COMPARISON OF DIFFERENT MODEL APPROACHES FOR THE SIMULATION OF MULTIPHASE PROCESSES.

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ELECTRONIC SUPPLEMENTARY MATERIAL (ESM)

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Electronic Supplementary Material

A.1 Initial gas phase concentration.

Species	Concentration [molec/cm^3]	Species	Concentration [molec/cm^3]
SO_2	1.81e+10	$HC5$	2.45e+10
CO	7.34e+12	$HC8$	2.45e+09
NO	1.89e+10	ETE	2.47e+10
NO_2	2.16e+11	OLT	2.45e+09
O_3	4.13e+11	TOL	6.92e+10
$HONO$	2.86e+09	CSL	2.45e+07
HNO_3	2.75e+09	XYL	5.87e+10
$ORA1$	4.40e+09	PAN	1.22e+10
$ORA2$	6.29e+09	$OP1$	2.45e+10
GLY	6.36e+08	$OP2$	2.45e+09
$MGLY$	8.81e+08	PAA	2.45e+07
ALD	3.41e+10	NH_3	2.45e+10
$MACR$	1.88e+09	HCL	4.89e+09
KET	2.06e+10	CH_3OH	1.22e+11
$HKET$	5.87e+08	$ETOH$	2.45e+10
H_2O_2	2.45e+08	API	9.78e+08
$HCH0$	2.86e+10	$LIMN$	4.89e+08
H_2	1.22e+13	ISO	1.30e+10
CH_4	4.16e+13	$[H_2O]$	4.89e+17
CO_2	8.73e+15	$[O2]$	4.89e+18
ETH	3.40e+10	$[N2]$	1.91e+19
$HC3$	4.89e+10		

The photolysis rates are determined for the corresponding mechanism from the start time at 45^0 N for summer solstice with a damping factor of 0.5. Simulations start at 9:00 AM (UTC).

A.2 Parameters of the initial aerosol distribution

Modes	Number [mg^{-1}]	Radius [nm]	Geom σ
First mode	2971.5	34	1.86
Second mode	161.1	167.5	1.39

A.3 Initial aerosol concentration

Species	Molar mass [g/mol]	First mode [g/g]	Second mode [g/g]
SO_4^{2-}	96.00	5.99522e-2	1.62205e-1
NO_3^-	62.00	9.70520e-3	4.33233e-1
NO_2^-	46.00	6.44347e-3	5.65258e-3
Cl^-	35.50	0.00000e+0	7.54111e-3
NH_4^+	18.00	3.32982e-2	8.91392e-2
Mn^{3+}	55.00	5.31060e-5	4.65870e-5
Fe^{3+}	56.00	2.64820e-4	2.32315e-4
Cu^{2+}	63.50	2.11714e-4	1.85728e-4
Na^+	23.00	0.00000e+0	5.24309e-4
K^+	39.00	3.93256e-3	4.01641e-3
Ca^{2+}	40.00	6.29720e-4	3.33050e-4
Zn^{2+}	65.00	5.82745e-4	5.11217e-4
$C_2O_4^{2-}$	88.00	3.07109e-3	3.40404e-3
$WSOC^-$	121.50	1.41869e-3	7.38041e-3
$aWSOC$	100.00	1.27109e-1	6.80049e-2
$sWISOC$	250.00	8.01933e-2	4.80122e-2
sEC	12.00	1.02812e-1	4.72648e-2
$sUNSOL$	61.00	5.70322e-1	1.22313e-1

$WSOC^-$ is the representing element for the ionic water soluble organic compounds. $aWSOC$ and $sWISOC$ stand for non-ionic water soluble organic compounds and non-soluble organic compounds, respectively. sEC is the non-soluble black carbon and $sUNSOL$ represents the rest measured non-soluble elements.

A.4 RISING and WAVE scenarios schematic description

RISING

Vertical velocity: $0.5 \, \text{m s}^{-1}$

Start altitude: 600 m

Cloud base: +98 m

Cloud top: +1200 m

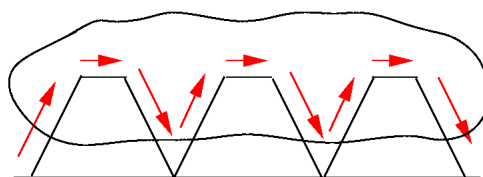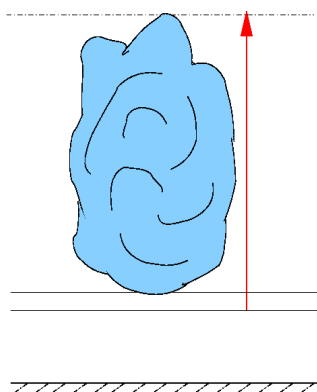**Meteorological initial values**:

Absolute temperature: 285.2 K

Relative humidity: 95 %

Pressure: 950 hPa

Temperature (cloud base): 284.2 K

Pressure (cloud base): 939 hPa

Air density (cloud base): $1.15 \, \text{kg m}^{-3}$

WAVE

3 cycles (traveling time = 1 h)

Upwards traveling time: 500 s

Mountain residence time: 200 s

Downwards traveling time: 500 s

Altitude (valley): 600 m

Altitude (mountain): 1000 m

Meteorological initial values :

Absolute temperature: 280 K

Relative humidity: 95 %

Air density: $1.15 \, \text{kg m}^{-3}$

Pressure (valley): 950 hPa

Pressure (mountain): 910 hPa

B.1 INORG mechanism

The gas phase reacting system is RACM (Stockwell et al., 1997).

Aqueous Phase Reactions

Number	Reaction	k_{298}	$-\frac{E_A}{R}$
A(1)	$HSO_3^- + H_2O_2 + H^+ \rightarrow SO_4^{2-} + 2H^+ + H_2O$	6.9×10^7	-4000.
A(2)	$SO_2 + O_3 \rightarrow HSO_4^- + H^+ + O_2 - H_2O$	2.4×10^4	0.
A(3)	$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2$	3.7×10^5	0.
A(4)	$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$	1.5×10^9	-5280.

Reaction rates are of the form $k = k_{298} exp[-\frac{E_A}{R}(\frac{1}{T} - \frac{1}{298})]$.

Henry's law equilibria

Number	Reaction	k_{298}	$-\frac{\Delta H}{R}$
E(1)	$O_3(g) \rightleftharpoons O_3(aq)$	1.1×10^{-2}	2300.
E(2)	$H_2O_2(g) \rightleftharpoons H_2O_2(aq)$	1.0×10^5	2300.
E(3)	$NH_3(g) \rightleftharpoons NH_3(aq)$	60.7	3920.
E(4)	$HCL(g) \rightleftharpoons HCL(aq)$	1.1	2020.
E(5)	$HNO_3(g) \rightleftharpoons HNO_3(aq)$	2.1×10^5	8700.
E(6)	$CO_2(g) \rightleftharpoons CO_2(aq)$	3.1×10^{-2}	2423.
E(7)	$SO_2(g) \rightleftharpoons SO_2(aq)$	1.24	3300.
E(8)	$H_2SO_4(g) \rightleftharpoons H_2SO_4(aq)$	1.1×10^{-2}	2300.

Reaction rates are of the form $k = k_{298} exp[-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{298})]$.

Dissociation equilibria

Number	Reaction	A	B	C
E(9)	$H_2SO_4(aq) \rightleftharpoons HSO_4^- + H^+$	1000.	0.	$5. \times 10^{10}$.
E(10)	$NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH_-$	$3.17 \times 10_{-7}$	-560.	3.47×10^{10}
E(11)	$HCL(aq) \rightleftharpoons Cl^- + H^+$	1.72×10^6	6890.	2.9×10^5
E(12)	$HNO_3(aq) \rightleftharpoons NO_3 + H^+$	22.	1800.	5.0×10^{10}
E(13)	$CO_2(aq) \rightleftharpoons HCO_3 + H^+$	4.3×10^{-7}	-913.	5.6×10^4
E(14)	$HCO_3^-(aq) + \rightleftharpoons CO_3^{2-} + H^+$	$4.7 \times 10_{-11}$	-1820.	$5. \times 10^{10}$
E(15)	$SO_2(aq) + H_2O \rightleftharpoons HSO_3^- + H^+$	$3.15 \times 10_{-4}$	1940.	$2. \times 10^8$
E(16)	$HSO_3^-(aq) + \rightleftharpoons SO_3^{2-} + H^+$	$6.22 \times 10_{-8}$	1960.	$5. \times 10^{10}$
E(16)	$HSO_4^-(aq) + \rightleftharpoons SO_4^{2-} + H^+$	$1.02 \times 10_{-2}$	-2700.	$1. \times 10^{11}$

Equilibrium reaction rates are of the form $k_e = \frac{k_+}{k_-} = A\, exp[-\frac{B}{T}]$ and the backward reaction rate $k_- = C$.

B.2 BARTH mechanism

In the sulfur free mechanism (Barth et al., 2003), called BARTH here, the gas phase reacting system was replaced by RACM (Stockwell et al., 1997).

Aqueous Phase Reactions (Photolysis)

Number	Reaction	A	B	C
A(1)	$O_3 + h\nu + \rightarrow H_2O2 + O_2$	3.83×10^{-5}	4.11188	7.7335×10^{-1}
A(2)	$H_2O_2 + h\nu \rightarrow 2OH$	11.47×10^{-6}	2.35766	7.6470×10^{-1}

Units for the photolysis frequencies are s^{-1}. Reaction rates are of the form $k = A\ exp(y)$, where $y = B\ [1 - \frac{1}{\cos z}]$ and $z = e\ C$. The parameter e represents the zenith angle in [Rad].

Aqueous Phase Reactions

Number	Reaction	k_{298}	$-\frac{E_A}{R}$
A(3)	$CH_2(OH)_2 + OH + O_2 \rightarrow HCOOH + HO_2 + H_2O$	2.0×10^9	-1500.
A(4)	$HCOOH + OH + O_2 \rightarrow CO_2 + HO_2 + H_2O$	1.6×10^8	-1500.
A(5)	$HCOO^- + OH + O_2 \rightarrow CO_2 + HO_2 + OH^-$	2.5×10^9	-1500.
A(6)	$CH_3OO + O_2^- + H_2O \rightarrow CH_3OOH + OH^- + O_2$	5.0×10^7	-1600.
A(7)	$CH_3OOH + OH \rightarrow CH_3OO + H_2O$	2.7×10^7	-1700.
A(8)	$CH_3OOH + OH \rightarrow CH_2(OH)_2 + OH$	1.9×10^7	-1900.
A(9)	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$	1.0×10^8	-1500.
A(10)	$HO_2^- + H^+ \rightarrow HO_2O_2$	5.0×10^{10}	-1500.
A(11)	$OH + OH \rightarrow H_2O_2$	5.2×10^9	-1500.
A(12)	$O_3 + O_2^- + H_2O \rightarrow OH + 2O_2 + OH^-$	1.5×10^9	-1500
A(13)	$O_3 + OH \rightarrow HO_2 + O_2$	3.0×10^9	-1500
A(14)	$H_2O_2 + OH \rightarrow HO_2 + H_2O$	2.7×10^7	-1700
A(15)	$OH + O_2^- \rightarrow OH^- + O_2$	1.0×10^{10}	-1500.
A(16)	$HCO_3^- + OH \rightarrow CO_3^- + H_2O$	1.0×10^7	-1500.
A(17)	$HCO_3^- + O_2^- \rightarrow CO_3^- + HO_2^-$	1.5×10^6	-1500.
A(18)	$CO_3^- + H_2O_2 \rightarrow HCO_3^- + HO_2$	8.0×10^5	-2800.
A(19)	$CO_3^- + O_2^- \rightarrow HCO_3^- + O_2 + OH^-$	4.0×10^8	-1500.
A(20)	$HO_2 + Cl_2^- \rightarrow 2Cl^- + O_2 + H^+$	4.5×10^9	-1500.
A(21)	$O_2^- + Cl_2^- \rightarrow 2Cl^- + O_2$	1.0×10^9	-1500.
A(22)	$H_2O_2 + Cl_2^- \rightarrow 2Cl^- + HO_2 + H^+$	1.4×10^5	-3400.
A(23)	$H_2O_2 + Cl \rightarrow Cl^- + HO_2 + H^+$	4.5×10^7	0.
A(24)	$NO_3 + Cl^- \rightarrow NO_3^- + Cl$	1.0×10^8	-1500.
A(25)	$NO_3 + O_2^- \rightarrow NO_3^- + O_2$	1.0×10^9	-1500.
A(26)	$N_2O_5(aq) + H_2O \rightarrow 2H^+ + 2NO_3^-$	$5. \times 10^9$	-1800.

Reaction rates are of the form $k = k_{298} exp[-\frac{E_A}{R}(\frac{1}{T} - \frac{1}{298}]$.

The aqueous phase reacting system was slightly modified and adapted to the intercomparison study. Thus, the hydroloysis rates were not kept constant, but replaced by the corresponding

Henry's law equilibria

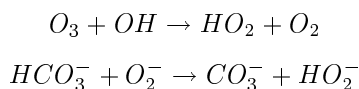| Number	Reaction	k_{298}	$-\frac{\Delta H}{R}$
E(1)	$O_3(g) \rightleftharpoons O_3(aq)$	1.1×10^{-2}	2300.
E(2)	$H_2O_2(g) \rightleftharpoons H_2O_2(aq)$	8.3×10^4	7400.
E(3)	$OH(g) \rightleftharpoons OH(aq)$	30.	4500.
E(4)	$HO_2(g) \rightleftharpoons HO_2(aq)$	$4. \times 10^3$	5900.
E(5)	$CH_3OO(g) \rightleftharpoons CH_3OO(aq)$	15.	5600.
E(6)	$CH_3OOH(g) \rightleftharpoons CH_3OOH(aq)$	3.1×10^2	5200.
E(7)	$CH_2O(g) \rightleftharpoons CH(OH)_2(aq)$	3.2×10^3	6800.
E(8)	$HCOOH(g) \rightleftharpoons HCOOH(aq)$	5.4×10^3	5700.
E(9)	$NO(g) \rightleftharpoons NO(aq)$	1.9×10^{-3}	1500.
E(10)	$NO_2(g) \rightleftharpoons NO_2(aq)$	6.4×10^{-3}	2500.
E(11)	$HNO_3(g) \rightleftharpoons HNO_3(aq)$	2.4×10^6	8700.
E(12)	$N_2O_5(g) \rightarrow N_2O_5(aq)$	1.4	0.
E(13)	$NO_3(g) \rightleftharpoons NO_3(aq)$	1.8	2000.
E(14)	$CO_2(g) \rightleftharpoons CO_2(aq)$	3.6×10^{-2}	2200.

Reaction rates are of the form $k = k_{298} exp[-\frac{\Delta H}{R}(\frac{1}{T} - \frac{1}{298}]$.
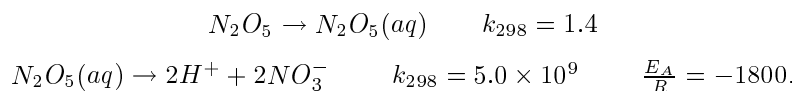
Dissociation equilibria

Number	Reaction	A	B	C
E(16)	$H_2O_2(aq) \rightarrow HO_2^- + H^+$	$11. \times 10^{-2}$	0.	-5200.
E(17)	$HO_2(aq) \rightleftharpoons O_2^- + H^+$	3.5×10^{-5}	0.	$5. \times 10^{10}$
E(18)	$HCOOH(aq) \rightleftharpoons HCOO^- + H^+$	1.8×10^{-4}	-1500.	$5. \times 10^{10}$
E(19)	$HNO_3(aq) \rightleftharpoons NO_3 + H^+$	15.	0.	$5. \times 10^{10}$
E(20)	$CO_2(aq) \rightleftharpoons HCO_3 + H^+$	4.5×10^{-7}	-1000.	5.6×10^4
E(21)	$Cl_2^-(aq) \rightleftharpoons Cl^- + Cl(aq)$	5.3×10^{-6}	0.	$6. \times 10^4$

Equilibrium reaction rates are of the form $k_e = \frac{k_+}{k_-} = A\ exp[-\frac{B}{T}]$ and the backward reaction rate $k_- = C$.
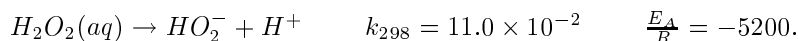
zenith angle dependent ones from the gas phase increased by a factor of 1.5. To ensure the electroneutrality reactions $(A13)$ and $(A17)$ in the original mechanism were replaced by

$$O_3 + OH \rightarrow HO_2 + O_2$$
$$HCO_3^- + O_2^- \rightarrow CO_3^- + HO_2^-$$

N_2O_5 phase transfer reaction $(E12)$ was replaced by

$$N_2O_5 \rightarrow N_2O_5(aq) \qquad k_{298} = 1.4$$
$$N_2O_5(aq) \rightarrow 2H^+ + 2NO_3^- \qquad k_{298} = 5.0 \times 10^9 \qquad \frac{E_A}{R} = -1800.$$

H_2O_2 dissociation reaction $(E15)$ was replaced by the forward reaction with the corresponding rate due to the presence of reaction $(A10)$ in the aqueous phase.

$$H_2O_2(aq) \rightarrow HO_2^- + H^+ \qquad k_{298} = 11.0 \times 10^{-2} \qquad \frac{E_A}{R} = -5200.$$

Reactions rates are of the form $k = k_{298} \; exp[-\frac{E_A}{R}(\frac{1}{298} - \frac{1}{T})]$.

B.3 CAPRAM2.3 mechanism

The aqueous phase reacting mechanism CAPRAM2.3 (Chemical Aqueous Phase RAdical Mechanism, Hermann et al., 2000) contains an explicit description of aqueous phase chemical transformation of tropospheric constituants initiated by primary radicals and secondary radical anions such as OH, NO_3, SO_4^-, Cl_2^-, Br_2^- or CO_3^-. In addition, a module of halogen activation is also included. Apart from that, CAPRAM2.3 considers organic compounds up to two carbon atoms. Starting from the alcohols, methanol and ethanol, the aldehydes and acids are produced. The gas phase in CAPRAM2.3 is described by RACM. The mechanism is available in electronic form under http://projects.tropos.de:8088/capram/