Supplement of Geosci. Model Dev., 10, 1587–1605, 2017
http://www.geosci-model-dev.net/10/1587/2017/
doi:10.5194/gmd-10-1587-2017-supplement
© Author(s) 2017. CC Attribution 3.0 License.

Geoscientific
Model Development
Open Access

Supplement of

A framework for expanding aqueous chemistry in the Community Multiscale Air Quality (CMAQ) model version 5.1

Kathleen M. Fahey et al.

Correspondence to: Kathleen M. Fahey (fahey.kathleen@epa.gov)

The copyright of individual parts of the supplement might differ from the CC-BY 3.0 licence.

Supplemental Information for "A framework for expanding aqueous chemistry in the Community Multiscale Air Quality (CMAQ) model version 5.1"

Table S1. Gas phase species• that participate in phase transfer and associated gas phase diffusion and accommodation coefficients. Unless otherwise indicated, Henry's Law coefficients are the base model's original values (from CMAQ subroutine hlconst.F).

Reaction	H_{law} (M/atm)	$-\Delta H/R$ (K)	α[a]	D_g (m^2/s) x 10^{5}[b]
$SO_{2\ (gas)} \leftrightarrow SO_{2\ (aq)}$	1.4	2.9E+03	1.10×10^{-1}	1.28
$HNO_{3\ (gas)} \leftrightarrow HNO_{3\ (aq)}$	2.1E+05	8.7E+03	8.68×10^{-2}	1.32
$CO_{2\ (gas)} \leftrightarrow H_2CO_{3\ (aq)}$	3.6E-02	2.2E+03	1.50×10^{-4}	1.55
$NH_{3\ (gas)} \leftrightarrow NH_4OH_{\ (aq)}$	6.1E+01	4.2E+03	9.10×10^{-2}	2.30
$H_2O_{2\ (gas)} \leftrightarrow H_2O_{2\ (aq)}$	8.3E+04	7.4E+03	1.53×10^{-1}	1.46
$O_{3\ (gas)} \leftrightarrow O_{3\ (aq)}$	1.14E-02	2.3E+03	1.00×10^{-1}	1.48
$HCOOH_{\ (gas)} \leftrightarrow HCOOH_{\ (aq)}$	8.9E+03	6.1E+03	2.29×10^{-2}	1.53
$MHP_{\ (gas)} \leftrightarrow MHP_{\ (aq)}$	3.1E+02	5.2E+03	6.76×10^{-3}	1.31
$PAA_{\ (gas)} \leftrightarrow PAA_{\ (aq)}$	8.4E+02	5.3E+03	1.90×10^{-2}	1.02
$HCl_{\ (gas)} \leftrightarrow HCl_{\ (aq)}$	1.9E+01	6.0E+02	1.16×10^{-1}	1.89
$GLY_{\ (gas)} \leftrightarrow GLY_{\ (aq)}$	3.6E+05		2.30×10^{-2}[c]	1.15[a]
$MGLY_{\ (gas)} \leftrightarrow MGLY_{\ (aq)}$	3.2E+04[e]		2.30×10^{-2}[c]	1.15[d]
$IEPOX_{\ (gas)} \leftrightarrow IEPOX_{\ (aq)}$	2.7E+06[f]		2.00×10^{-2}[f]	1.00[f]
$MAE_{\ (gas)} \leftrightarrow MAE_{\ (aq)}$	1.2E+05[f]		2.00×10^{-2}[f]	1.00[f]
$HMML_{\ (gas)} \leftrightarrow HMML_{\ (aq)}$	1.2E+05[f]		2.00×10^{-2}[f]	1.00[f]

•H_2SO_4 is instantaneously transferred to aerosol SO_4 and N_2O_5 to $HNO_{3\ (gas)}$ at the start of cloud processing. [a]CAPRAM 2.4 tables (http://projects.tropos.de/capram/capram_24.html)*. [b]Herrmann et al. (2000)*. [c]Lim et al. (2005)*. [d]Assumed equal to D_g for glyoxal. [e]The Henry's Law coefficient for methylglyoxal is replaced with that of glyoxal when the CB05 gas phase mechanism is used (Carlton et al., 2010). [f]Pye et al. (2013). *and the original sources therein

Table S2. Dissociation reactions and equilibrium constants. Ionic species are considered explicitly and dissociation equilibrium reactions are described as a set of forward and backward reactions. Activity coefficients are rolled into the forward and backward reaction rates.

Reaction	$K_{eq,298}$[a] [M]	$-\Delta E_a/R$ [K][#]	k_b[a,d] [$M^{-1}\ s^{-1}$]
$SO_2 \leftrightarrow HSO_3^- + H^+$	1.39×10^{-2}	1.87×10^{3}	2.0×10^{8}
$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$	6.72×10^{-8}	3.55×10^{2}	5.0×10^{10}
$HNO_3 \leftrightarrow NO_3^- + H^+$	1.7×10^{1}		5.0×10^{10}
$NH_4OH \leftrightarrow NH_4^+ + OH^-$	1.77×10^{-5}	-7.10×10^{2}	3.4×10^{10}
$H_2CO_3 \leftrightarrow HCO_3^- + H^+$	4.3×10^{-7}	-9.95×10^{2}	6.4×10^{4}
$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	4.68×10^{-11}	-1.79×10^{3}	5.0×10^{10}
$HCOOH \leftrightarrow HCOO^- + H^+$	1.8×10^{-4}[b]	-2.00×10^{1}	5.0×10^{10}
$HCl \leftrightarrow Cl^- + H^+$	1.74×10^{6}[b]	6.90×10^{3}	5.0×10^{10}
$H_2O \leftrightarrow OH^- + H^+$	1.8×10^{-16}[c]	-6.95×10^{3}	1.4×10^{11}
$H_2SO_4 \leftrightarrow HSO_4^- + H^+$	1.0×10^{3}[b]		5.0×10^{10}
$HSO_4^- \leftrightarrow SO_4^{2-} + H^+$	1.02×10^{-2}	2.45×10^{3}	1.0×10^{11}

[a]Warneck and Williams (2012)*. [b]Seinfeld and Pandis(2006)*. [c]Removed [H_2O] concentration of 55.5 M from the original equilibrium constant. [d]Graedel and Weschler (1981)*. *and the original sources therein

$k_f = Keq_{i,T} \times k_b$ [#]Note that while there are some minor differences between some of the equilibrium constants used here compared to AQCHEM, box model tests indicate that these small differences only have a minimal impact on predicted concentrations

Table S3. Chemical kinetic reactions.

Reaction	Rate coefficient in appropriate units of M,s (298K); $-E_a/R$ (K) $^{\$}$		Notes
$HSO_3^- + H_2O_2 + H^+ \rightarrow SO_4^{2-} + 2 H^+$	7.45E+7 / (1 + 13 [H+]); -4756.08		
$SO_2 + O_3 \rightarrow SO_4^{2-} + 2 H^+$	2.4E+4; 0.0		Q
$HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+$	3.7E+5; -5530.88		Q
$SO_3^{2-} + O_3 \rightarrow SO_4^{2-}$	1.5E+9; -5280.56		Q
$HSO_3^- + MHP + H^+ \rightarrow SO_4^{2-} + 2 H^+$	1.9E+7; -3799.5		
$^{*}HSO_3^- + PAA + H^+ \rightarrow SO_4^{2-} + 2 H^+$	3.6E+7; -3999.2		*
$^{*}HSO_3^- + PAA \rightarrow SO_4^{2-} + H^+$	7E+2; 0.0		
SO_2 (+ Mn(II)) $\rightarrow SO_4^{2-} + 2 H^+$	7.5E+2; 0.0		#
HSO_3^- (+ Mn(II)) $\rightarrow SO_4^{2-} + H^+$	7.5E+2; 0.0		#
SO_3^{2-} (+ Mn(II)) $\rightarrow SO_4^{2-}$	7.5E+2; 0.0		#
SO_2 (+ Fe(III)) $\rightarrow SO_4^{2-} + 2 H^+$	2.6E+3; 0.0		#
HSO_3^- (+ Fe(III)) $\rightarrow SO_4^{2-} + H^+$	2.6E+3; 0.0		#
SO_3^{2-} (+ Fe(III)) $\rightarrow SO_4^{2-}$	2.6E+3; 0.0		#
SO_2 (+Mn(II) + Fe(III)) $\rightarrow SO_4^{2-} + 2 H^+$	1E+10; 0.0		#
HSO_3^- (+ Mn(II) + Fe(III)) $\rightarrow SO_4^{2-} + H^+$	1E+10; 0.0		#
SO_3^{2-} (+ Mn(II) + Fe(III)) $\rightarrow SO_4^{2-}$	1E+10; 0.0		#
GLY + OH• → 0.04 ORGC	3E+10; 0.0		Fixed OH•
MGLY + OH• → 0.04 ORGC	3E+10; 0.0		Fixed OH•
	k_1 ($M^{-2}s^{-1}$)	k_2 ($M^{-2}s^{-1}$)	
IEPOX + H_2O → 2-methyltetrol	9E-04	1.3E-05	Rate = KIEPOX * Parent Hydrocarbon * Nucleophile * Q where KIEPOX = k_1*[H^+] + k_2*[$HSO4^-$] H_2O concentration remains fixed (55.5 M)
IEPOX + SO_4^{2-} → IEPOX_OS	2E-04	2.9E-06	
IEPOX + NO_3^- → IEPOX_ON[§]	2E-04	2.9E-06	
IEPOX + 2-methyltetrol → dimers	2E-04	2.9E-06	
IEPOX + IEPOX_OS → dimers	2E-04	2.9E-06	
IEPOX + IEPOX_ON → dimers[§]	2E-04	2.9E-06	
MAE + H_2O → 2-MG	9E-04	1.3E-05	
MAE + SO_4^{2-} → MPAN_OS	2E-04	2.9E-06	
MAE + NO_3^- → MPAN_ON[§]	2E-04	2.9E-06	
MAE + 2-MG → dimers[§]	2E-04	2.9E-06	
MAE + MPAN_OS→ dimers[§]	2E-04	2.9E-06	
MAE + MPAN_ON → dimers[§]	2E-04	2.9E-06	
HMML + H_2O → 2-MG	9E-04	1.3E-05	
HMML + SO_4^{2-} → MPAN_OS	2E-04	2.9E-06	
HMML + NO_3^- → MPAN_ON[§]	2E-04	2.9E-06	
HMML + 2-MG → dimers[§]	2E-04	2.9E-06	
HMML + MPAN_OS → dimers[§]	2E-04	2.9E-06	
HMML + MPAN_ON → dimers[§]	2E-04	2.9E-06	

$^{\$}$Rate coefficients are equal to those used in the standard version of AQCHEM. [Q] Aqueous diffusion correction factor applied; [*]included here as two reactions to accommodate the original single rate expression which included pH dependent and pH independent elements. [#]A S(VI) inhibition factor of the following form is applied to these reaction rates: $(1+75[S(VI)]^{0.67})^{-1}$. (Species in parentheses on the left hand side of the rate expression indicate species that affect the reaction rate calculation but whose concentrations are not consumed in the reaction.) [§]Included here but not included in the version of AQCHEM-KMTI released with CMAQv5.1

Table S4. CMAQ species and local AQCHEM-KMT(I) species. The “G”, “L”, “A”, and “WD” prefixes in column 1 refer to the gas-phase, aqueous-phase, Aitken aerosol, and wet deposition portion of the species respectively. Shaded cells include species specific to AQCHEM-KMTI. CMAQ aerosol concentration and wet deposition indices are of the form: [species, mode].

AQCHEM-KMT(I) local dynamic species	CMAQ species	Name and Notes
G_SO2, L_SO2, WD_SO2	GAS(LSO2), GASWDEP(LSO2)	Sulfur dioxide
G_HNO3, L_HNO3, WD_HNO3	GAS(LHNO3)/AEROSOL(LNO3, 2/3), GASWDEP(LHNO3)	Nitric acid, nitrate
G_CO2, L_H2CO3, WD_CO2	GAS(LCO2), GASWDEP(LCO2)	Carbon dioxide
G_NH3, L_NH4OH, WD_NH4OH	GAS(LNH3), AEROSOL(LNH4, 2/3), GASWDEP(LNH3)	Ammonia, ammonium
G_H2O2, L_H2O2, WD_H2O2	GAS(LH2O2), GASWDEP(LH2O2)	Hydrogen peroxide
G_O3, L_O3, WD_O3	GAS(LO3), GASWDEP(LO3)	Ozone
G_HCOOH, L_HCOOH, WD_HCOOH	GAS(LFOA), GASWDEP(LFOA)	Formic acid
G_MHP, L_MHP, WD_MHP	GAS(LMHP), GASWDEP(LMHP)	Methylhydroxyperoxide (CH3OOH)
G_PAA, L_PAA, WD_PAA	GAS(LPAA), GASWDEP(LPAA)	peroxyacetic acid (CH3C(O)OOH)
G_HCL, L_HCL, WD_HCL	GAS(HCL), GASWDEP(HCL)	Hydrochloric acid
G_GLY, L_GLY, WD_GLY	GAS(LGLY), GASWDEP(LGLY)	Glyoxal
G_MGLY, L_MGLY, WD_MGLY	GAS(LMGLY), GASWDEP(LMGLY)	Methylglyoxal
A_NO3AKN	AEROSOL(LNO3,1)	Aitken nitrate
A_NH4AKN	AEROSOL(LNH4,1)	Aitken ammonium
A_CLAKN	AEROSOL(LCL,1)	Aitken chloride
A_NAAKN	AEROSOL(LNA,1)	Aitken sodium
A_SO4AKN	AEROSOL(LSO4,1)	Aitken sulfate
A_PECAKN	AEROSOL(LEC,1)	Aitken elemental carbon
A_POAAKN	AEROSOL(LPOA,1)	Aitken primary OA
A_PRIAKN	AEROSOL(LPRI,1)	Aitken other primary
L_SO4MIN2, WD_H2SO4	AEROSOL(LSO4, 2/3), AERWDEP(LSO4, 2/3)	Sulfate
L_NO3MIN, WD_NO3MIN	GAS(LHNO3), AEROSOL(LNO3, 2/3), AERWDEP(LNO3, 2/3)	Nitrate
L_NH4PLUS, WD_NH4PLUS	GAS(LNH3), AEROSOL(LNH4, 2 and 3), AERWDEP(LNH4, 2/3)	Ammonium
L_CLMIN, WD_CLMIN	AEROSOL(LCL, 2/3), AERWDEP(LCL, 2/3)	Chloride
L_PRIACC, WD_PRIACC	AEROSOL(LPRI, 2), AERWDEP(LPRI, 2)	Other primary
L_PECACC, WD_PECACC	AEROSOL(LEC, 2), AERWDEP(LEC, 2)	Elemental carbon
L_ORGC, WD_ORGC	AEROSOL(LORGC, 2), AERWDEP(LORGC, 2)	Cloud SOA
L_POAACC, WD_POAACC	AEROSOL(LPOA, 2), AERWDEP(LPOA, 2)	Primary OA
L_HPLUS, WD_HPLUS	HPWDEP	H^+
L_OHMIN	--	OH^-

L_FEPLUS3, WD_FEPLUS3$^{\%}$	AEROSOL(LFEACC, 2), AERWDEP(LFEACC, 2), AEROSOL(LSOILC, 3), AERWDEP(LSOILC, 3), AEROSOL(LANTHC, 3), AERWDEP(LANTHC, 3)	Soluble iron($^{3+}$); $^{\%}$AQCHEM species include contributions from coarse aerosol
L_MNPLUS2, WD_MNPLUS2$^{\%}$	AEROSOL(LMNACC, 2), AERWDEP(LMNACC, 2) , AEROSOL(LSOILC, 3), AERWDEP(LSOILC, 3), AEROSOL(LANTHC, 3), AERWDEP(LANTHC, 3)	Soluble manganese($^{2+}$); $^{\%}$AQCHEM species include contributions from coarse aerosol
L_HSO3MIN, (WD_SO2)	GAS(LSO2)	Bisulfite
L_SO3MIN2, (WD_SO2)	GAS(LSO2)	Sulfite
L_HCO3MIN, (WD_CO2)	GAS(LCO2)	Bicarbonate
L_CO3MIN2, (WD_CO2)	GAS(LCO2)	Carbonate
L_HCOOMIN, (WD_HCOOH)	GAS(LFOA)	Formate
L_HSO4MIN, (WD_H2SO4)	AEROSOL(LSO4, 2/3)	Bisulfate
L_CAPLUS2, WD_CAPLUS2$^{\%}$	AEROSOL(LCAACC, 2), AERWDEP(LCAACC, 2), AEROSOL(LSOILC, 3), AERWDEP(LSOILC, 3), AEROSOL(LANTHC, 3), AERWDEP(LANTHC, 3), AEROSOL(LSEASC, 3), AERWDEP(LSEASC, 3)	Calcium($^{2+}$); $^{\%}$AQCHEM species include contributions from coarse aerosol
L_MGPLUS2, WD_MGPLUS2$^{\%}$	AEROSOL(LMGACC, 2), AERWDEP(LMGACC, 2), AEROSOL(LSOILC, 3), AERWDEP(LSOILC, 3), AEROSOL(LANTHC, 3), AERWDEP(LANTHC, 3), AEROSOL(LSEASC, 3), AERWDEP(LSEASC, 3)	Magnesium($^{2+}$); $^{\%}$AQCHEM species include contributions from coarse aerosol
L_KPLUS, WD_KPLUS$^{\%}$	AEROSOL(LKACC, 2), AERWDEP(LKACC, 2), AEROSOL(LSOILC, 3), AERWDEP(LSOILC, 3), AEROSOL(LANTHC, 3), AERWDEP(LANTHC, 3), AEROSOL(LSEASC, 3), AERWDEP(LSEASC, 3)	Potassium($^{+}$); $^{\%}$AQCHEM species include contributions from coarse aerosol
L_NAPLUS, WD_NAPLUS$^{\%}$	AEROSOL(LNA, 2), AERWDEP(LNA, 2), AEROSOL(LSOILC, 3), AERWDEP(LSOILC, 3), AEROSOL(LANTHC, 3), AERWDEP(LANTHC, 3), AEROSOL(LSEASC, 3), AERWDEP(LSEASC, 3)	Sodium($^{+}$); $^{\%}$AQCHEM species include contributions from coarse aerosol
G_IEPOX, L_IEPOX, WD_IEPOX	GAS(LIEPOX), GASWDEP(LIEPOX)	Isoprene epoxydiols

G_IMAE, L_IMAE, WD_IMAE	GAS(LIMAE), GASWDEP(LIMAE)	Methacrylic acid epoxide
G_IHMML, L_IHMML, WD_IHMML	GAS(LIHMML), GASWDEP(LIHMML)	Hydroxymethylmethyl-α-lactone
L_IETET, WD_IETET	AEROSOL(LIETET, 2), AERWDEP(LIETET, 2)	2-methyltetrols
L_IEOS, WD_IEOS	AEROSOL(LIEOS, 2), AERWDEP(LIEOS, 2)	IEPOX-derived organosulfate
L_IEON, WD_IEON**	AEROSOL(LIEON, 2), AERWDEP(LIEON, 2)	IEPOX-derived organonitrate. **not included in CMAQv5.1 but used here
L_DIMER, WD_DIMER	AEROSOL(LDIMER, 2), AERWDEP(LDIMER, 2)	dimers
L_IMGA, WD_IMGA	AEROSOL(LIMGA, 2), AERWDEP(LIMGA, 2)	2-methylglyceric acid
L_IMOS, WD_IMOS	AEROSOL(LIMOS, 2), AERWDEP(LIMOS, 2)	MPAN-derived organosulfate
L_IMON, WD_IMON**	AEROSOL(LIMON, 2), AERWDEP(LIMON, 2)	MPAN-derived organonitrate. **not included in CMAQv5.1 but used here
G_OH, L_OH*	GAS(LHO)	Hydroxyl radical. *Mapped in from CMAQ but kept constant during/after cloud processing

Table S5. Box model test scenarios. Initial aerosol species concentrations are held constant for the variable scenarios and are associated with an initial droplet pH of ~5. Default gas concentrations were set at 1 ppb and modal aerosol species concentrations were set to 0.1 μg/m^3, with the following exceptions: O_3 = 50 ppb, CO_2 = 340 ppm, H_2SO_4 = 0.1 ppb, N_2O_5 = 0.1 ppb, SO_4^{2-} = 4.2 μg/m^3, Primary inorganic (inert) = 2.1 μg/m^3, Primary OA = 1.1 μg/m^3, SOA = 2.1 μg/m^3, EC = 1.1 μg/m^3, Cl^- = 2.3 μg/m^3, NH_4^+ = 2.2 μg/m^3, NO_3^- = 4.1 μg/m^3, Na, accumulation mode Fe, Mn, Ca = 0.3 μg/m^3, coarse soil and anthropogenic coarse = 2 μg/m^3, coarse sea salt cations = 1 μg/m^3, Pressure = 1 atm.

Variable input	**Values**
Liquid Water content (g/m^3)	0.05, 0.1, 0.2, 0.3
Precipitation rate (mm/hr)	0, 2
Temperature (K)	270, 283
Daylight (binary)	0, 1
Integration time (s)	60, 300, 720
SO_2 (ppb)	1, 5, 10
H_2O_2 (ppb)	0.1, 1, 5
(M)GLY (ppb)	0.5, 2
OH (ppb)	10^{-3}, 10^{-5}, 10^{-7}
NH_3 (ppb)	1, 5
HNO_3 (ppb)	1, 5

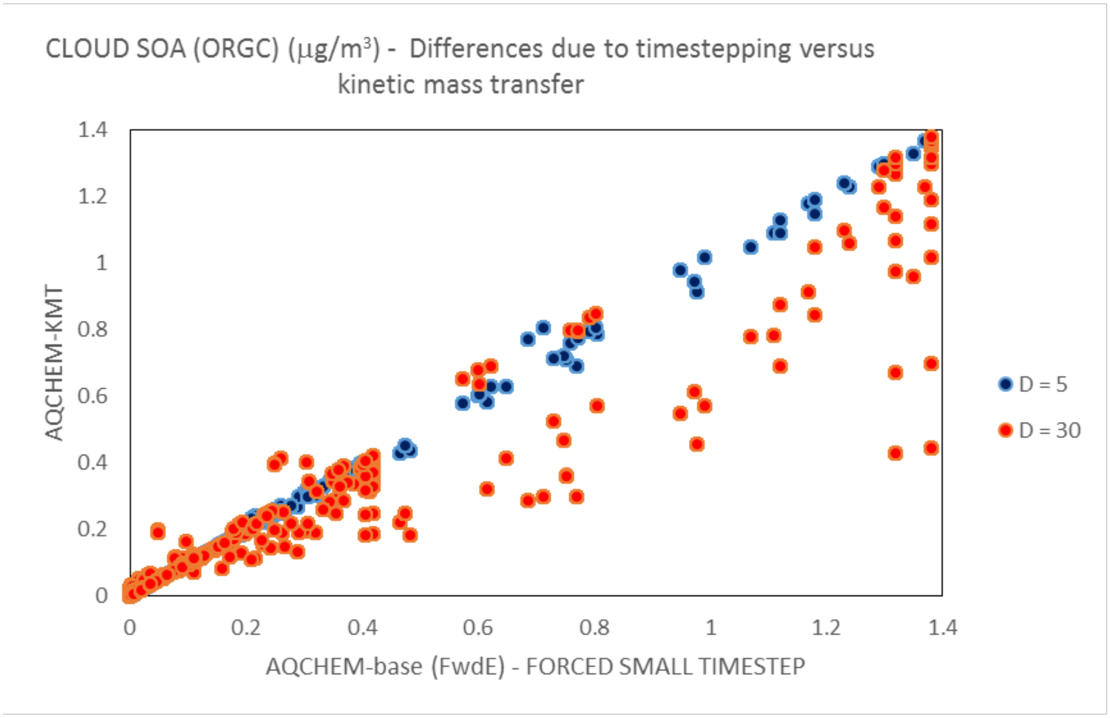

Figure S1: Cloud SOA (ORGC) predicted by AQCHEM-KMT at 5 (blue) and 30 µm (red) droplet diameters versus standard AQCHEM with a forced small time step. Compared to Figure 2 where AQCHEM is run with its standard time-stepping procedure, it appears that the differences between the models for ORGC are driven by both mass transfer limitations as well as the time-stepping procedure (which in standard AQCHEM is based on sulfate production only).

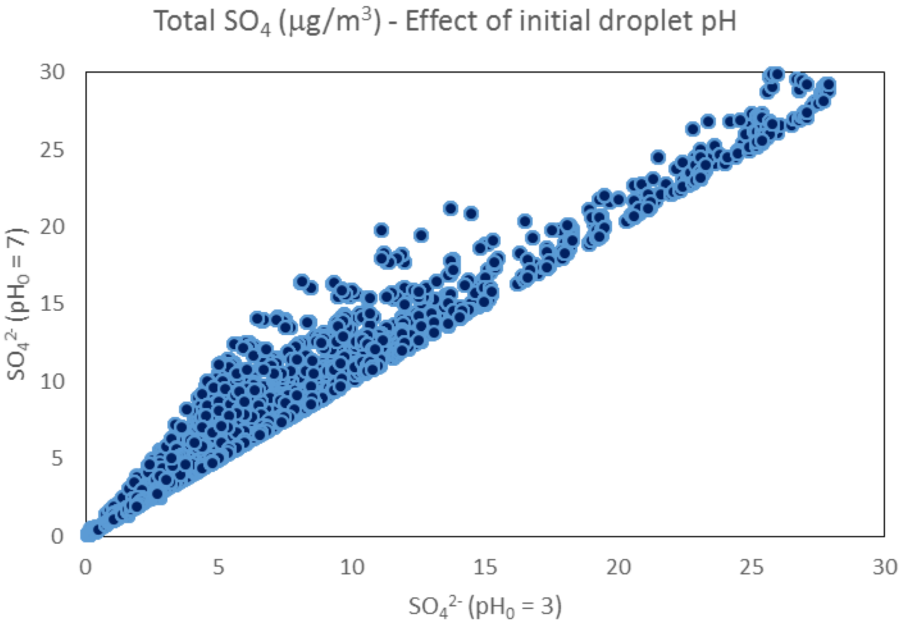

Figure S2: Predicted SO_4^{2-} concentrations for AQCHEM-KMT for initial pH of 7 versus 3.

References:

Carlton, A.G., Bhave, P.V., Napelenok, S.L., Edney, E.O., Sarwar, G., Pinder, R.W., Pouliot, G.A., and Houyoux, M.: Model representation of secondary organic aerosol in CMAQv4.7, Environ. Sci. Technol., 44, 8553-8560, doi: 10.1021/es100636q, 2010.

Graedel, T.E. and Weschler, C.J.: Chemistry within aqueous atmospheric aerosols and raindrops, Reviews of Geophysics, 19(4), 505-539, doi:10.1029/RG019i004p00505, 1981.

Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P., and Zellner, R.: A chemical aqueous phase radical mechanism for tropospheric chemistry, J. Atmos. Chem., 36, 231–284, doi:10.1023/A:1006318622743, 2000.

Lim, H., Carlton, A.G., and Turpin, B.J.: Isoprene forms secondary organic aerosol through cloud processing: model simulations, Environ. Sci. Technol., 39, 4441-4446, doi:10.1021/es048039h, 2005.

Pye, H.O.T., Pinder, R.W., Piletic, P.R., Xie, Y., Capps, S. L., Lin, Y., Surratt, J.D., Zhang, Z., Gold, A., Luecken, D.J., Hutzell, W.T., Jaoui, M., Offenberg, J.H., Kleindienst, T.E., Lewandoswki M., and Edney, E.O.: Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation, Environ. Sci. Technol., 47, 11056-11064, doi: 10.1021/es402106h, 2013.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd Edn., John Wiley and Sons, Inc., 2006.

Warneck, P. and Williams, J.: The Atmospheric Chemist’s Companion: Numerical Data for Use in the Atmospheric Sciences, Springer, 2012.