Supplement of

The number fraction of iron-containing particles affects OH, HO_2 and H_2O_2 budgets in the atmospheric aqueous phase

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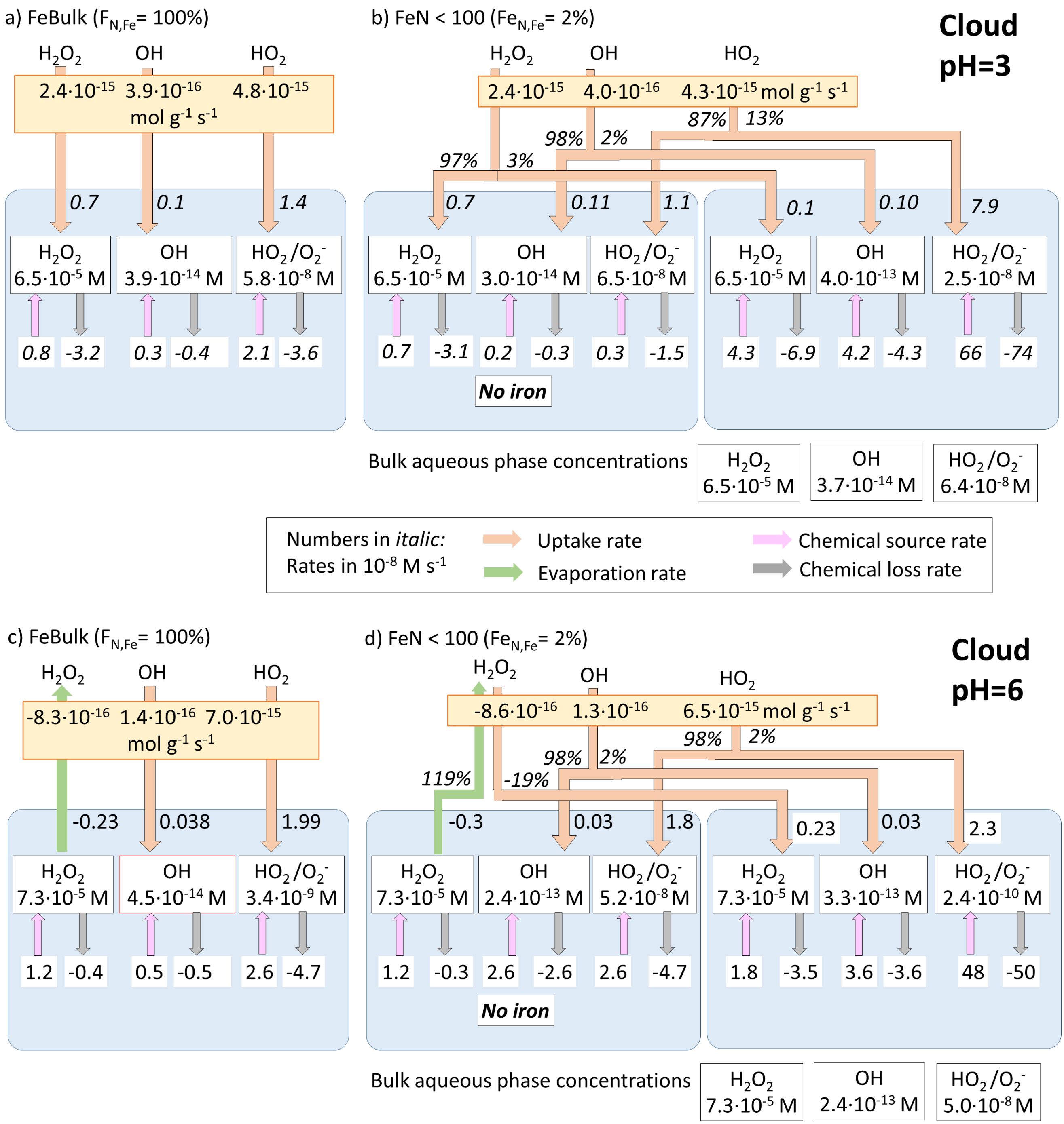

Figure S1. Same as Figure 2 (cloud case) but for a, b) pH = 3 and c, d) pH = 6 (lower part)

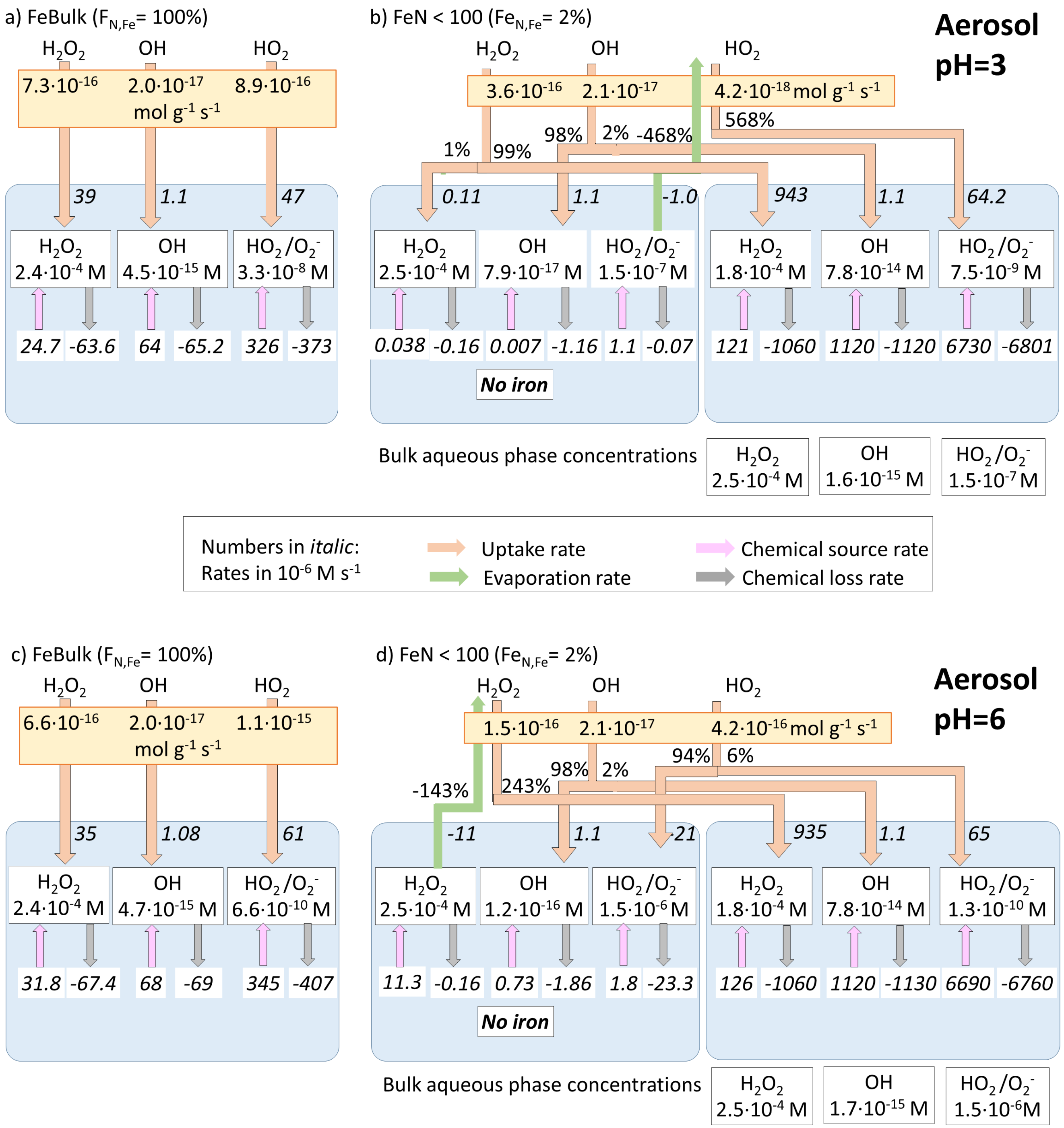

Figure S2. Same as Figure 3 (aerosol case) but for a, b) pH = 3 and c, d) pH = 6 (lower part)

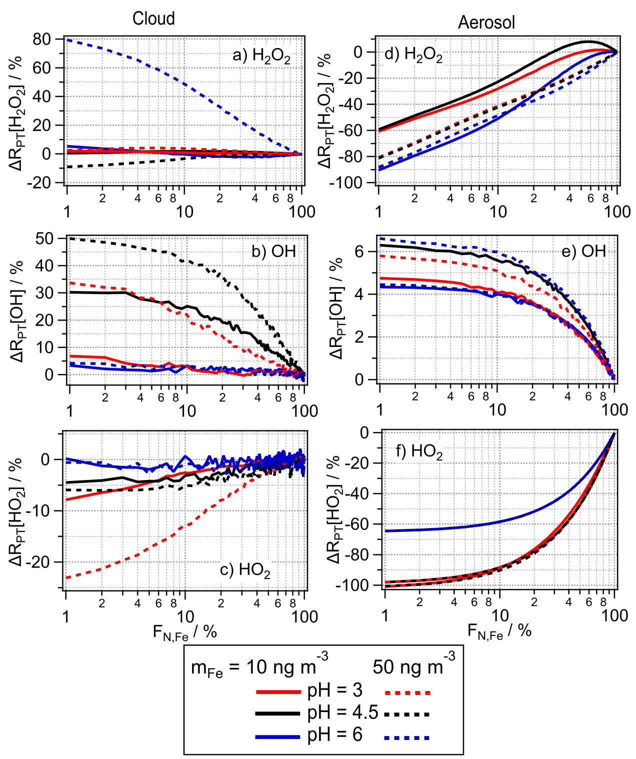

Figure S3. Relative difference [%] of net phase transfer rates ΔR_{PT} (Equation E.6) for (a-c) cloud and (d-f) aerosol case

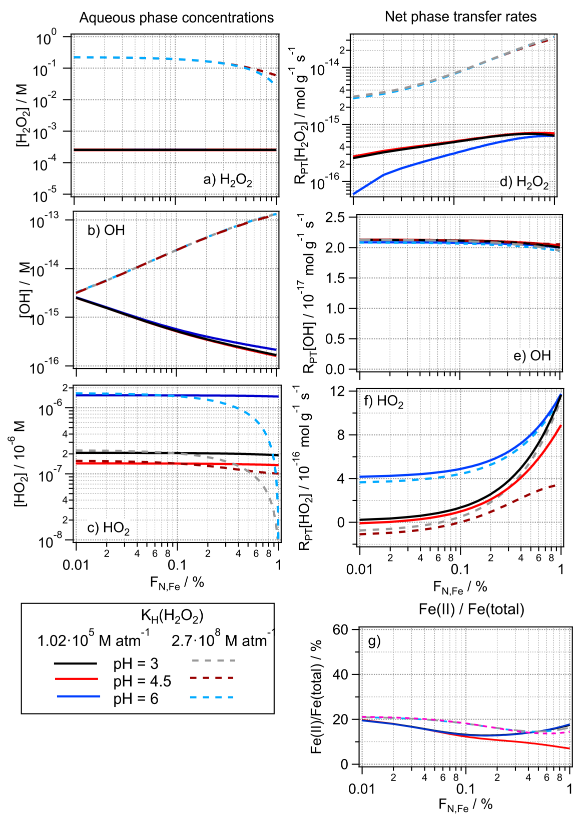

Figure S4. Comparison of aqueous phase concentrations and phase transfer rates for a) OH, b) HO_2, c) H_2O_2 using the physical Henry's law constant for H_2O_2 ($K_H = 1.02 \cdot 10^5$ M atm^{-1}) and the effective Henry's law constant ($K_{Heff} = 2.7 \cdot 10^8$ M atm^{-1}) as determined based on measurements of gas and particle H_2O_2 concentrations

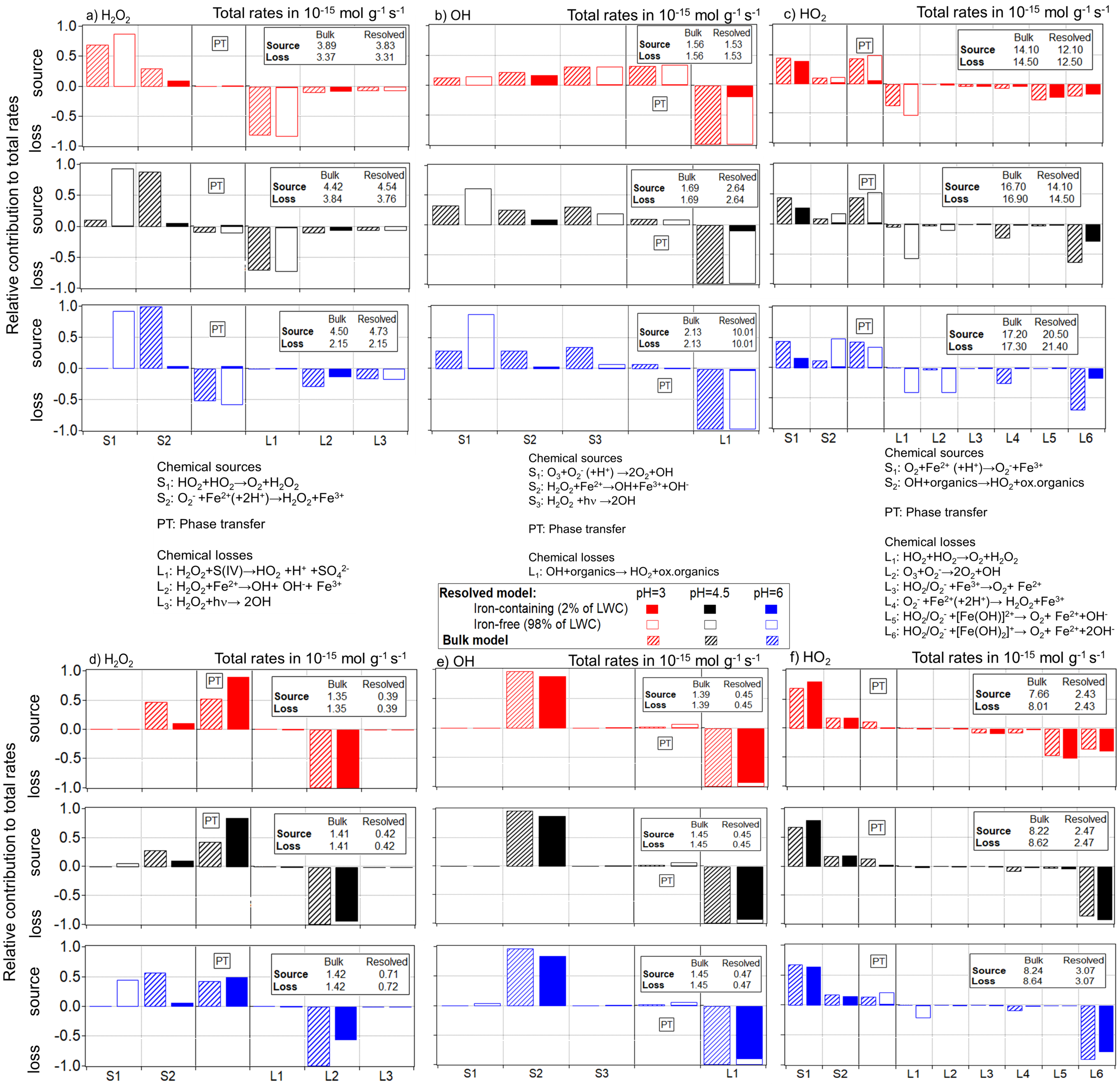

Figure S5. Relative contributions of chemical and phase transfer rates to the total sources and losses of the three ROS. The total rates [mol g_{air}^{-1} s^{-1}] are shown in boxes of each panel; for the FeN<100 approach, the contribution in iron-free and iron-containing droplets (particles) are displayed as open and dashed bars. Simulations were performed at constant pH values of pH = 3 (red), 4.5 (black). and 6 (blue) for cloud conditions: a) H_2O_2, b) OH, c) HO_2 and aerosol conditions: d) H_2O_2, e) OH, f) HO_2. The chemical source (S) and loss (L) reactions in the aqueous phase are listed between the panels. These results show the rates at t = 2000 s.

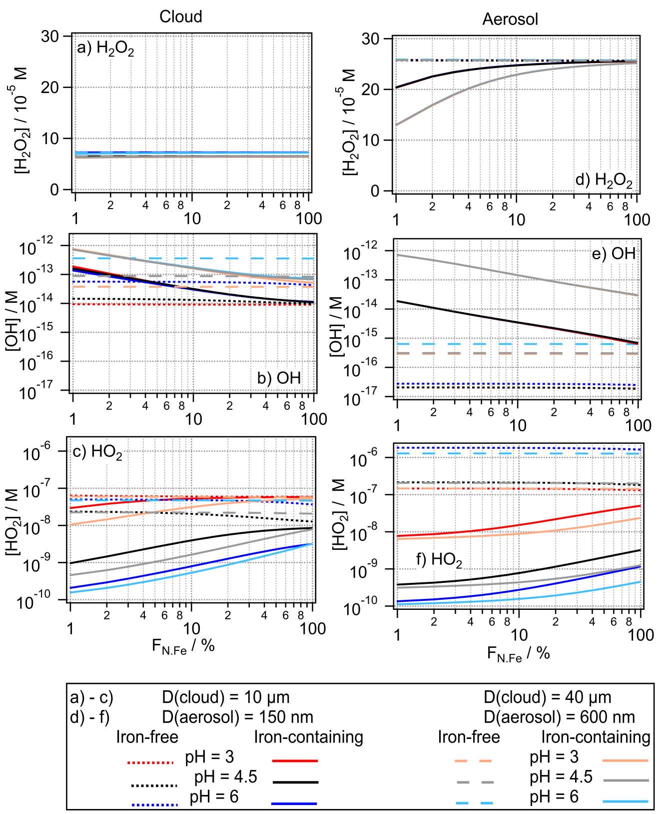

Figure S6. ROS aqueous phase concentrations for a-c) cloud case and d-f) aerosol case for droplet and particle diameters that differ by a factor of 0.5 and 2, respectively, from those of the base case.

Table S1. Irreversible aqueous reactions

	Reactants		Products	k [M^{-1} s^{-1}]	E_a/R [K]
R1	$SO_2 + O_3$	→	$S(VI) + O_2$	$2.4 \cdot 10^4$	
R2	$HSO_3^- + O_3$	→	$S(VI) + O_2$	$3.7 \cdot 10^5$	5530
R3	$SO_3^{2-} + O_3$	→	$S(VI) + O_2$	$1.5 \cdot 10^9$	5280
R4	$H_2O_2 + HSO_3^- + H^+$	→	$S(VI) + H_2O$	$7.2 \cdot 10^7$ M^{-2} s^{-1}	4000
R5	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	$8.3 \cdot 10^5$	2720
R6	$O_2^- + HO_2$	→	$H_2O_2 + O_2$	$9.7 \cdot 10^7$	1060
R7	$OH + CH_2O$	→	$HO_2 + HCOOH$	$1 \cdot 10^9$	1000
R8	$OH + CH_3OOH$	→	$CH_3O_2 + H_2O$	$2.4 \cdot 10^7$	1680
R9	$OH + CH_3OOH$	→	$HO_2 + HCOOH$	$6 \cdot 10^6$	1680
R10	$O_3 + O_2^-$ (+ H^+)	→	$OH + 2\ O_2$	$1.5 \cdot 10^9$	2200
R11	$OH + CHOCHO$	→	$HO_2 + CHOCOOH$	$1.1 \cdot 10^9$	1516
R12	$OH + CHOCOOH$	→	$HO_2 + H_2C_2O_4$	$3.6 \cdot 10^8$	1000
R13	$OH + CHOCOO^-$	→	$H_2C_2O_4$-	$2.9 \cdot 10^9$	4300
R14	$OH + C_2O_4^{2-}$	→	$O_2^- + 2\ CO_2 + OH^-$	$1.6 \cdot 10^8$	4300
R15	$OH + HC_2O_4^-$	→	$HO_2 + 2\ CO_2 + OH^-$	$1.9 \cdot 10^8$	2800
R16	$OH + H_2C_2O_4$	→	$HO_2 + 2\ CO_2 + H_2O$	$1.4 \cdot 10^6$	
R17	$OH + CH_3C(O)COOH$	→	$HO_2 + CO_2 + CH_3COO^-$	$7 \cdot 10^8$	
R18	$OH + CH_3COCOOH$	→	$HO_2 + H_2O + CH_3COOH$	$1.2 \cdot 10^8$	
R19	$OH + CHOCHO$	→	$HO_2 + CHOCOOH$	$1.1 \cdot 10^9$	1516
R20	$OH + HCOO^-$	→	$HO_2 + CO_2 + H_2O$	$3.2 \cdot 10^9$	1000
R21	$OH + HCOOH$	→	$HO_2 + CO_2 + H_2O$	$1.3 \cdot 10^8$	1000
R22	$CH_3O_2 + CH_3O_2$	→	$CH_2O + CH_3OH + HO_2$	$1.7 \cdot 10^8$	2200
R23	$H_2O_2 + OH$	→	$HO_2 + H_2O$	$3 \cdot 10^7$	1680
R24	OH + WSOC	→	WSOC + HO_2	$3.8 \cdot 10^8$	
R25	$Fe^{2+} + H_2O_2$	→	Fe^{3+} +OH+OH^-	55	
R26	$Fe^{3+} + HO_2$	→	$Fe^{2+} + O_2 + H^+$	$1.3 \cdot 10^5$	
R27	$Fe^{3+} + O_2^-$	→	$Fe^{2+} + O_2$	$1.5 \cdot 10^8$	
R28	$Fe^{3+} + H_2O_2$	→	$Fe^{2+} + HO_2 + H^+$	0.002	
R29	$Fe^{2+} + H_2O_2$	→	$Fe^{4+} + H_2O$	0.06	
R30	$Fe^{2+} + O_2$	→	$O_2^- + Fe^{3+}$	200	
R31	$Fe^{2+} + O_2^-$ (+2H^+)	→	$Fe^{3+} + H_2O_2$	$1 \cdot 10^7$	
R32	$Fe^{3+} + C_2O_4^{2-}$	→	$[Fe(C_2O_4)]^+$	$2.9 \cdot 10^9$	
R33	$[Fe(C_2O_4)^+] + C_2O_4^{2-}$	→	$[Fe(C_2O_4)]^{2-}$	$1.89 \cdot 10^4$	
R34	$[Fe(C_2O_4)^{2-}] + C_2O_4^{2-}$	→	$[Fe(C_2O_4)_2]^{3-}$	114	
R35	$[Fe(OH)]^{2+} + O_2^-$	→	$O_2 + Fe^{2+} + OH^-$	$1.5 \cdot 10^8$	
R36	[Fe(OH)]2++ HO_2	→	$O_2 + Fe^{2+} + H_2O$	$1.3 \cdot 10^5$	
R37	$[Fe(OH)_2]$+ + O_2^-	→	$O_2 + Fe^{2+} + 2\ OH^-$	$1.5 \cdot 10^8$	
R38	$[Fe(OH)_2]$+ + HO_2	→	$O_2^- + Fe^{2+} + H_2O$	$1.3 \cdot 10^5$	
R39	$Fe^{3+} + H_2O$	→	$[Fe(OH)]^{2+} + H^+$	$4.7 \cdot 10^4$	
R40	$[Fe(OH)]^{2+} + H_2O$	→	$[Fe(OH)_2]^+ + H^+$	$1.1 \cdot 10^3$	
R41	$[Fe(OH)]^{2+} + H^+$	→	Fe^{3+} + +H_2O	$4.3 \cdot 10^8$	
R42	$[Fe(OH)_2]^+ + H^+$	→	$[Fe(OH)]^{2+}$ +H_2O	$8 \cdot 10^7$	
R43	Fe^{2+} + OH	→	$[Fe(OH)]^{2+}$	$4.3 \cdot 10^8$	

Table S2. Aqueous phase equilibria

				K_a [M]
E1	H_2O	$\rightleftharpoons$	$OH^- + H^+$	$1.0 \cdot 10^{-14}$
E2	HO_2	$\rightleftharpoons$	$O_2^- + H^+$	$1.60 \cdot 10^{-5}$
E3	CHOCOOH	$\rightleftharpoons$	$CHOCOO^- + H^+$	$6.60 \cdot 10^{-4}$
E4	HCOOH	$\rightleftharpoons$	$HCOO^- + H^+$	$1.77 \cdot 10^{-4}$
E5	$H_2C_2O_4$	$\rightleftharpoons$	$HC_2O_4^- + H^+$	$6.40 \cdot 10^{-2}$
E6	$HC_2O_4^-$	$\rightleftharpoons$	$C_2O_4^{2-} + H^+$	$5.25 \cdot 10^{-5}$
E7	HNO_3	$\rightleftharpoons$	$NO_3^- + H^+$	22
E8	$SO_2 + H_2O$	$\rightleftharpoons$	$HSO_3^- + H^+$	0.013
E9	HSO_3^-	$\rightleftharpoons$	$SO_3^{2-} + H^+$	$6.60 \cdot 10^{-8}$
E10	H_2SO_4	$\rightleftharpoons$	$HSO_4^- + H^+$	1000
E11	HSO_4^-	$\rightleftharpoons$	$SO_4^{2-} + H^+$	0.102
E12	NH_3	$\rightleftharpoons$	$NH_4^+ + OH^-$	$1.76 \cdot 10^{-5}$

Table S3. Photolyses in the aqueous phase

	Reaction			J [s^{-1}]
P1	$[Fe(OH)^{2+}] + h\nu$	$\rightarrow$	$Fe^{2+} + OH$	$1.83 \cdot 10^{-4}$
P2	$[Fe(OH)_2]^+ + h\nu$	$\rightarrow$	$Fe^{2+} + OH + OH^-$	$1.83 \cdot 10^{-4}$
P3	$[Fe(C_2O_4)_2]^- + h\nu$	$\rightarrow$	$Fe^{2+} + C_2O_4^{2-} + C_2O_4^-$	$9.19 \cdot 10^{-4}$
P4	$[Fe(C_2O_4)_3]^{3-} + h\nu$	$\rightarrow$	$Fe^{2+} + 2\ C_2O_4^{2-} + C_2O_4^-$	$9.19 \cdot 10^{-4}$
P5	$H_2O_2 + h\nu$	$\rightarrow$	2 OH	$8.13 \cdot 10^{-6}$

Table S4. Phase transfer parameters, used in Eq-1 and Eq-2, molecular weight M_g [mol g^{-1}, mass accommodation coefficient α (dimensionless), gas phase diffusion coefficient D_g [cm s^{-1}] and Henry's law constant K_H [M atm^{-1}]

Species	M_g	α	D_g	K_H
O_3	48	0.05	0.148	$1.14 \cdot 10^{-2}$
H_2O_2	34	0.1	0.118	$1.02 \cdot 10^{5}$
OH	17	0.05	0.153	25
HO_2	33	0.01	0.104	$9 \cdot 10^{3}$
HCHO	30	0.02	0.164	$4.99 \cdot 10^{3}$
CH_3O_2	47	0.0038	0.135	310
CH_3OOH	48	0.0038	0.135	310
HNO_3	63	0.054	0.132	$2.1 \cdot 10^{5}$
N_2O_5	108	0.0037	0.110	1.4
SO_2	64	0.035	0.128	1.23
HCOOH	46	0.012	0.153	$1.77 \cdot 10^{-4}$
$(CHO)_2$	58	0.023	0.115	$4.19 \cdot 10^{5}$
CH_3COCHO	72	0.1	0.115	$3.2 \cdot 10^{4}$
NH_3	17	0.1	0.1	60.7

Table S5. Initial gas phase mixing ratios [ppb]; all other species are not initialized

Species	Mixing ratio
O_3	30
H_2O_2	1
HCHO	1
HNO_3	1
SO_2	0.5
NH_3	1
NO	2
CO	150
C_5H_8	2
C_7H_8	2
C_2H_4	0.5