}) = 1 + a\zeta + b\zeta(1+c-d\zeta)\exp(-d\zeta) \tag{S5}$$

where $a = 0.7$, $b = 0.75$, $c = 5$ and $d = 0.35$ for the stated applicability range of $0 \leq \zeta \leq 10$, and the second alternative set was adopted from Grachev et al. (2007):

$$\Phi_{\mathrm{M}} = 1 + \frac{a_m\zeta(1+\zeta)^{1/3}}{1+b_m\zeta} \tag{S6}$$

$$\Phi_{\mathrm{H}} = 1 + \frac{a_h\zeta + b_h\zeta^2}{1+c_h\zeta+\zeta^2} \tag{S7}$$

where $a_m = 5$, $b_m = a_m/6.5$, $a_h = 5$, $b_h = 5$ and $c_h = 3$ for the stated applicability range of $\zeta \geq 0$ (i.e., the entire stability range from neutral to very stable conditions). One useful metric to show the characteristics of stability functions is the turbulent Prandtl number (Pr_*) defined by the ratio between turbulent viscos-

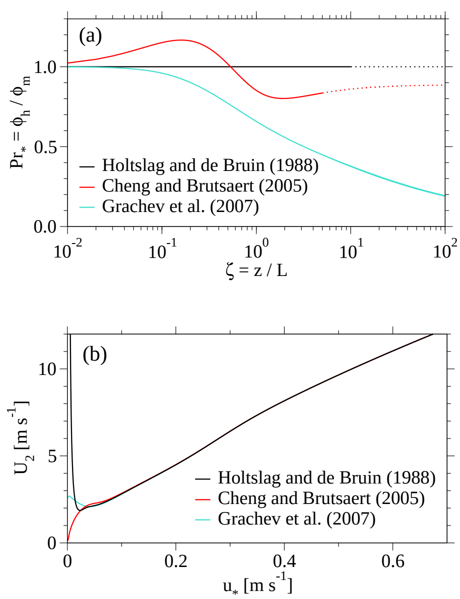

Fig. S1. **(a)** Turbulent Prandtl number (Pr_*) as a function of ζ as calculated by three different sets of stability functions; **(b)** The same as (a) but for wind speed diagnosed at a reference height of 2 m as a function of friction velocity (u_*) with the sensible heat flux specified at $-9\,\mathrm{W\,m^{-2}}$.

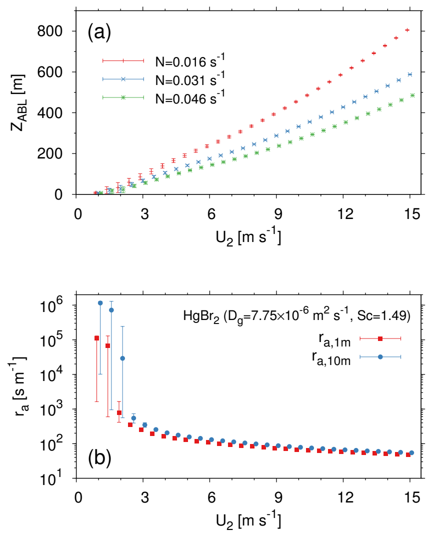

Fig. S2. The same as Fig. 2 in the main paper on the diagnosed properties of turbulence and vertical mass transfer in the ABL, but here by using stability functions from Holtslag and de Bruin (1988); **(a)** Changes in the diagnosed height of the turbulent ABL (Z_{ABL}) with surface wind speeds (U_2) between $1{\sim}15\,\mathrm{m\,s^{-1}}$ and Brunt–Väisälä frequencies in the free troposphere (N) between $0.016 \sim 0.046\,\mathrm{s^{-1}}$. Cross marks denote daily mean values while bars indicate the range of diurnal variations; **(b)** aerodynamic resistance for $HgBr_2$ from the snow surface to the height of either 1 m or 10 m in ambient air for $U_2 = 1{\sim}15\,\mathrm{m\,s^{-1}}$ at $N = 0.031\,\mathrm{s^{-1}}$. Filled squares and circles denote daily mean values while bars indicate the range of diurnal variations. Note, however, when using the stability functions other than from Cheng and Brutsaert (2005), our diagnostic equations for Z_{ABL} often become ill-posed for relatively large negative values of sensible heat flux (F_{SH}) at low wind speeds ($U_2 \lesssim 2\,\mathrm{m\,s^{-1}}$), in which case a solution for Z_{ABL} is intrinsically non-existent. Under such circumstances, the vertical diffusivity of trace gases is represented by molecular diffusivity ($D_{\mathrm{g,\,mol}}$) in the entire model domain of the atmosphere.

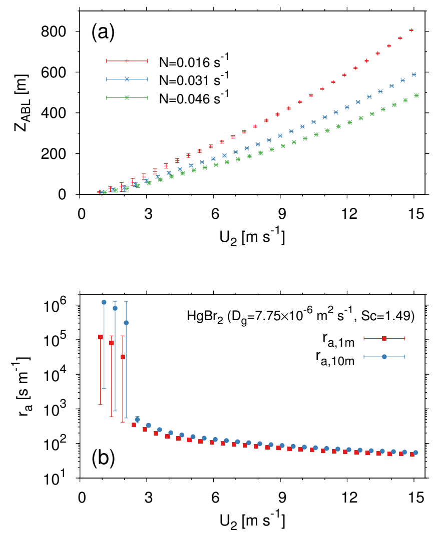

Fig. S3. The same as Fig. S2 but by using stability functions from Grachev et al. (2007).

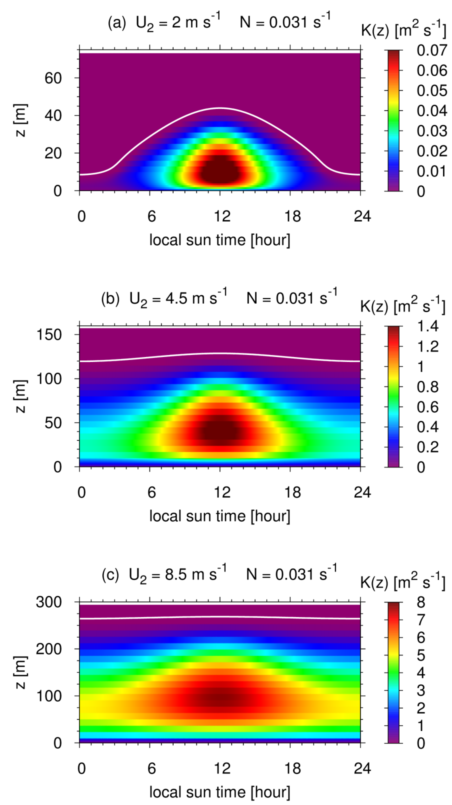

Fig. S4. The same as Fig. 3 in the main paper on vertical diffusivity diagnosed in the atmosphere, but here by using stability functions from Holtslag and de Bruin (1988); Profiles and their diurnal variations of vertical diffusivity in the atmosphere prescribed by assuming $N = 0.031\,\mathrm{s^{-1}}$ and $U_2 = 2\,\mathrm{m\,s^{-1}}$ **(a)**, $4.5\,\mathrm{m\,s^{-1}}$ **(b)** and $8.5\,\mathrm{m\,s^{-1}}$ **(c)**. The white line in each graph indicates the level of Z_{ABL}, above which the vertical diffusion is assumed to be controlled by molecular diffusion for gases or by Brownian diffusion for aerosols.

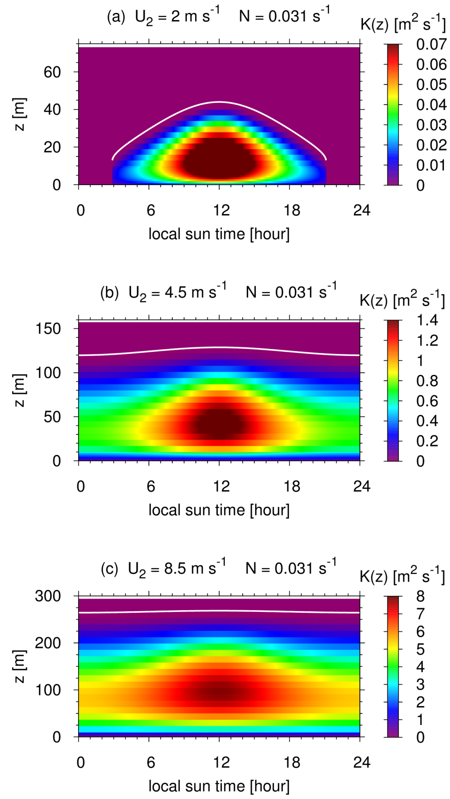

Fig. S5. The same as Fig. S2 but by using stability functions from Grachev et al. (2007). Note that a solution for Z_{ABL} becomes non-existent for relatively large negative values of F_{SH} at $U_2 = 2\,\mathrm{m\,s^{-1}}$, as indicated by an incomplete diurnal cycle obtained for Z_{ABL} (white line) **(a)**.

ity (k_{M}) and turbulent thermal diffusivity (k_{H}):

$$\mathrm{Pr}_* = \frac{k_{\mathrm{M}}}{k_{\mathrm{H}}} = \frac{\Phi_{\mathrm{H}}}{\Phi_{\mathrm{M}}} \tag{S8}$$

which is plotted as a function of ζ in Fig. S1a. Pr_* exceeds unity at small ζ if one employs stability functions from Cheng and Brutsaert (2005). This behavior is at odds with an assertion that Pr_* is most likely unity or smaller in the stable boundary layer (e.g., Brost and Wyngaard, 1978; Andreas, 2002). However, a major benefit of using the Cheng and Brutsaert (2005) functions, at least for our present practical purpose, is that numerical solutions for Eqs. (13)–(15) (see Sect. 2.7 in the main paper) exist for any U_{ref} values, whereas a consistent set of U_{ref} and z_0 do not exist at low U_{ref} ($\lesssim 2\,\mathrm{m\,s^{-1}}$) when using the stability functions taken from Holtslag and de Bruin (1988) and Grachev et al. (2007) (see Figs. S1b and S5a). Resultant profiles of $K(z)$ from the alternative formulas were found not to be different enough to significantly change general trends of model behavior discussed in this study (Figs. S2–S5).

S3 Mass conservation issue in our numerical integration method

Since the LSODES solver (used for the temporal integration of chemical source/sink terms) employs multi-step backward differ-

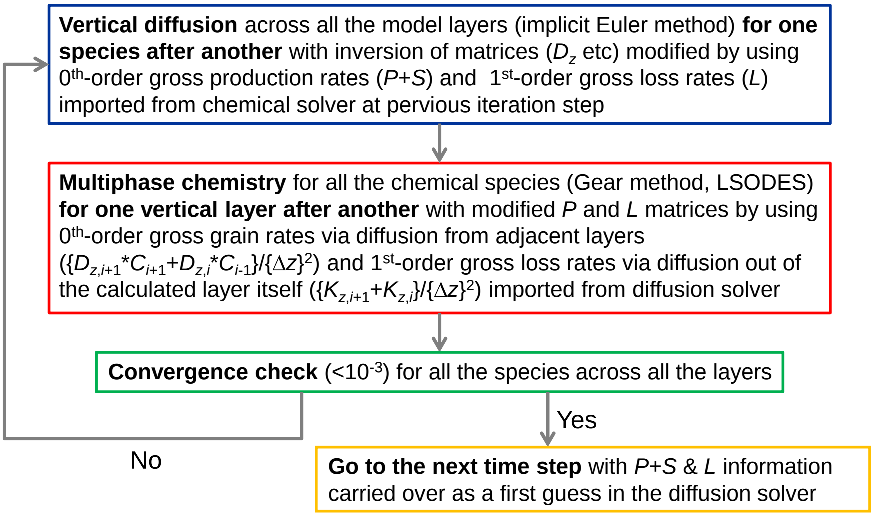

Fig. S6. Overview of a linearly coupled operator splitting with iteration between chemistry and diffusion solvers. C: tracer concentrations, P: chemical production rates, L: chemical loss rate constants, S: (parameterized) emission rates, and D_z: vertical diffusivity.

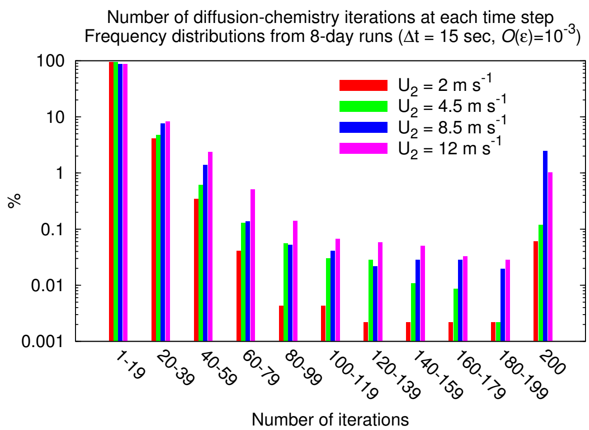

Fig. S7. Frequency distributions (over 8 model days) of iteration times spent by our numerical scheme with linearly coupled iteration between diffusion and chemistry solvers at each time step in model runs with $U_2 = 2\,\mathrm{m\,s^{-1}}$, $4.5\,\mathrm{m\,s^{-1}}$, $8.5\,\mathrm{m\,s^{-1}}$, and $12\,\mathrm{m\,s^{-1}}$. $N = 0.031\,\mathrm{s^{-1}}$ for all the model runs.

entiation formulas for representing the time differentiation of the mass continuity equations along with a capacity of automatic time-step control inside the solver (Hindmarsh, 1983), our method of iteration with a linear coupling between the chemistry solver and the diffusion solver (employing a single-step backward differentiation formula based on a fixed time-step) risks mass conservation in the system (see Fig. S6 for a diagram of the iteration procedure). One manifestation of this problem is that, on about 1 % of the time steps, iteration between the diffusion and chemistry solvers achieves the relative tolerance of 10^{-2} but never down to the level of 10^{-3}. Therefore, at each time step, the iteration is terminated if it is done 200 times even without achieving the desired relative tolerance of 10^{-3} (Fig. S7).

Basically, our model runs maintain non-zero vertical fluxes of gaseous and aerosol composition across the top lid of the model atmosphere by assuming molecular and Brownian diffusions for gases and aerosols, respectively, with fixed "free tropospheric" mixing ratios assumed above the top lid. By switching off these fluxes across the top lid, we tested the capability of our numerical scheme in terms of mass conservation in the system. Changes from the initial state in total bromine mass in the whole system of the atmosphere and the snowpack were found to be up to 2 % over 8 model days, whereas changes in total mercury mass approached 10 % in some model runs. Given that the present study aims at the mechanistic understanding of processes, this level of mass inconsistency is considered to be acceptable. However, this numerical aspect will need to be improved if physical and chemical processes governing the air–snowpack exchange of reactive species are to be incorporated in such a way as in our 1-D model to large-scale models for assessment purposes (e.g., impacts of atmospheric mercury deposition on the ecosystem), because mass conservation should be controlled more stringently in such models.

S4 Unsuccessful model run of potential relevance to snowpack bromine chemistry at Summit, Greenland

Thomas et al. (2011) developed a 1-D model of chemistry and transport between snowpack and overlying ambient air in a framework similar to our model, PHANTAS. The focus of the Thomas et al. study was to simulate to the release of gaseous bromine and nitrogen oxides to the air as a result of snowpack photochemistry atop the Greenland ice sheet in the summer. Their model run predicted predicted the mixing ratios of BrO up to $15\,\mathrm{pmol\,mol^{-1}}$ in the snowpack interstitial air (SIA) and up to $3\,\mathrm{pmol\,mol^{-1}}$ in the near-surface ambient air. Although the context of their study was somewhat different from ours (in which we simulate chemistry and transport leading to ODEs and AMDEs in the springtime Arctic boundary layer as a result of snowpack photochemistry on sea ice), it seemed to be useful to understand what may have resulted in more conservative activation of bromine chemistry in the model snow-

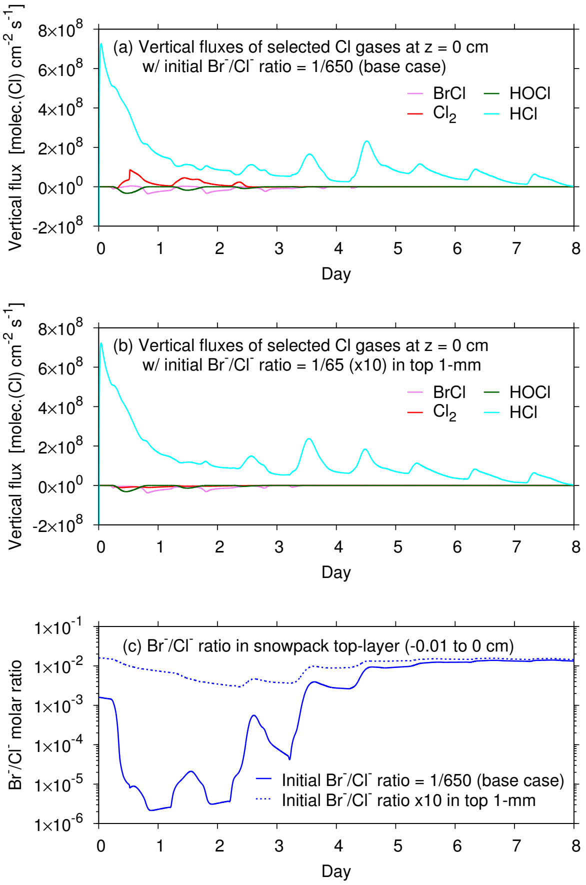

Fig. S8. Vertical air-snow fluxes (positive if the flux is from snow to air) of selected gaseous chlorine species, HCl, HOCl, BrCl and Cl_2, as simulated in two model runs both at $U_2 = 4.5\,m\,s^{-1}$ and $N = 0.031\,s^{-1}$, employing **(a)** our baseline scenario with initial Br^-/Cl^- molar ratio at 1/650 in the entire snowpack and **(b)** an adapted scenario in which initial Br^- concentration in the snowpack between 0 mm and 1 mm in depth (i.e., top two layers in the model snowpack) is raised by a factor of 10 from our baseline scenario. Also shown in **(c)** are the time series of simulated molar ratios between Br^- and Cl^- in the topmost layer of the snowpack (i.e., between 0 mm and 0.1 mm in depth) from each model run.

pack by Thomas et al. (2011) than ours. We therefore attempted a model run using the same initial condition in dissolved ion concentrations and the volume fraction of liquid-like layer (LLL) on snow grains as in Thomas et al. (2011). Unfortunately, our chemical solver crashed for numerical reasons that we could not control very well before proceeding sufficient time steps to gain anything informative.

One critical difference in simulated conditions between the two models is that ion concentrations in the LLL are generally more dilute in the Thomas et al. model than in ours. In part, this results from lower (initial) bulk concentrations for Cl^- and Br^- by factors of 127 and 11, respectively, used by Thomas et al. (2011) to represent the surface snow chemistry data from Summit. But, more importantly, these authors considered the LLL fraction (f_q) in the snowpack to be a turning parameter and chose $f_q = 3.3 \times 10^{-5}$, which is 3 times higher than the f_q value calculated here on the basis of a thermodynamic relation to dissolved ion concentrations (see Table 3 in the main paper). Given the uncertainty in factors controlling the physics and chemistry of the LLL (see Sect. 2.5 in the main paper), we do not claim which of the two modeling approaches is superior to another. This is certainly one of the critical areas that need to be studied further. As discussed by Piot and von Glasow (2008) in the simulations of halogen chemistry in the polar boundary layer, cloud droplets, owing to diluted halide concentrations, are much less conducive than sea-salt aerosols to producing reactive halogens. We therefore speculate that the difference in halide concentrations between our model and the Thomas et al. model can at least partly explain rather conservative in-snow bromine activation simulated by the latter model.

S5 Simulated air-snow fluxes and surface-air mixing ratios of reactive chlorine species

To supplement our discussion in Sect. 3.2 of the main paper, we present simulated time series in the air-snow fluxes of selected chlorine gases viz. HCl, HOCl, BrCl and Cl_2 (Fig. S8a–b), the mixing ratios of HOCl, BrCl and Cl_2 at the height of 1.5 m in the ambient air (Fig. S9a–b) and Br^-/Cl^- molar ratios in the topmost layer of the snowpack (Fig. S8c). These results were obtained from two model runs, one with our baseline scenario on the initial concentration of Br^- (i.e., Br^-/Cl^- molar ratio = 1/650) in the snowpack and the other with a 10-fold higher initial concentration of Br^- in the top 1-mm layer of the snowpack than our baseline scenario.

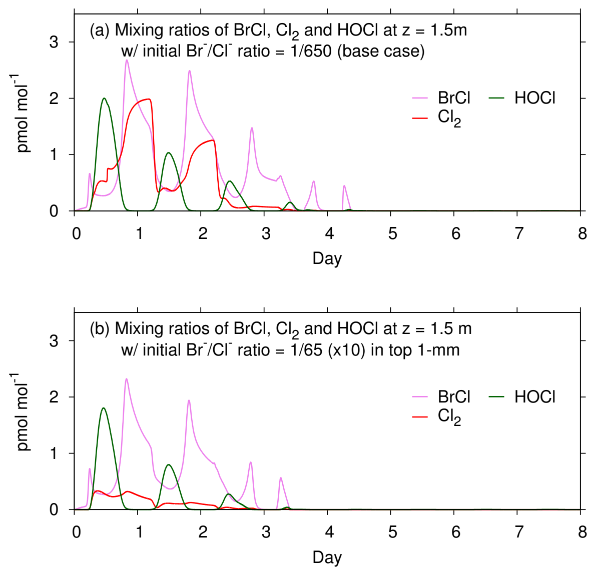

Fig. S9. Mixing ratios of HOCl, BrCl and Cl_2 in ambient air at the height of 1.5 m as simulated in two model runs both at $U_2 = 4.5\,m\,s^{-1}$ and $N = 0.031\,s^{-1}$, employing **(a)** our baseline scenario with initial Br^-/Cl^- molar ratio at 1/650 in the entire snowpack and **(b)** an adapted scenario in which initial Br^- concentration in the snowpack between 0 mm and 1 mm in depth (i.e., top two layers in the model snowpack) is raised by a factor of 10 from our baseline scenario.

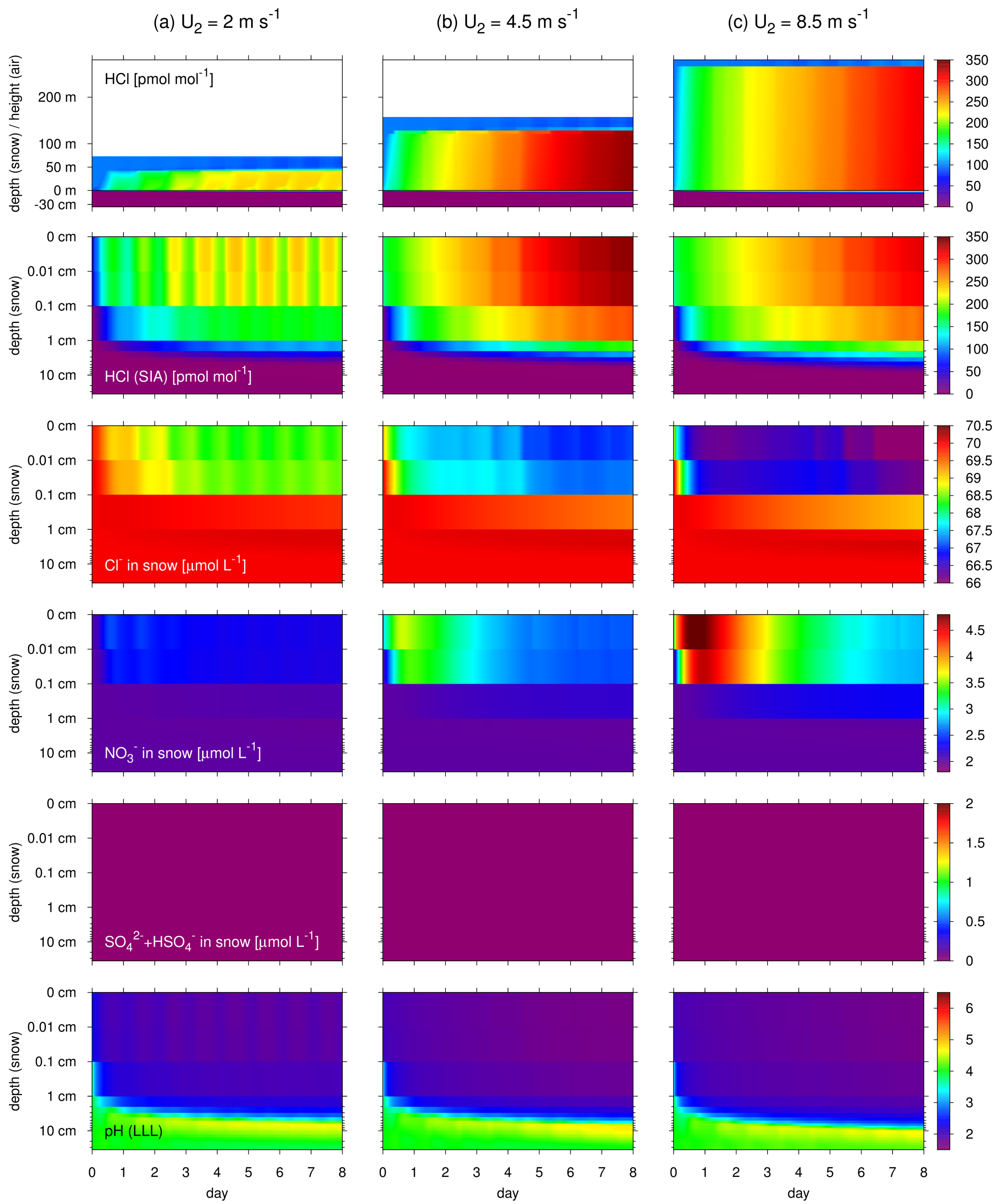

Fig. S10. Time-height cross sections for the mixing ratios of HCl (top row for the entire model domain from the bottom of the SIA and to the top of the atmosphere and second row for the SIA only), bulk concentrations of chloride (Cl^-, third row), nitrate (NO_3^-, fourth row) and sulfate ($SO_4^{2-}+HSO_4^-$, fifth row) in snowpack grains, and pH in the LLL on the surface of snowpack grains (bottom row) from sensitivity runs where SO_4^{2-} being produced in and/or entering the LLL of the snowpack is assumed to be lost irreversibly at the first-order rate of $10^3\,s^{-1}$ as an ad-hoc representation of the precipitation of mirabilite ($Na_2SO_4 \cdot 10\,H_2O$) from a brine with high sodium content: $U_2 = 2\,m\,s^{-1}$ **(a)**, $4.5\,m\,s^{-1}$ **(b)**, and $8.5\,m\,s^{-1}$ **(c)**. $N = 0.031\,s^{-1}$ for all the model runs.

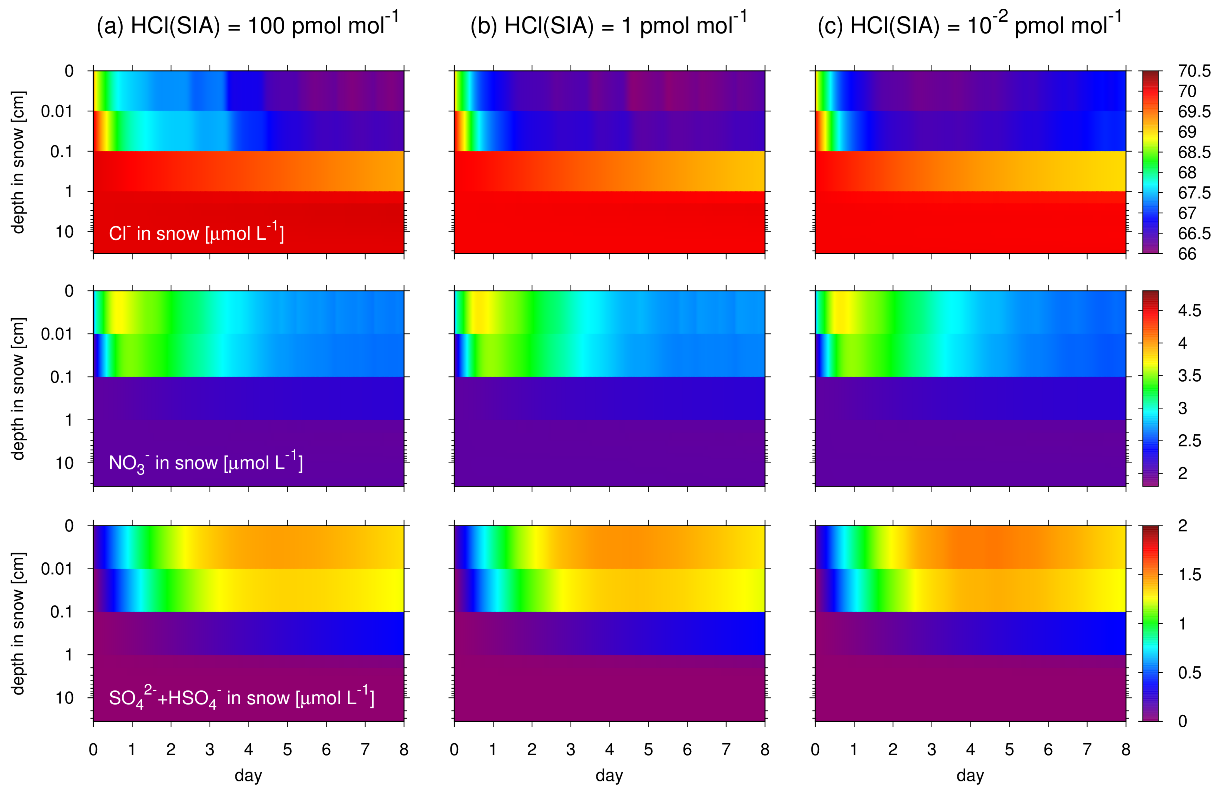

Fig. S11. The same as Fig. S10 but without plots for the mixing ratios of gas-phase HCl and the pH values in the LLL from model runs in which gas-phase HCl mixing ratio in the SIA is fixed deliberately at 100 pmol mol^{-1} **(a)**, 1 pmol mol^{-1} **(b)**, and 0.01 pmol mol^{-1} **(c)**, while in the ambient air it is fixed at 100 pmol mol^{-1} for all the cases. $U_2 = 4.5$ m s^{-1} and $N = 0.031$ s^{-1} for all the model runs.

S6 Sensitivity runs with a simple formulation of mirabilite ($Na_2SO_4 \cdot 10H_2O$) precipitation from LLL

As the temperature of brine is lowered, seawater composition dissolved in the brine can precipitate as various salts at different temperatures according to the eutectic of precipitating salts. At present, PHANTAS neglects this process, which is one of the main reasons for the restriction of our simulation scenarios to a single temperature value, viz. 253 K, about 3 K above the eutectic of hydrohalite ($NaCl \cdot 2H_2O$) (e.g., Weeks and Hibler III, 2010, see Chap. 6). However, mirabilite ($Na_2SO_4 \cdot 10H_2O$) is known to precipitate from the brine at ∼267 K. Hence we do not properly account for the fate of sulfate entering Na^+-containing brine on snow grains either via dry deposition of "haze" aerosols or via aqueous-phase production from gaseous SO_2 after its dry deposition from the atmosphere.

Fortunately, this does not appear to pose a major problem for our prediction of pH in the LLL, because the formation of mirabilite will simply leave behind H^+, which originates from HSO_4^- and H_2SO_4 in aerosols, in the LLL. Here we show results from sensitivity models runs where the effect of mirabilite precipitation from the LLL is represented in a very simple manner, viz. SO_4^{2-} being produced in and/or entering the LLL of the snowpack is assumed to be lost irreversibly at the arbitrarily-chosen, first-order rate of 10^3 s^{-1} (Fig. S10a–c). We find only minor difference in composition and pH in the LLL of the snowpack from our simulations discussed in the main paper (cf. Fig. 11 in the main paper).

S7 Sensitivity runs by using fixed mixing ratios of HCl

To supplement our discussion in Sect. 3.3 of the main paper, we present simulated time-depth cross sections for chloride, nitrate and sulfate concentrations in the snowpack (Fig. S11a–c) and simulated time-depth/height cross sections for the concentrations of ozone and bromine from the bottom of the snowpack to the top of the atmosphere in the model (Fig. S12a–c, for comparison with Fig. 4b in the main paper). These results were obtained from three model runs in which the mixing ratio of gaseous HCl was fixed at different levels (100 pmol mol^{-1}, 1 pmol mol^{-1} or 0.01 pmol mol^{-1}) in the SIA deliberately to control pH values in the snowpack LLL.

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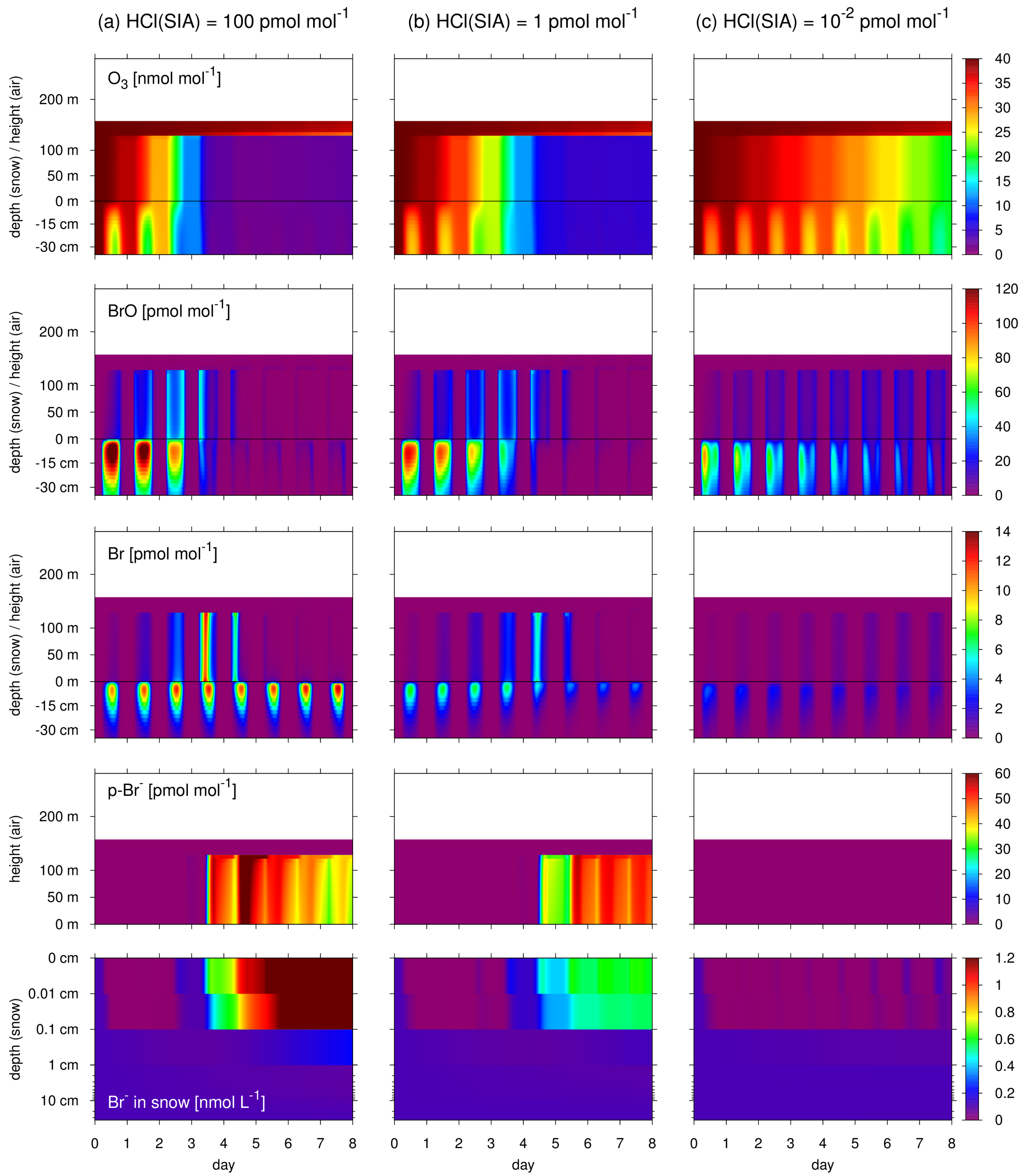

Fig. S12. Time-height cross sections for the mixing ratios of O_3 (top row), BrO (second row), Br-atom (third row), and aerosol bromide (p-Br^-, fourth row), and for the bulk concentrations of bromide in snowpack grains (bottom row) from the same model runs presented in Fig. S11, i.e. at $U_2 = 4.5\,\mathrm{m\,s^{-1}}$ and using the fixed mixing ratios of HCl in the SIA at 100 pmol mol^{-1} **(a)**, 1 pmol mol^{-1} **(b)** and 0.01 pmol mol^{-1} **(c)**, while in the ambient air at 100 pmol mol^{-1} for all the cases.

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