3.3 Acids: formation reactions and cloud chemistry

3.3.1 Sulfuric acid formation in the gas-phase

Formation of sulfuric acid in the (A) gas-phase:

(1) $SO_2 + OH\cdot \rightarrow HSO_3\cdot$

(2) $HSO_3\cdot + O_2 \rightarrow SO_3 + HO_2\cdot$

(3) $SO_3 + 2\ H_2O \rightarrow H_2SO_4{*}H_2O$

net:

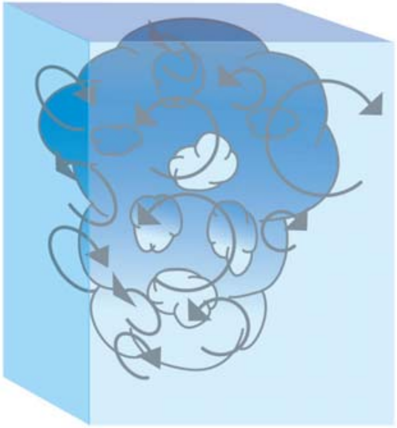
(1-3) $SO_2 + OH\cdot + O_2 + 2\ H_2O \rightarrow H_2SO_4{*}H_2O + HO_2\cdot$

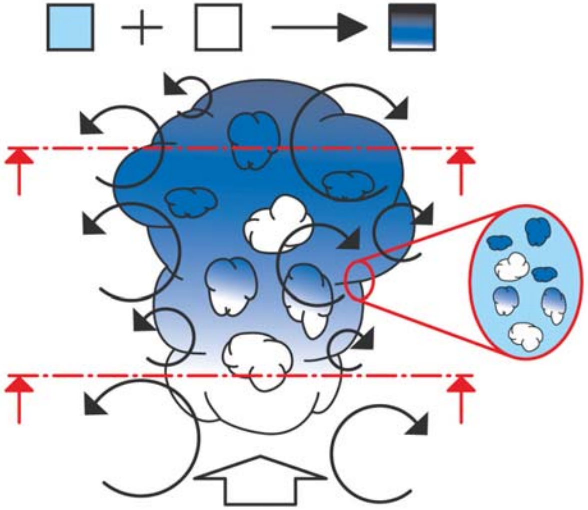
Then very fast phase change by nucleation (→ *3.1 Aer*), condensation

Only 15% of S(VI) is formed in the gas-phase globally, 85% is formed (B) in cloud droplets and humid aerosol particles

3.3.2 Cloudwater - introduction, significance

- 15% of the volume of the troposphere filled with clouds
- liquid water content $L = 0.1\text{-}2 \times 10^{-6}\ V_{water}/V_{air} = 0.1\text{-}2\ g/m^3$ $= (0.1\text{-}2) \times 10^{-3}\ L/m^3 < 10\%$ of total water content ($10\text{-}40\ g/m^3$!)
- only ≈ 10% of clouds will rain out, while 90% will recycle aerosol particles
- lifetime of clouds hours-days, of cloud droplets ($D = 5\text{-}50\ \mu m$) minutes
- aqueous composition: dissolved ($c_i \approx 10^{-6} - 10^{-3}$ M) + eventually non-dissolved constituents, droplet-size dependent, $c_i(D)$
- humidity/supersaturation S (:=rh-1) is altitude (above cloud base)-dependent





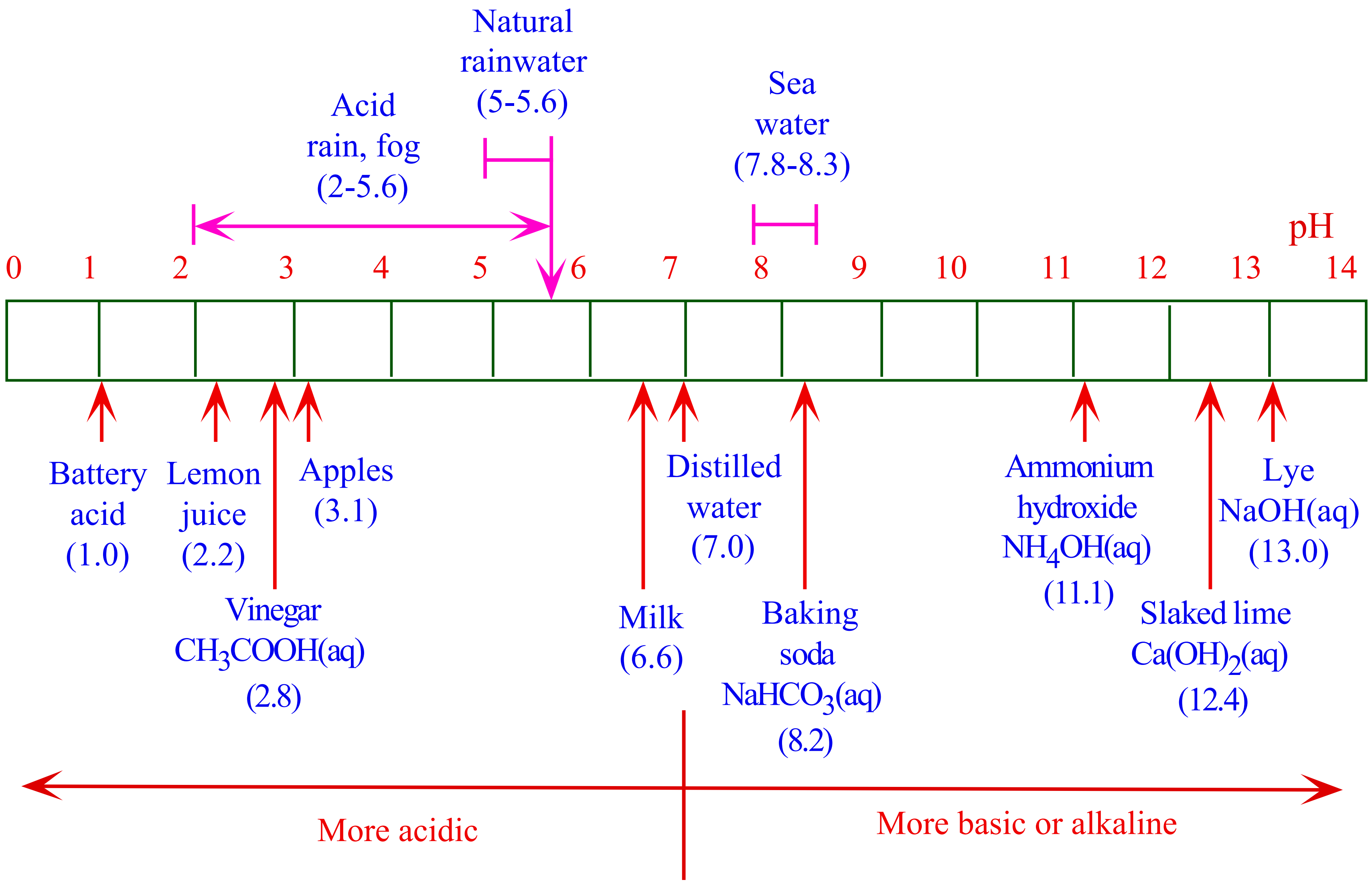
Terminology:

- Hydrometeors = cloud droplets + ice particles + rain droplets + snow flakes + graupel + ...
- Wash-out = below-cloud scavenging + in-cloud scavenging of both gases and particles
- in-cloud scavenging of gases = dissolution
- Wet deposition = rain + snow fall + rime
- occult deposition = droplet deposition from clouds, fogs

some units:

- 1 M = 1mol/L
- pH 7 ↔ $c_{H3O+} = 10^{-7}$ M
- 1 atm = 10^5 Pa = 10^5 Nm^{-2} = 1 bar

pH scale



Natural rainwater (5-5.6)

Acid rain, fog (2-5.6)

Sea water (7.8-8.3)

pH

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Battery acid (1.0)

Lemon juice (2.2)

Vinegar $CH_3COOH(aq)$ (2.8)

Apples (3.1)

Milk (6.6)

Distilled water (7.0)

Baking soda $NaHCO_3(aq)$ (8.2)

Ammonium hydroxide $NH_4OH(aq)$ (11.1)

Slaked lime $Ca(OH)_2(aq)$ (12.4)

Lye $NaOH(aq)$ (13.0)

More acidic

More basic or alkaline

Courtesy: Jacobson

3.3.3 Sulfuric acid formation in the aqueous phase

3.3.3.1 Dissolution of gases - thermodynamic equilibrium

...with diluted solutions (ideal behaviour).

The scavenging efficiency of gaseous molecules is dependent on water solubility:

$$\varepsilon_{i(g)\,Lsg} = n_{(sol)} / (n_{(sol)} + n_{(g)}) = n_{(sol)} / [n_{(sol)} + p_i V_{air}/(R_g T)] =$$
$$= n_{(sol)} / [n_{(sol)} + H_i n_{(sol)} V_{air}/(R_g T n_{H2O})] =$$
$$= [1 + H_i M_w/(R_g\, T\, L)]^{-1}$$

with: Henry coefficient H_i [atm] $= p_i/x_i = p_i/(c_i/10^3/M_w)$,

liquid water content L [g/m³]

solubility $s(T) = s(T_0) * \exp[-\Delta H_{sol}/R * (1/T-1/T_0)]$

gas constant R_g, M_w[g/mol], 10^3[cm³/L], (Warneck, 1986)

Another, very common Henry coefficient:

K_H [M bar^{-1}] $= 10^2\, s/M_w p = (10^3/M_w)*\rho_{H2O}/H$

s [mg/L], $R_g = 8.206*10^{-5}$ m³ atm/mol/K

... confusing: there are more common so-called ‚Henry coefficients‘:

Air-water partitioning coefficient:

K_{aw} [ ] $= M_w p/(10^5\, R_g T s) = 1/\,(10^3\, R_g T K_H)$

Henry coefficients

Solubility increases with decreasing temperatures,
e.g. 78, 63 and 53% of O_2 at 0°C is soluble at 10, 20 and 30°C, respectively.

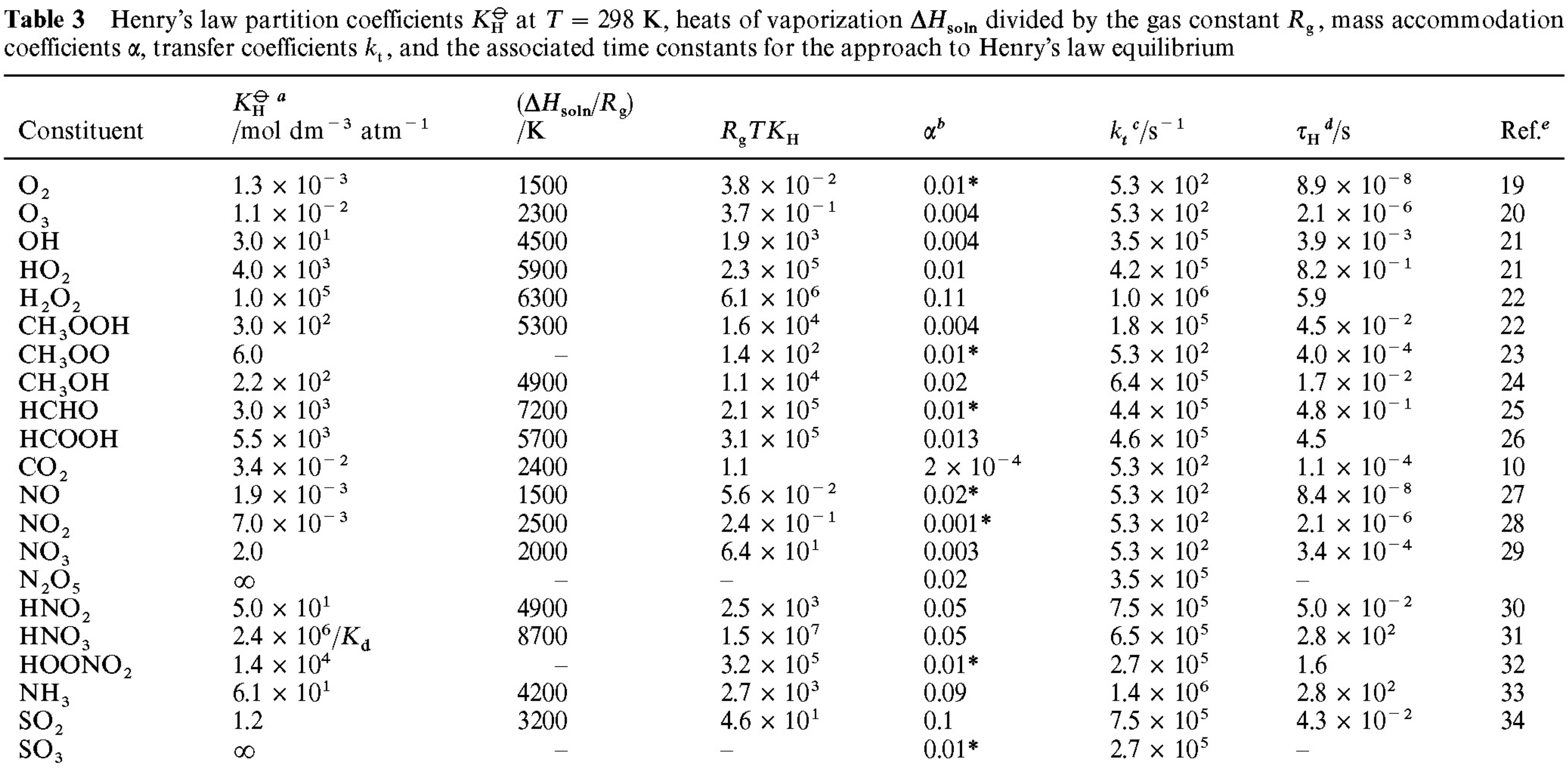


Table 3 Henry's law partition coefficients $K_H^\ominus$ at T = 298 K, heats of vaporization ΔH_{soln} divided by the gas constant R_g, mass accommodation coefficients α, transfer coefficients k_t, and the associated time constants for the approach to Henry's law equilibrium

Constituent	$K_H^\ominus$ [a] /mol dm^{-3} atm^{-1}	$(\Delta H_{soln}/R_g)$ /K	$R_g T K_H$	α[b]	k_t[c]/s^{-1}	τ_H[d]/s	Ref.[e]
O_2	1.3×10^{-3}	1500	3.8×10^{-2}	0.01*	5.3×10^2	8.9×10^{-8}	19
O_3	1.1×10^{-2}	2300	3.7×10^{-1}	0.004	5.3×10^2	2.1×10^{-6}	20
OH	3.0×10^1	4500	1.9×10^3	0.004	3.5×10^5	3.9×10^{-3}	21
HO_2	4.0×10^3	5900	2.3×10^5	0.01	4.2×10^5	8.2×10^{-1}	21
H_2O_2	1.0×10^5	6300	6.1×10^6	0.11	1.0×10^6	5.9	22
CH_3OOH	3.0×10^2	5300	1.6×10^4	0.004	1.8×10^5	4.5×10^{-2}	22
CH_3OO	6.0	–	1.4×10^2	0.01*	5.3×10^2	4.0×10^{-4}	23
CH_3OH	2.2×10^2	4900	1.1×10^4	0.02	6.4×10^5	1.7×10^{-2}	24
HCHO	3.0×10^3	7200	2.1×10^5	0.01*	4.4×10^5	4.8×10^{-1}	25
HCOOH	5.5×10^3	5700	3.1×10^5	0.013	4.6×10^5	4.5	26
CO_2	3.4×10^{-2}	2400	1.1	2×10^{-4}	5.3×10^2	1.1×10^{-4}	10
NO	1.9×10^{-3}	1500	5.6×10^{-2}	0.02*	5.3×10^2	8.4×10^{-8}	27
NO_2	7.0×10^{-3}	2500	2.4×10^{-1}	0.001*	5.3×10^2	2.1×10^{-6}	28
NO_3	2.0	2000	6.4×10^1	0.003	5.3×10^2	3.4×10^{-4}	29
N_2O_5	∞	–	–	0.02	3.5×10^5	–	
HNO_2	5.0×10^1	4900	2.5×10^3	0.05	7.5×10^5	5.0×10^{-2}	30
HNO_3	$2.4 \times 10^6/K_d$	8700	1.5×10^7	0.05	6.5×10^5	2.8×10^2	31
$HOONO_2$	1.4×10^4	–	3.2×10^5	0.01*	2.7×10^5	1.6	32
NH_3	6.1×10^1	4200	2.7×10^3	0.09	1.4×10^6	2.8×10^2	33
SO_2	1.2	3200	4.6×10^1	0.1	7.5×10^5	4.3×10^{-2}	34
SO_3	∞	–	–	0.01*	2.7×10^5	–	

Compilation of K_H :
- Warneck, Phys. Chem. Chem. Phys. 1 (1999) 5471-5483
- download from Rolf Sander's webpage, MPI-C

http://www.mpch-mainz.mpg.de/~sander/res/henry.html

$$CO_2(aq) + H_2O(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$$

$CO_2(aq)$	$H_2O(aq)$	$H_2CO_3(aq)$	H^+	HCO_3^-	$2H^+$	CO_3^{2-}
Dissolved carbon dioxide	Liquid water	Dissolved carbonic acid	Hydrogen ion	Bicarbonate ion	Hydrogen ion	Carbonate ion

Solubility of CO_2 (g) $\rightarrow CO_{2\ aqu} + 20$ kJ/mol

(1) $K_H = c_{CO2\ aqu} / p_{CO2} = 3.4\text{x}10^{-7}$ mol/L/Pa (298 K)

$CO_{2\ aqu} + H_2O \rightarrow HCO_3^- + H_3O^+$

(2) $K_{S1} = (c_{HCO3-}\ c_{H3O+}) / c_{CO2\ aqu} = 10^{-6.35}$

$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$

(3) $K_{S2} = (c_{CO3--}\ c_{H3O+}) / c_{HCO3-} = 10^{-10.33}$

Dissolved fraction is pH dependent, expressed as the effective Henry coeff. H*:

$K_{H\ CO2}^* = (c_{CO2\ aqu} + c_{HCO3-} + c_{CO3--}) / p$ (mol/l/Pa)

$K_H^* = K_H\ (1 + K_{S1} / c_{H3O+} + K_{S1}K_{S2} / c_{H3O+}^2)$

pH of water in the atmosphere in equilibrium with CO_2 ($p_{CO2} = 36$ Pa):

(1) in (2):

$c_{HCO3-}\ \ c_{H3O+} = K_{S1}\ H_{CO2}\ p_{CO2}$

$c_{HCO3-} = c_{H3O+}$

$c_{H3O+} = (K_{S1}\ \ H_{CO2}\ p_{CO2})^{0.5}$

$pH = -\ 0.5\ (-pK_{S1} - \log K_{H\ CO2} - \log p_{CO2})$

$pH = 0.5\ (6.35 - \log 3.4\text{x}10^{-7} - \log 36) = 5.63$

S(IV) phase equilibrium and reactions

determined by Henry coeff. K_H, pH, T

S(IV): = $SO_{2\ aqu.} + HSO_3^- + SO_3^{2-}$

Phase equilibrium (Henry coeff., physical solubility of SO_2):

$SO_2 = SO_{2\ aqu.}$ $K_{H\ (298K)} := c_{SO2}/p_{SO2} = 1.2x10^{-5}$ M/Pa

Dissociation equilibria:

$SO_{2\ aqu.} + 2\ H_2O = HSO_3^- + H_3O^+$ $K_{S1\ (298K)}=1.7x10^{-2}$ M

$HSO_3^- + H_2O = SO_3^{2-} + H_3O^+$ $K_{S2\ (298K)}=6.5x10^{-8}$ M

Substances which interact with water to form ions via acid-base dissociation equilibria K_H must be replaced by a modified coefficient K_H*:
(‚modified Henry coeff.‘):

$K_{H\ (298K)}{}^*:= c_{S(IV)}/p_{SO2} = K_H\ (1 + K_{S1}/c_{H3O+} + K_{S1}K_{S2}/c_{H3O+}{}^2) = f(pH)$

… and S(VI) phase equilibrium and dissociation

$$S(IV): = SO_{2\ aqu.} + HSO_3^- + SO_3^{2-}$$

Phase equilibrium (Henry coeff., physical solubility of SO_2):

$$SO_2 = SO_{2\ aqu.} = HSO_3^- + H_3O^+ = SO_3^{2-} + H_3O^+$$

Sulfur dioxide gas

dissolved sulfur dioxide

bisulfite

sulfite

$$S(VI) = SO_4^{2-}{}_{aqu} + HSO_4^-{}_{aqu} + H_2SO_4{*}(H_2O)_n$$

$$H_2SO_4(g) \longrightarrow H_2SO_4(aq) \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

Sulfuric acid gas

Dissolved sulfuric acid

Hydrogen ion

Bisulfate ion

Hydrogen ion

Sulfate ion

3.3.3.2 Bulk aqueous phase chemistry

Acid-base dissociation equilibrium

Reaction	K_{298}/mol dm^{-3}	K_{285}
$H_2O \rightleftharpoons H^+ + OH^-$	1.0×10^{-14}	3.6×10^{-15}
$HO_2 \rightleftharpoons H^+ + O_2^-$	1.6×10^{-5}	1.7×10^{-5}
$HCOOH \rightleftharpoons H^+ + HCOO^-$	1.8×10^{-4}	1.8×10^{-4}
$CO_{2a} \rightleftharpoons H^+ + HCO_3^-$	4.3×10^{-7}	3.6×10^{-7}
$HNO_2 \rightleftharpoons H^+ + NO_2^-$	6.1×10^{-4}	4.6×10^{-4}
$HNO_3 \rightleftharpoons H^+ + NO_3^-$	1.5×10^{1}	1.5×10^{1}
$HOONO_2 \rightleftharpoons H^+ + NO_4^-$	–	1.0×10^{-5}
$NH_3 + H_2O \rightleftharpoons OH^- + NH_4^+$	1.8×10^{-5}	1.7×10^{-5}
$SO_{2a} \rightleftharpoons H^+ + HSO_3^-$	1.7×10^{-2}	2.2×10^{-2}
$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	6.5×10^{-8}	7.7×10^{-8}
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.0×10^{-2}	1.5×10^{-2}

(Warneck, 1999)

Dissociated / undissociated species exist in ratios determined by acidity (pH) and the dissociation constant, K_S. E.g. $SO_{2\ \mathrm{aqu.}}$ for pH < $-\log K_{S1} = 1.7$, SO_3^{2-} for pH > $-\log K_{S2} = 7.1$ and HSO_3^- in between.

S(IV) oxidation reactions

(1) $SO_3^{2-}{}_{aqu} + HO_2^{\cdot}{}_{aqu} \rightarrow SO_4^{2-}{}_{aqu} + OH^{\cdot}{}_{aqu}$

(2) $+ OH^{\cdot}{}_{aqu} \rightarrow SO_3^{-\cdot}{}_{aqu} + OH^{-}{}_{aqu} \rightarrow SO_5^{-\cdot}{}_{aqu} \xrightarrow{HO_2 \text{ or } HSO_3^-} \rightarrow SO_4^{2-}{}_{aqu}$

(3a) $HSO_3^{-}{}_{aqu} + O_{3\,aqu} \rightarrow HSO_4^{-}{}_{aqu} + H_2O$ $k_{3a}=3.2\text{x}10^5\ M^{-1}s^{-1}$

(3b) $SO_3^{2-}{}_{aqu} + O_{3\,aqu} \rightarrow SO_4^{2-}{}_{aqu} + H_2O$ $k_{3b}=1.5\text{x}10^9\ M^{-1}s^{-1}$

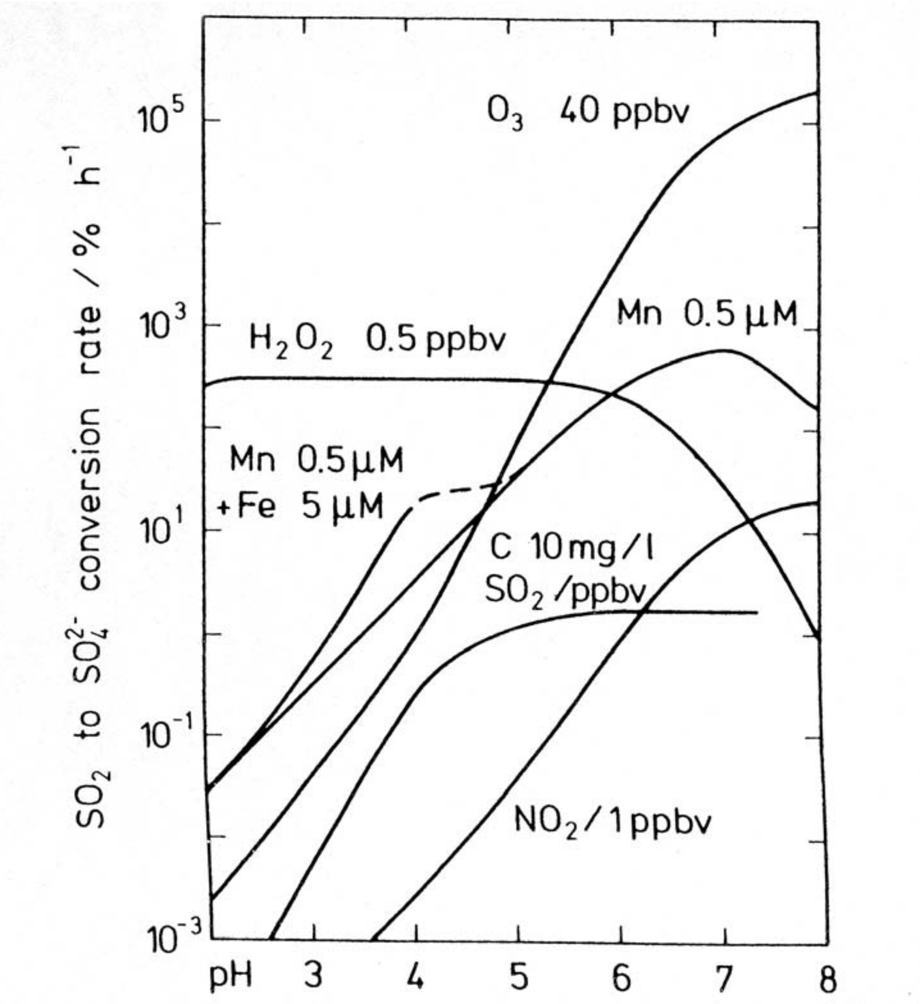
(4) $HSO_3^{-}{}_{aqu} + H_2O_{2\,aqu} \rightarrow HSO_4^{-}{}_{aqu} + H_2O$ $k_4=4.0\text{x}10^7\ c_{H+}\ M^{-1}s^{-1}$

(5) $2\ HSO_3^{-}{}_{aqu} + O_{2\,aqu} \xrightarrow{<M^{n+}>} 2\ HSO_4^{-}{}_{aqu}$ “autoxidation“ reactions

(Graedel & Weschler, 1981; Warneck, 1999)

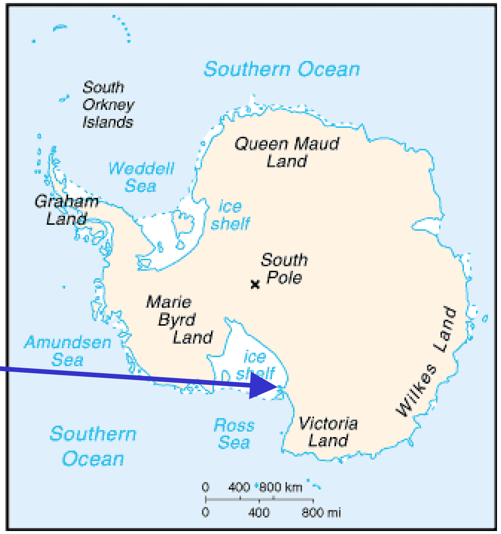
Acidity formation in the troposphere: sulfuric acid

pH dependent oxidations,
because in individual steps of the reactions of $SO_{2\,aqu}$, $HSO^{-}_{3\,aqu}$ and $SO^{2-}_{3\,aqu}$ (which are present in pH-dependent fraction according to K_{S1}, K_{S2}) is H^{+}_{aqu} consumed or formed.



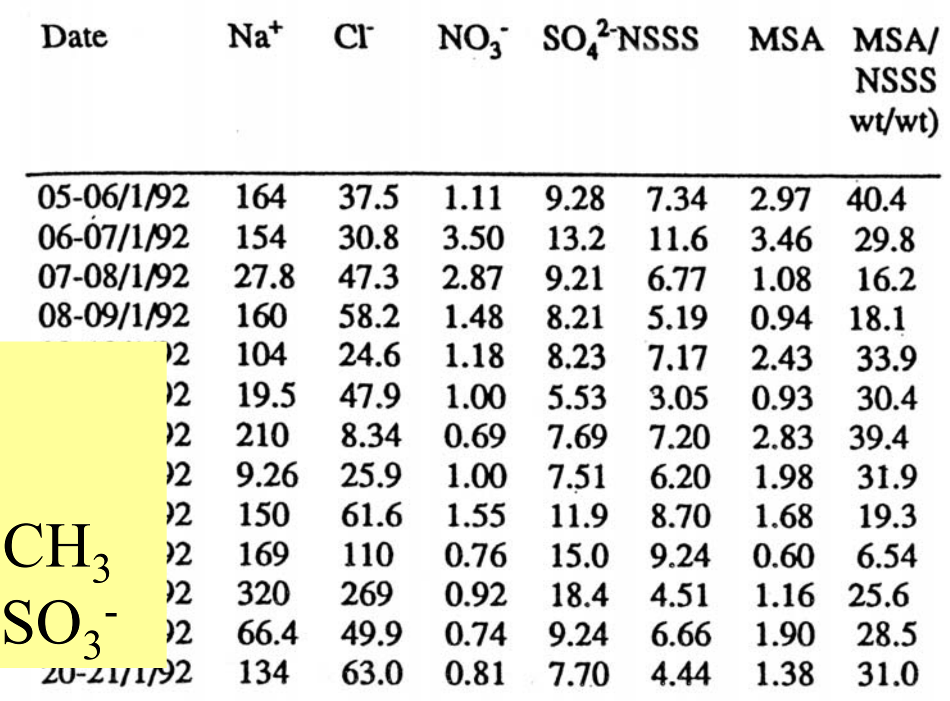
for $L = V_{H2O(l)}/V = 3x10^{-6}$ (Seinfeld, Calvert)

Sulfuric acid: precursors other than anthropogenic SO_2



Aerosol constituents
McDonald Beach
[nmol/m³]

seasalt-S(VI)/Cl^- = 0.051



Date	Na^+	Cl^-	NO_3^-	SO_4^{2-}	NSSS	MSA	MSA/ NSSS wt/wt)
05-06/1/92	164	37.5	1.11	9.28	7.34	2.97	40.4
06-07/1/92	154	30.8	3.50	13.2	11.6	3.46	29.8
07-08/1/92	27.8	47.3	2.87	9.21	6.77	1.08	16.2
08-09/1/92	160	58.2	1.48	8.21	5.19	0.94	18.1
2	104	24.6	1.18	8.23	7.17	2.43	33.9
2	19.5	47.9	1.00	5.53	3.05	0.93	30.4
2	210	8.34	0.69	7.69	7.20	2.83	39.4
2	9.26	25.9	1.00	7.51	6.20	1.98	31.9
2	150	61.6	1.55	11.9	8.70	1.68	19.3
2	169	110	0.76	15.0	9.24	0.60	6.54
2	320	269	0.92	18.4	4.51	1.16	25.6
2	66.4	49.9	0.74	9.24	6.66	1.90	28.5
20-21/1/92	134	63.0	0.81	7.70	4.44	1.38	31.0

Terminology:
- NSSS = non-sea salt sulfate
- DMS = dimethylsulfide , CH_3SCH_3
- MSA = methanesulfonate, $CH_3SO_3^-$

3.3.4 Dimethylsulfide

3.3.4.1 Formation of carbonyl sulfide

(Gas-phase chemistry)

(1) $CH_3SCH_3 + OH \rightarrow CH_3SCH_2\cdot + H_2O$

$CH_3SCH_2\cdot + O_2 + M \rightarrow CH_3SCH_2OO\cdot + M$

(2) $CH_3SCH_2OO\cdot + NO \rightarrow CH_3SCH_2O\cdot + NO_2$

(3a) $CH_3SCH_2O\cdot \rightarrow HCHO + \boxed{CH_3S\cdot}$ **major**

(3b) $+ O_2 \rightarrow CH_3SCHO + HO_2\cdot$ **minor**

(4b) $CH_3SCHO + OH\cdot \rightarrow CH_3\cdot + COS + H_2O$

In DMS oxidation the COS yield is much smaller than 1 COS/CH_3SCH_3 because of reaction decomposition of the alkoxy radical, CH_3SCH_2O, and as much of the intermediate products are washed out (τ < week)

Other carbonyl sulfide, COS, sources

(1a) $CS_2 + OH + O_2 \rightarrow COS + SO_2 + H\cdot$

(1b) $+ h\nu \rightarrow CS_2^*$

(2b) $CS_2^* + O_2 \rightarrow COS + O\cdot$

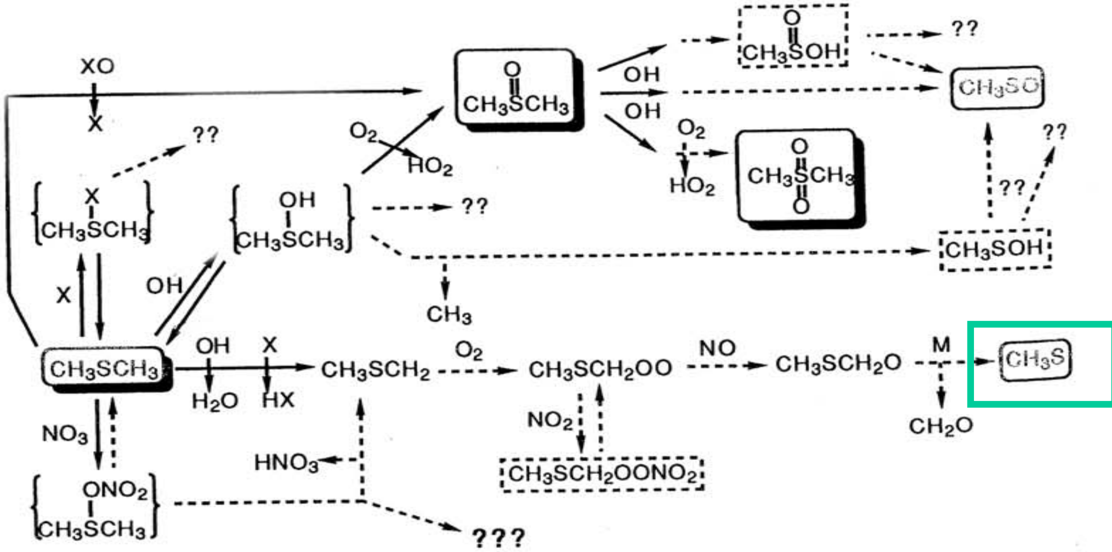
(Crutzen, 1983)

Significance of COS

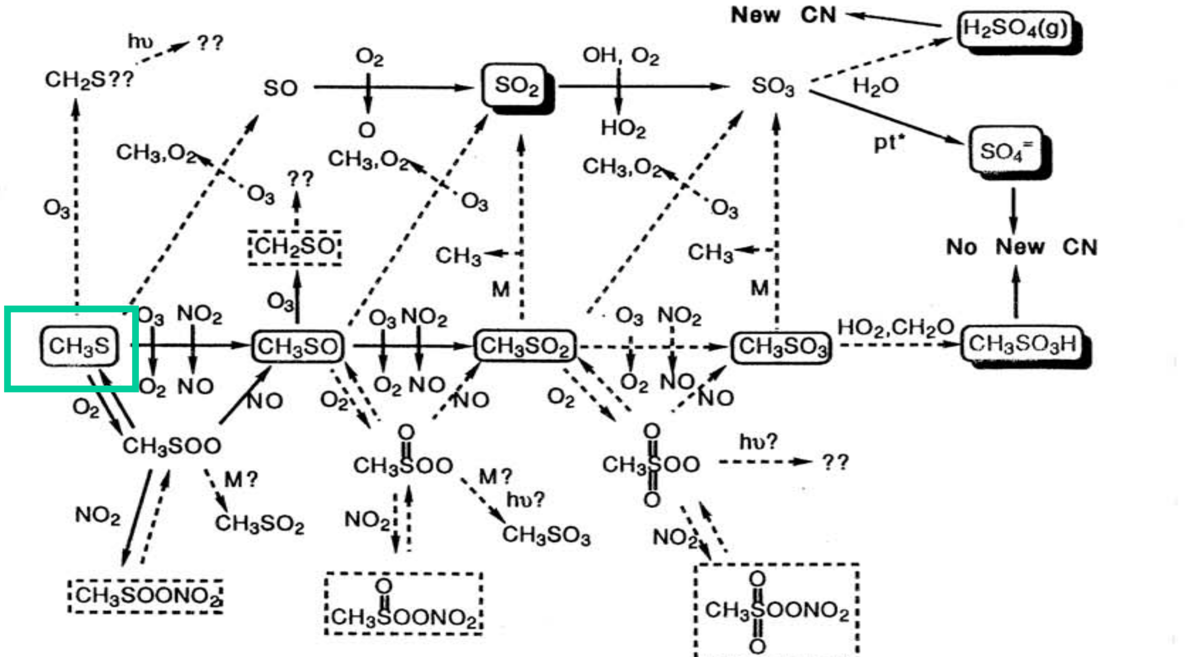
As $\tau_{COS} \approx$ years it is transported globally and reaches the stratosphere. Its photolysis there produces SO_2 and H_2SO_4 and explains the stratopsheric sulfate layer during periods of low volcanic activity

3.3.4.2 Formation of SO_2

in the marine boundary layer:
$CH_3SCH_3 \rightarrow \rightarrow CH_3S^{\cdot}$

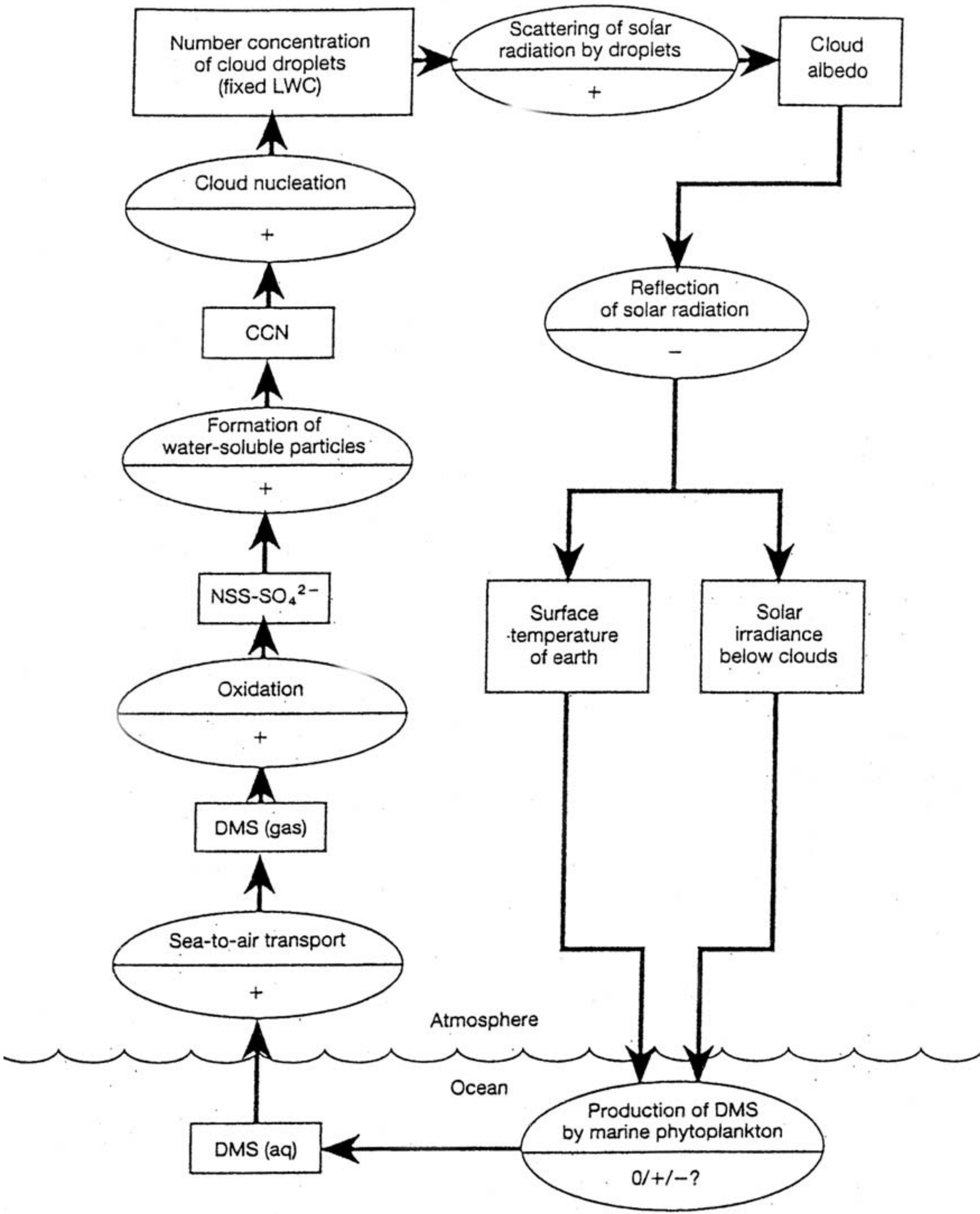


$CH_3S^{\cdot} \rightarrow \rightarrow$
$S(IV) \rightarrow \rightarrow S(VI)$



Hypothetical neg. feedback mechanism in the marine boundary layer (so-called CLAW hypothesis): CH_3SCH_3 → clouds →● radiation → phytoplankton →

(Charlson et al., 1987)



1.5.2 Heterogeneous reactions in the gas/water droplet system
1.5.2.1 In phase equilibrium

Acidity formation in the troposphere: sulfuric acid

Example: $c_{SO2} = 2$ nmol m^{-3}, $c_{H2O2} = 40$ nmol m^{-3}, T = 298 K
(near Bermuda 1988)

1. Gas-phase: $dc_{S(VI)}/dt = 5.6x10^{-6}$ nmol m^{-3} s^{-1}

2. Aqueous phase:

$$dc_{SO4--}/dt = k_4\, p_{H2O2}\, K_{H\ H2O2}\, p_{SO2}\, K^*_{H\ SO2}\ (M\ s^{-1})$$

$$K^*_{H\ SO2} = K_{H\ SO2}\ x\ (1 + K_{S1} / c_{H+} + K_{S1}K_{S2} / c^2_{H+})$$

$$dc_{S(VI)}/dt = dc_{S(VI)}/dt\ (M\ s^{-1})\ x\ L\ (L\ m^{-3})\ x\ 10^9\ (nmol\ mol^{-1}) =$$
$$= 32x10^{-6}\ nmol\ m^{-3}\ s^{-1}$$

1.5.2.2 Deviation from phase equilibrium due to kinetic limitations - mass transport considerations

Transfer from gas to aqueous phase treated like a chemical reaction (‚pseudo-reaction‘):

$$dc_{i\ aqu}/dt = k_{mt}\ (c_{i\ (g)} - c_{i\ aqu}/RTK_H^*)$$

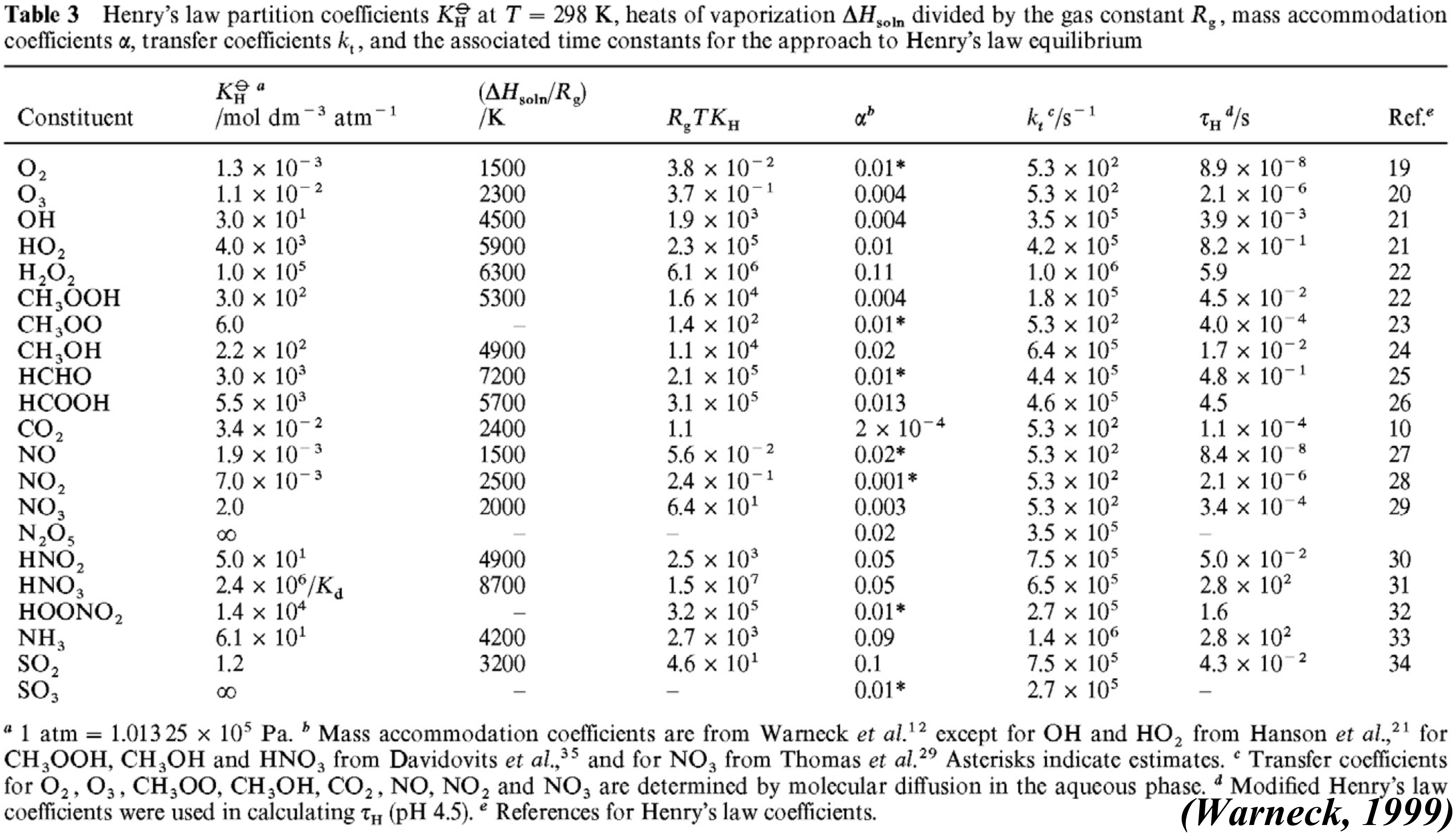


Table 3 Henry's law partition coefficients $K_H^{\ominus}$ at $T = 298$ K, heats of vaporization ΔH_{soln} divided by the gas constant R_g, mass accommodation coefficients α, transfer coefficients k_t, and the associated time constants for the approach to Henry's law equilibrium

Constituent	$K_H^{\ominus\ a}$ /mol dm^{-3} atm^{-1}	$(\Delta H_{soln}/R_g)$ /K	R_gTK_H	α^b	$k_t{}^c$/s^{-1}	$\tau_H{}^d$/s	Ref.^{e}
O_2	1.3×10^{-3}	1500	3.8×10^{-2}	0.01*	5.3×10^2	8.9×10^{-8}	19
O_3	1.1×10^{-2}	2300	3.7×10^{-1}	0.004	5.3×10^2	2.1×10^{-6}	20
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HO_2	4.0×10^3	5900	2.3×10^5	0.01	4.2×10^5	8.2×10^{-1}	21
H_2O_2	1.0×10^5	6300	6.1×10^6	0.11	1.0×10^6	5.9	22
CH_3OOH	3.0×10^2	5300	1.6×10^4	0.004	1.8×10^5	4.5×10^{-2}	22
CH_3OO	6.0	–	1.4×10^2	0.01*	5.3×10^2	4.0×10^{-4}	23
CH_3OH	2.2×10^2	4900	1.1×10^4	0.02	6.4×10^5	1.7×10^{-2}	24
HCHO	3.0×10^3	7200	2.1×10^5	0.01*	4.4×10^5	4.8×10^{-1}	25
HCOOH	5.5×10^3	5700	3.1×10^5	0.013	4.6×10^5	4.5	26
CO_2	3.4×10^{-2}	2400	1.1	2×10^{-4}	5.3×10^2	1.1×10^{-4}	10
NO	1.9×10^{-3}	1500	5.6×10^{-2}	0.02*	5.3×10^2	8.4×10^{-8}	27
NO_2	7.0×10^{-3}	2500	2.4×10^{-1}	0.001*	5.3×10^2	2.1×10^{-6}	28
NO_3	2.0	2000	6.4×10^1	0.003	5.3×10^2	3.4×10^{-4}	29
N_2O_5	∞	–	–	0.02	3.5×10^5	–	
HNO_2	5.0×10^1	4900	2.5×10^3	0.05	7.5×10^5	5.0×10^{-2}	30
HNO_3	$2.4 \times 10^6/K_d$	8700	1.5×10^7	0.05	6.5×10^5	2.8×10^2	31
$HOONO_2$	1.4×10^4	–	3.2×10^5	0.01*	2.7×10^5	1.6	32
NH_3	6.1×10^1	4200	2.7×10^3	0.09	1.4×10^6	2.8×10^2	33
SO_2	1.2	3200	4.6×10^1	0.1	7.5×10^5	4.3×10^{-2}	34
SO_3	∞	–	–	0.01*	2.7×10^5	–	

[a] 1 atm = 1.013 25 × 10^5 Pa. [b] Mass accommodation coefficients are from Warneck *et al.*[12] except for OH and HO_2 from Hanson *et al.*,[21] for CH_3OOH, CH_3OH and HNO_3 from Davidovits *et al.*,[35] and for NO_3 from Thomas *et al.*[29] Asterisks indicate estimates. [c] Transfer coefficients for O_2, O_3, CH_3OO, CH_3OH, CO_2, NO, NO_2 and NO_3 are determined by molecular diffusion in the aqueous phase. [d] Modified Henry's law coefficients were used in calculating τ_H (pH 4.5). [e] References for Henry's law coefficients.

(Warneck, 1999)

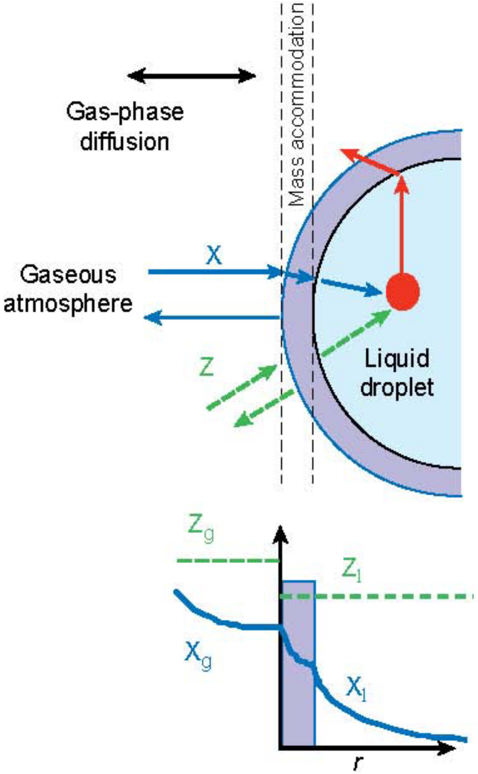
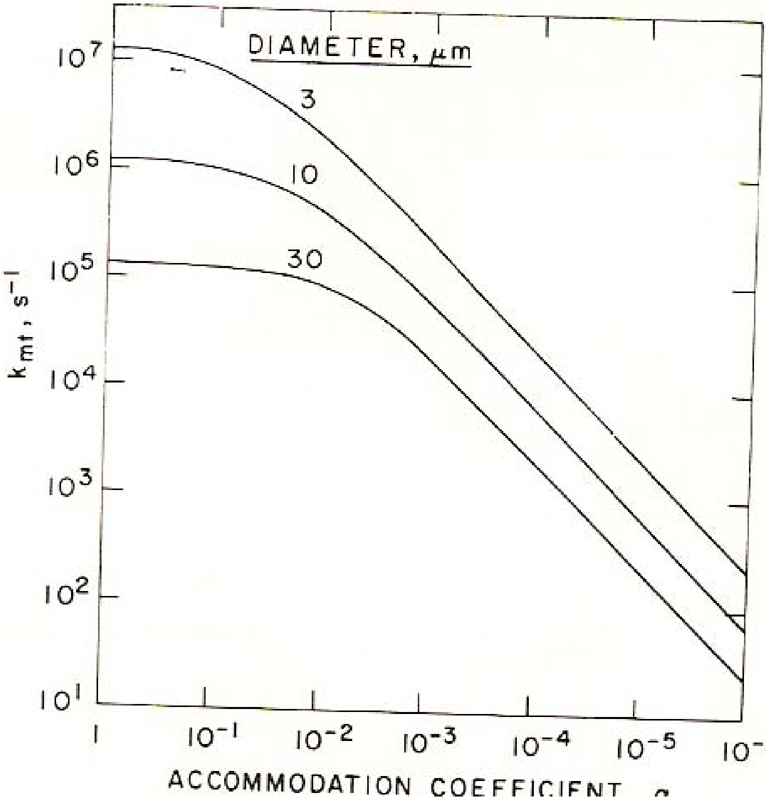


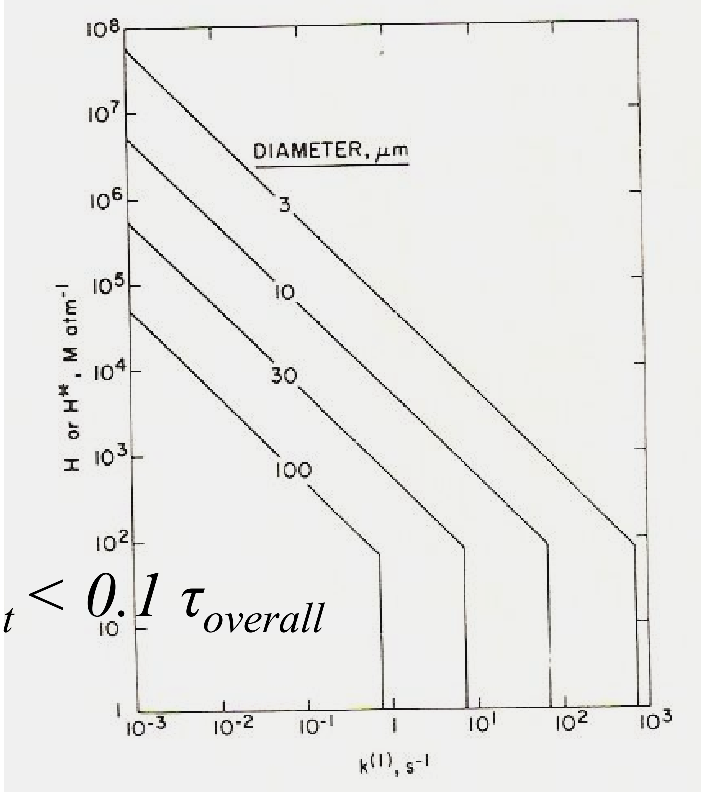
Fig. 4 (**Top**). Various physicochemical processes that control a multiphase reaction of a molecule X with another molecule Z in a liquid droplet. The subscripts *g* and l refer to gas and liquid phases. It is assumed that the concentration of Z in the liquid phase is controlled by the gas-phase abundance and its Henry's law solubility coefficient, *H*. The steps are described in the text and noted in the figure, except for the diffusion into and out of the liquid. (**Bottom**) The concentrations, in arbitrary units and different scales for gas and liquid phases, of species X and Z as a function of radial distance from the surface of a spherical droplet. It is assumed that there is no concentration gradient in either the gas or liquid

	Condensed phase: Liquid
Transport in the gas phase Initial interaction	$\Gamma_{g\,;}\ \tau_{dg} = r^2/(3D_g)$ Sat. after $K_H RT\ \tau_{dg}$
Reversible sorption	Accommodation coefficient α
Reaction on surface	*Reactive uptake coeff.* γ_r
Crossing of interface ('uptake', interfacial m.trp)	$\tau_i = 4r/(3<v>\alpha)$ Sat. after $\tau_H = K_H RT\ \tau_i$
Solvation Rapid chemical equilibrium	$\gamma_{sol} \approx 0$
Diffusion into bulk Reaction in bulk	$K_{aq;}\ \tau_{da} = r^2/(\pi^2 D_a)$
Reaction in bulk liquid	$\tau_r = c_A / (a\ \Delta c_A/\Delta t)$ for: $aA \rightarrow$

(Schwartz, 1986)

Kinetic description of mass transfer: water uptake





$\tau_{mt} < 0.1\ \tau_{overall}$

$k_{mt} = f(D, \alpha)$:

$K_{mt\ SO2} = 7.5\text{x}10^5\ s^{-1} (\alpha = 0.1)\ \tau_H = 0.043$ s

$K_{mt\ O3} = 5.3\text{x}10^2\ s^{-1} (\alpha = 0.004)\ \tau_H = 2.1\text{x}10^{-6}$ s

$K_{mt\ HCOOH} = 4.6\text{x}10^5\ s^{-1} (\alpha = 0.013)\ \tau_H = 4.5$ s

(Schwartz, 1986; Warneck, 1986)

Kinetic description of mass transfer: water uptake

Transfer from gas to aqueous phase treated like a chemical reaction (‚pseudo-reaction‘):

$$dc_{i\ aqu}/dt = k_{mt}\ (c_{i\ (g)} - c_{i\ aqu}/RTK_H{}^*)$$

with mass transfer rate coefficient $k_{mt} = (\Sigma_i\ \tau_{\ i})^{-1}$

- Slightly soluble gases (i.e. $RTK_H < 750$): Henry‘s law equilibrium rapidly established at the drop surface, transport rate limiting is diffusion within the drop: $k_{mt} \approx \tau_{da} = r^2/(\pi^2 D_a)$
- Soluble gases (i.e. $RTK_H > 750$): Henry‘s law equilibrium establishment limited by diffusion in the gas-phase and by transport through the interface: $k_{mt} \approx \tau_{da} = [r^2/(3D_g) + 4r/(3\alpha<v>)]^{\ -1}$

(Schwartz, 1986)

In more detail including dependency on mass transport kinetics
(accommodation coefficient α; Calvert et al., 1985):
L = 1 g/m³

Oxidants

a = 50 ppbv O_3 at –5°C
b = 50 ppbv O_3 at +15°C
c = 10^{-5} M Fe(III), 10^{-6} M Mn(II)
d = 10^{-7} M Fe(III), 10^{-8} M Mn(II)
e = OH_{aqu} α = 0.1,0.01, or 0.001
f = 1ppbv H_2O_2 at –5°C
g = 1ppbv H_2O_2 at +15°C
h = 1ppbv CH_3OOH at –5°C
i = 1ppbv CH_3OOH at +15°C
j = 1ppbv $CH_3C(O)OOH$ at –5°C
k = 1ppbv $CH_3C(O)OOH$ at +15°C

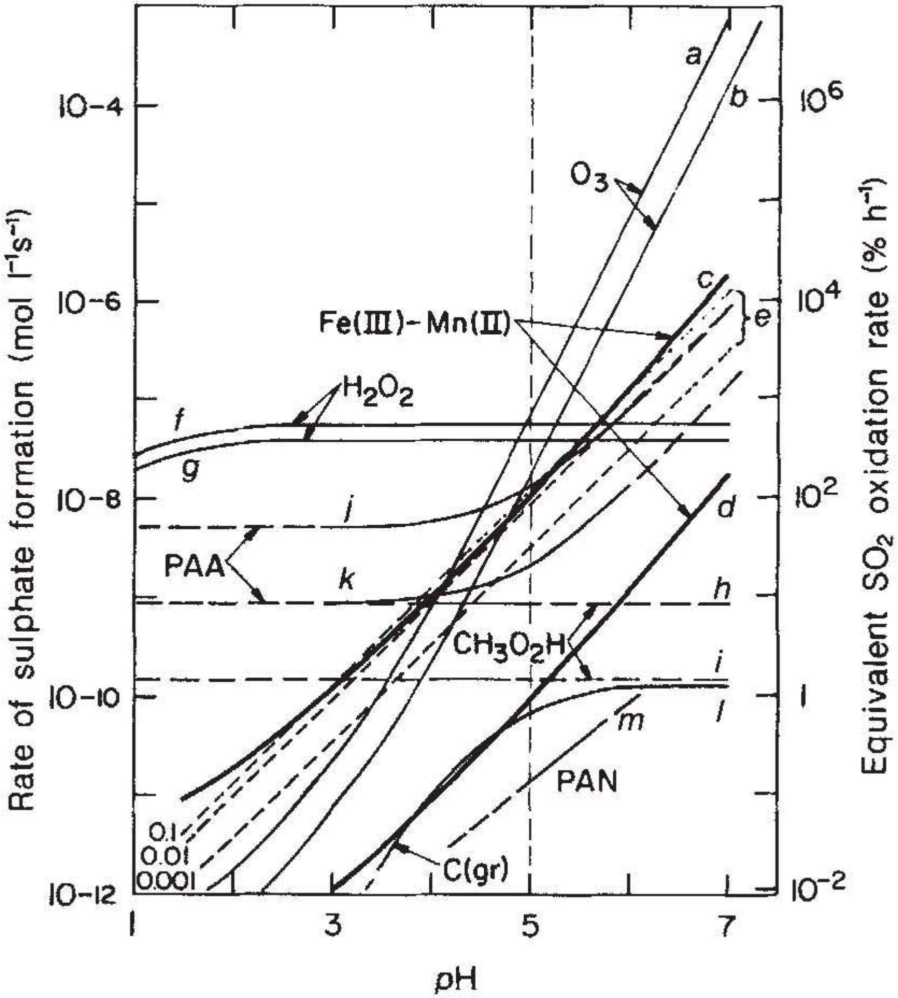


Fig. 6 Theoretical instantaneous rates of liquid-phase oxidation of S(IV); $SO_2(g)$ at 1 p.p.b. in equilibrium with cloud water; left-hand ordinate gives rates independent of the liquid water content (L) of the cloud; right-hand ordinate gives the equivalent gas-phase oxidation rate for SO_2 for a cloud with $L = 1\,g\,m^{-3}$; see text for the specific reactant conditions chosen for the calculations in curves a–m.

3.3.5 Deviation from air/water equilibrium due to organic films

Apart from kinetic control: Another reason for apparent deviation from gas-aqueous phase equilibrium is lipophilicity in combination with (organic) surface films

Example:
Fogwater in agricultural area, California, 1986

$c_{(g)}/c_{aqu}$
predicted (K_{aw}) vs. observed (D)

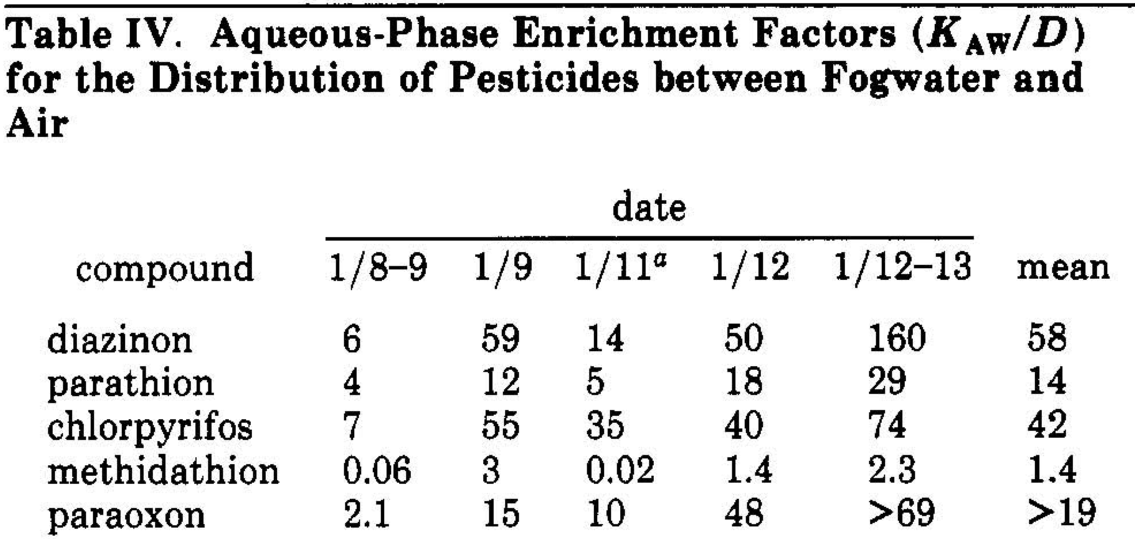
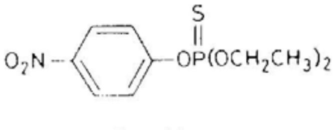
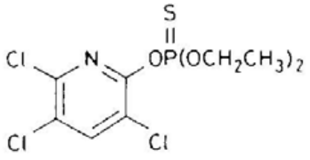


Table IV. Aqueous-Phase Enrichment Factors (K_{AW}/D) for the Distribution of Pesticides between Fogwater and Air

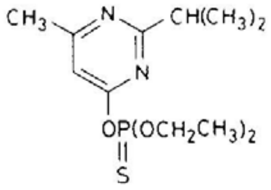
compound	date 1/8–9	 1/9	 1/11[a]	 1/12	 1/12–13	mean
diazinon	6	59	14	50	160	58
parathion	4	12	5	18	29	14
chlorpyrifos	7	55	35	40	74	42
methidathion	0.06	3	0.02	1.4	2.3	1.4
paraoxon	2.1	15	10	48	>69	>19



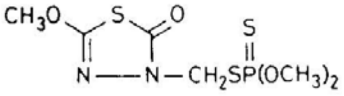
Parathion



Chlorpyrifos



Diazinon



Methidathion

(Glotfelty et al., 1990)

3.3.6 Tropospheric ozone and clouds

Ozone reactions

(1a) $O_{3\,aqu} + OH^-_{aqu} \rightarrow O^-_{2\,aqu} + HO_2{\cdot}_{aqu}$

(1b) $+ HO_2{\cdot}_{aqu} \rightarrow 2\,O_{2\,aqu} + OH{\cdot}_{aqu}$

(1c) $+ OH{\cdot}_{aqu} \rightarrow O_{2\,aqu} + HO_2{\cdot}_{aqu}$

(2a) $HO_2{\cdot}_{aqu} + OH{\cdot}_{aqu} \rightarrow O_{2\,aqu} + H_2O$

(2b) $+ HO_2{\cdot}_{aqu} \rightarrow O_{2\,aqu} + H_2O_2$

(3b) $H_2O_2 + h\nu \rightarrow 2\,OH{\cdot}_{aqu}$

TABLE 1 Gas-phase, gas–liquid equilibrium and aqueous-phase reactions

Gas-phase reactions				Rate constant*		Ref.
G1	$O_3 + h\nu$	$\rightarrow$	$O(^1D) + O_2$	1.6×10^{-5}		27
G2	$O_3 + h\nu$	$\rightarrow$	$O + O_2$	3.6×10^{-4}		27
G3	$NO_2 + h\nu$	$\rightarrow$	$NO + O$	5.6×10^{-3}		27
G4	$H_2O_2 + h\nu$	$\rightarrow$	$2OH$	4.6×10^{-6}		27
G5	$CH_2O + h\nu + 2O_2$	$\rightarrow$	$2HO_2 + CO$	1.7×10^{-5}		27
G6	$CH_2O + h\nu$	$\rightarrow$	$H_2 + CO$	3.3×10^{-5}		27
G7	$CH_3OOH + h\nu + O_2$	$\rightarrow$	$CH_2O + HO_2 + OH$	4.6×10^{-6}		27
G8	$NO_3 + h\nu$	$\rightarrow$	$NO + O_2$	1.4×10^{-2}		27
G9	$NO_3 + h\nu + O_2$	$\rightarrow$	$NO_2 + O_3$	1.2×10^{-1}		27
G10	$HNO_3 + h\nu$	$\rightarrow$	$NO_2 + OH$	3.2×10^{-7}		27
G11	$N_2O_5 + h\nu$	$\rightarrow$	$NO_2 + NO_3$	2.7×10^{-5}		27
G12	$O(^1D) + M$	$\rightarrow$	$O + M$	$2.0 \times 10^{-11} \exp(100/T)$		27
G13	$O + O_2(+M)$	$\rightarrow$	$O_3(+M)$	1.5×10^{-15}		27
G14	$O(^1D) + H_2O$	$\rightarrow$	$2OH$	2.2×10^{-10}		27
G15	$O_3 + NO$	$\rightarrow$	$NO_2 + O_2$	$2.0 \times 10^{-12} \exp(-1{,}400/T)$		27
G16	$O_3 + HO_2$	$\rightarrow$	$OH + 2O_2$	$1.1 \times 10^{-14} \exp(-500/T)$		27
G17	$O_3 + OH$	$\rightarrow$	$HO_2 + O_2$	$1.6 \times 10^{-12} \exp(-940/T)$		27
G18	$NO_2 + OH(+M)$	$\rightarrow$	$HNO_3(+M)$	1.2×10^{-11}		27
G19	$HO_2 + OH$	$\rightarrow$	$H_2O + O_2$	$4.6 \times 10^{-11} \exp(230/T)$		27
G20	$H_2O_2 + OH$	$\rightarrow$	$HO_2 + H_2O$	$3.3 \times 10^{-12} \exp(-200/T)$		27
G21	$HO_2 + HO_2$	$\rightarrow$	$H_2O_2 + O_2$	$2.3 \times 10^{-13} \exp(600/T)$		27
G22	$HO_2 + NO$	$\rightarrow$	$NO_2 + OH$	$3.7 \times 10^{-12} \exp(240/T)$		27
G23	$NO_2 + O_3$	$\rightarrow$	$NO_3 + O_2$	$1.4 \times 10^{-13} \exp(-2{,}500/T)$		27
G24	$NO + NO_3$	$\rightarrow$	$2NO_2$	$1.7 \times 10^{-11} \exp(150/T)$		27
G25	$NO_2 + NO_3(+M)$	$\rightarrow$	$N_2O_5(+M)$	$8.1 \times 10^{-11} (T/300)^{-4.1}$		28
G26	$N_2O_5(+M)$	$\rightarrow$	$NO_2 + NO_3(+M)$	$4.6 \times 10^{16} (T/300)^{-4.4} \exp(-11{,}080/T)$		28
G27	$CH_4 + OH + O_2(+M)$	$\rightarrow$	$CH_3O_2 + H_2O\ (+M)$	$2.3 \times 10^{-12} \exp(-1{,}700/T)$		27
G28	$CH_3O_2 + NO + O_2$	$\rightarrow$	$CH_2O + HO_2 + NO_2$	$4.2 \times 10^{-12} \exp(180/T)$		27
G29	$CH_3O_2 + HO_2$	$\rightarrow$	$CH_3OOH + O_2$	4.0×10^{-12}		29
G30	$CH_3O_2 + HO_2$	$\rightarrow$	$CH_2O + H_2O + O_2$	2.0×10^{-12}		29
G31	$CH_2O + OH + O_2$	$\rightarrow$	$HO_2 + H_2O + CO$	1.1×10^{-11}		28
G32	$CH_3OOH + OH$	$\rightarrow$	$CH_2O + OH + H_2O$	4.4×10^{-12}		30
G33	$CH_3OOH + OH$	$\rightarrow$	$CH_3O_2 + H_2O$	5.6×10^{-12}		30
G34	$CO + OH + O_2$	$\rightarrow$	$CO_2 + HO_2$	2.4×10^{-13}		27
G35	$CH_3O_2 + CH_3O_2 + O_2$	$\rightarrow$	$2CH_2O + 2HO_2$	$1.9 \times 10^{-13} \exp(220/T)$		27
Gas–aqueous and aqueous-phase equilibria				K_{298}†	$-\Delta H/R$	Ref.
E1	HO_2 (gas)	$\rightleftharpoons$	HO_2 (aq)	2.0×10^{3}	6,600	31
E2	HO_2 (aq)	$\rightleftharpoons$	$O_2^- + H^+$	3.5×10^{-5}		32
E3	H_2O_2 (gas)	$\rightleftharpoons$	H_2O_2 (aq)	7.4×10^{4}	6,615	33
E4	O_3 (gas)	$\rightleftharpoons$	O_3 (aq)	1.1×10^{-2}	2,300	34
E5	CH_2O (gas)	$\rightleftharpoons$	$CH_2(OH)_2$	6.3×10^{3}	6,425	8
E6	$HCOOH$ (gas)	$\rightleftharpoons$	$HCOOH$ (aq)	3.7×10^{3}	5,700	35
E7	$HCOOH$ (aq)	$\rightleftharpoons$	$HCOO^- + H^+$	1.8×10^{-4}	−1,510	35
E8	CH_3OOH (gas)	$\rightleftharpoons$	CH_3OOH (aq)	2.2×10^{2}	5,653	33
E9	CH_3O_2 (gas)	$\rightleftharpoons$	CH_3O_2 (aq)	2.0×10^{3}	6,600	E9=E1‡
E10	HNO_3 (gas)	$\rightleftharpoons$	HNO_3 (aq)	2.1×10^{5}	8,700	36
E11	HNO_3 (aq)	$\rightleftharpoons$	$NO_3^- + H^+$	15.4		36
E12	NO (gas)	$\rightleftharpoons$	NO (aq)	1.9×10^{-3}	1,480	36
E13	NO_2 (gas)	$\rightleftharpoons$	NO_2 (aq)	6.4×10^{-3}	2,500	37
E14	NO_3 (gas)	$\rightleftharpoons$	NO_3 (aq)	15.0		12
E15	OH (gas)	$\rightleftharpoons$	OH (aq)	9.0×10^{3}		38
E16	CO_2 (gas)	$\rightleftharpoons$	CO_2 (aq)	3.4×10^{-2}	2,420	39
E17	CO_2 (aq)	$\rightleftharpoons$	$HCO_3^- + H^+$	4.5×10^{-7}	−1,000	39
Aqueous-phase reactions				K_{298}*	$-E_a/R$§	Ref.
A1	$H_2O_2 + h\nu$	$\rightarrow$	$2OH$	9.2×10^{-6}		‖
A2	$O_3 + h\nu + H_2O$	$\rightarrow$	$H_2O_2 + O_2$	3.2×10^{-5}		‖
A3	$CH_2(OH)_2 + OH + O_2$	$\rightarrow$	$H_2O + HCOOH + HO_2$	2.0×10^{9}	−1,500	40, 41
A4	$HCOOH + OH + O_2$	$\rightarrow$	$CO_2 + H_2O + HO_2$	1.6×10^{8}	−1,500	42
A5	$HCOO^- + OH + O_2$	$\rightarrow$	$CO_2 + OH^- + HO_2$	2.5×10^{9}	−1,500	43
A6	$O_3 + O_2^- + H_2O$	$\rightarrow$	$OH + 2O_2 + OH^-$	1.5×10^{9}	−1,500	44, 45
A7	$HO_2 + O_2^-$	$\rightarrow$	$HO_2^- + O_2$	1.0×10^{8}	−1,500	46
A8	$HO_2^- + H^+$	$\rightarrow$	H_2O_2	5.0×10^{10}	−1,500	2
A9	$H_2O_2 + OH$	$\rightarrow$	$HO_2 + H_2O$	2.7×10^{7}	−1,715	47
A10	$N_2O_5 + H_2O$	$\rightarrow$	$2HNO_3$			¶
A11	$CH_3O_2 + O_2^- + H_2O$	$\rightarrow$	$CH_3OOH + O_2 + OH^-$	5.0×10^{7}	−1,610	4
A12	$CH_3OOH + OH$	$\rightarrow$	$CH_3O_2 + H_2O$	2.7×10^{7}	−1,715	4
A13	$CH_3OOH + OH$	$\rightarrow$	$CH_2(OH)_2 + OH$	1.9×10^{7}	−1,860	4
A14	$HCO_3^- + OH$	$\rightarrow$	$H_2O + CO_3^-$	1.0×10^{7}	−1,500	48
A15	$HCO_3^- + O_2^-$	$\rightarrow$	$HO_2^- + CO_3^-$	1.5×10^{6}	−1,500	48
A16	$CO_3^- + H_2O_2$	$\rightarrow$	$HO_2 + HCO_3^-$	8.0×10^{5}	−2,800	49
A17	$CO_3^- + O_2^-$	$\rightarrow$	$O_2 + CO_3^{2-}$	4.0×10^{8}	−1,500	49

G, E and A are gas-phase reactions, gas–liquid equilibrium and aqueous-phase reactions, respectively. These are the most important reactions from the more extended reaction scheme n the model. Some reactions summarize several reaction steps. Aqueous-phase processes at mid-latitudes in the Northern Hemisphere are simulated at pH 4.5, for other latitudes in Table 2 pH 5 is adopted[50]. Photolysis rate coefficients and water vapour concentrations in clouds are kept equal to those during clear sky to emphasize photochemical differences. Daytime average hotolysis rates are applied. Accommodation coefficients, as used for gas-to-aqueous-phase transfer processes[14], are taken from refs 51–56. For those components with unknown ccommodation coefficients we assume a value of 0.05.

* Reaction rate constants of first-order reactions are in s^{-1}, of second-order reactions in the gas phase (G) in molecule $^{-1}$ cm^3 s^{-1}, in the aqueous phase (A) in mol^{-1} l s^{-1}. Photodissociation ate constants are calculated per season, latitude and altitude. The given values pertain to the Equator in July, at 700 mbar.

† K_{298} is in mol l^{-1} atm^{-1} for Henry's law constants and in mol l^{-1} for aqueous-phase equilibria. The temperature dependence is calculated by $K = K_{298} \exp[(-\Delta H/R)((1/T) - (1/298))]$.

‡ Assumed.

§ E_a values are taken from ref. 4.

‖ J.L., thesis in preparation.

¶ Gas-to-aqueous-phase transfer of N_2O_5 is limited by gas-phase diffusion and transfer through the interface. We assume that reaction A10 then occurs instantaneously, so that dissolution s irreversible.

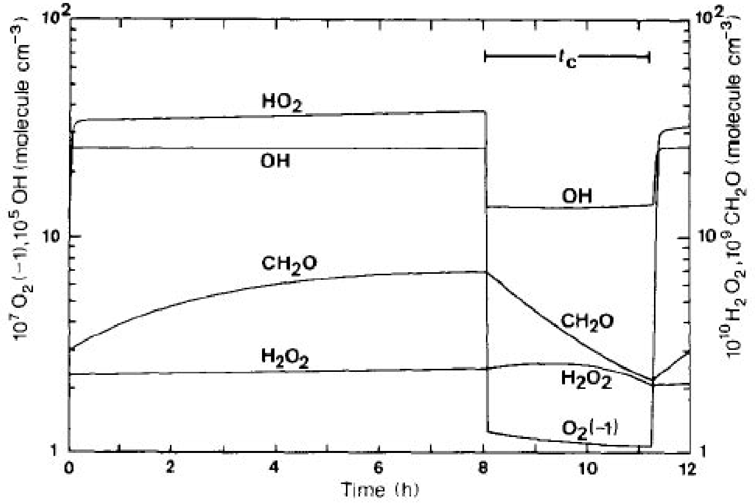


FIG. 2 Concentrations of some gases during sunlit hours of day 14 of the simulations, pertaining to the Equator at 3 km altitude (case 6, Table 2 and 3*a*), with NO_x fixed. For the cloudy period (t_c) total gas-phase plus aqueous-phase concentrations are depicted. $O_2(-1) = HO_2(gas) + HO_2(aq) + O_2^-$.

Differences in solubility and chemical reactivity in the aqueous phase result in changed (overall) chemistry of the atmosphe

pH dependent O_3 sink, e.g. A6 (Lelieveld & Crutzen, 1990)

3.3.7 Nitrogen compounds in the aqueous phase

Acidity formation in the troposphere: N

during the day: $NO_2 + OH \rightarrow HNO_3$
during night: $NO_2 + NO_3 = N_2O_5$

phase equilibria of N(-III), N(IV), N(V) species:
$NH_3 = NH_{3\ aqu.}$
$HNO_3 = HNO_{3\ aqu}$
$N_2O_5 = N_2O_{5\ aqu}$

dissociation, hydration N(-III), N(V):
$NH_{3\ aqu} + H_2O \rightarrow NH_4^+{}_{aqu} + OH^-{}_{aqu}$
$HNO_{3\ aqu} + H_2O \rightarrow H_3O^+{}_{aqu} + NO_3^-{}_{aqu}$
$2\ NO_2 + 3\ H_2O \rightarrow NO_2^-{}_{aqu} + NO_3^-{}_{aqu} + 2\ H_3O^+{}_{aqu;}$ slow (Lee & Schwartz, 1981)
$N_2O_{5\ aqu} + 3\ H_2O \rightarrow 2\ H_3O^+{}_{aqu} + 2\ NO_3^-{}_{aqu}$

more phase equilibria of N(-III), N(IV), N(V) species:

$HNO_2 = HNO_{2\ aqu}$

$HNO_4 = HNO_{4\ aqu}$

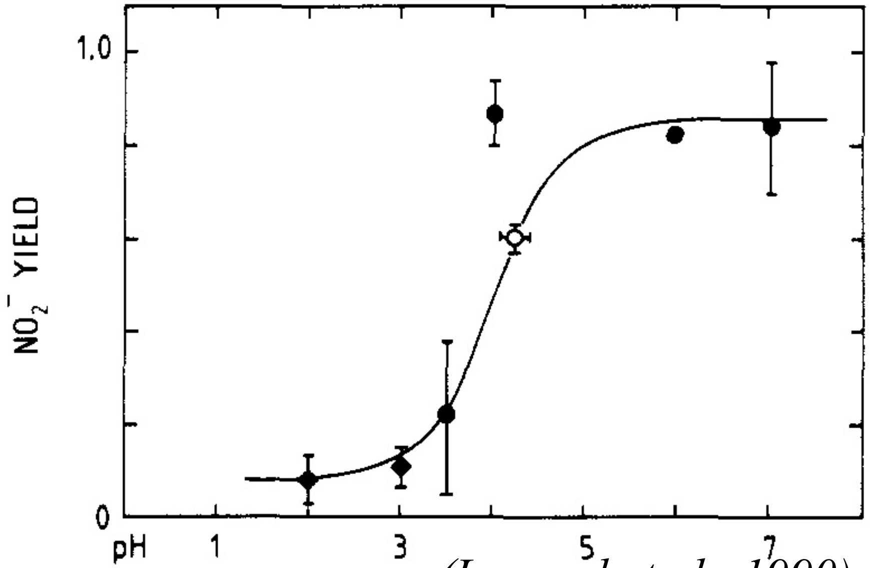
dissociation, hydration N(-III), N(V):

$HNO_{2\ aqu} + H_2O = H_3O^+_{aqu} + NO_2^-{}_{aqu}$ $K_S = 0.6\text{x}10^{-5}$ M

$HNO_{4\ aqu} + H_2O = H_3O^+_{aqu} + NO_4^-{}_{aqu}$ $K_S = 1.0\text{x}10^{-5}$ M

$HNO_{4\ aqu} = HO_2\cdot_{aqu} + NO_{2\ aqu}$ $K_S = 4.6\text{x}10^{-10}$ M

$NO_4^-{}_{aqu} \rightarrow O_{2\ aqu} + NO_2^-{}_{aqu}$ $k = 1.4\text{x}10^{-2}\ s^{-1}$



(Lammel et al., 1990)

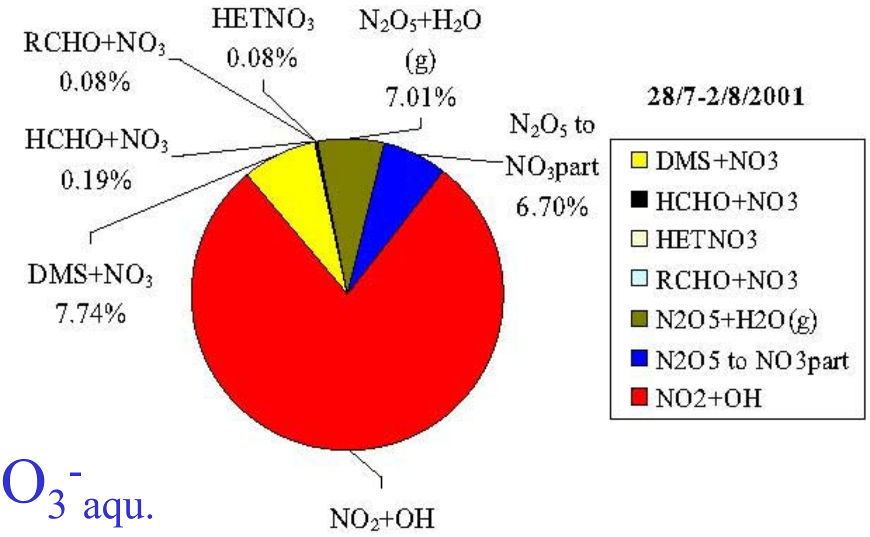
HNO_3 production: sources

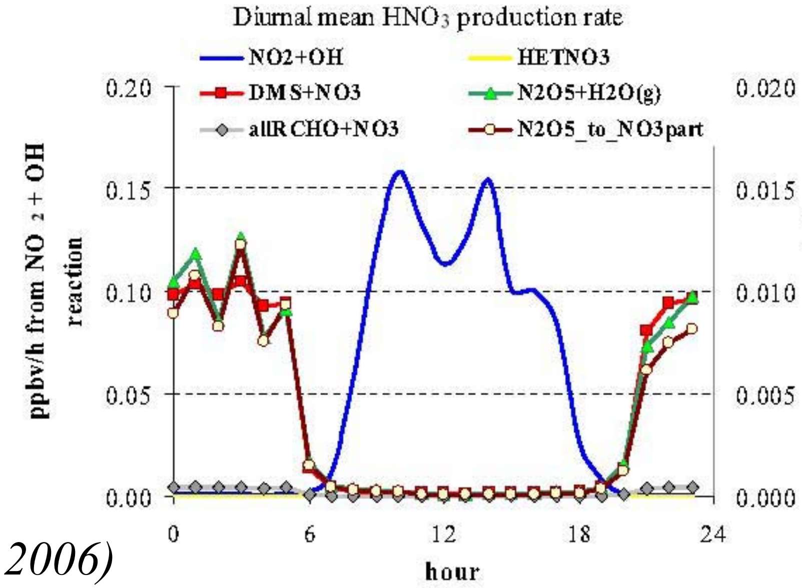
(1a) $NO_2 + {}^{\cdot}OH \rightarrow HNO_3$ *(day)*

(1b) $NO_2 + NO_3^{\cdot} = N_2O_5$ *(night)*

(2b) dissolution + hydration:

$N_2O_5 + 2\ H_2O \rightarrow 2\ H_3O^+_{aqu.} + 2\ NO_3^-{}_{aqu.}$





Crete, 2001-03 *(Vrekoussis et al., 2006)*

N(III) and N(V) chemical sinks in the aqueous phase

(1) $HNO_{2\ aqu} + h\nu\ (< 390\ \mathrm{nm}) \rightarrow NO + OH\cdot_{aqu}$
(2) $+ OH\cdot_{aqu} \rightarrow NO_{2\ aqu} + H_2O$
(3) $+ R_2NH_{aqu} \rightarrow R_2NNO_{aqu} + H_2O$
(4) $NO_2^-{}_{aqu} + OH\cdot_{aqu} \rightarrow NO_{2\ aqu} + OH^-{}_{aqu}$
(5) $+ O_{2\ aqu} \rightarrow NO_3^-{}_{aqu} + O_{3\ aqu}$

(6) $NO_3^-{}_{aqu} + h\nu\ (< 350\ \mathrm{nm}) \rightarrow NO_2^-{}_{aqu} + OH\cdot_{aqu}$
(7) $\rightarrow NO_{2\ aqu} + O^-{}_{aqu}$

(Graedel & Weschler, 1981)

→ **Slower, than deposition**

3.3.8 Organic chemistry in the aqueous phase

Oxidation of organics

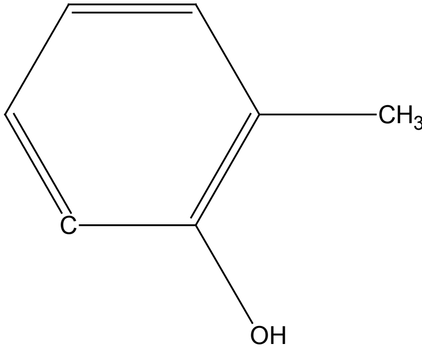
Aliphatic hydrocarbons:

(1) $RCH_{3\ aqu} + OH\cdot_{aqu} \rightarrow RCH_2\cdot_{aqu} + H_2O$

(1) $RCH_2OH_{aqu} + OH\cdot_{aqu} \rightarrow RCH\cdot OH_{aqu} + H_2O$
(2) $RCH\cdot OH_{aqu} + O_{2\ aqu} \rightarrow RCHO_{aqu} + HO_2\cdot_{aqu}$
(3) $RCHO_{aqu} + H_2O = RCH(OH)_{2\ aqu}$

Aromatic hydrocarbons:

(1) $\phi CH_3 + OH\cdot_{aqu} \rightarrow \phi CH_3(OH)\cdot$
(2) $\phi CH_3(OH)\cdot + O_{2\ aqu} \rightarrow \phi CH_3(OH) + HO_2\cdot_{aqu}$
$2\ HO_2\cdot_{aqu} \rightarrow O_{2\ aqu} + H_2O_2$
(6) $H_2O_2 + h\nu \rightarrow 2\ OH\cdot_{aqu}$



→ Similar to gas-phase chemistry in many regards, - but without NO

Acidity formation in the troposphere: carboxylic acids, example HCOOH

$NO_3^{\cdot} = NO_{3\,aqu}^{\cdot}$

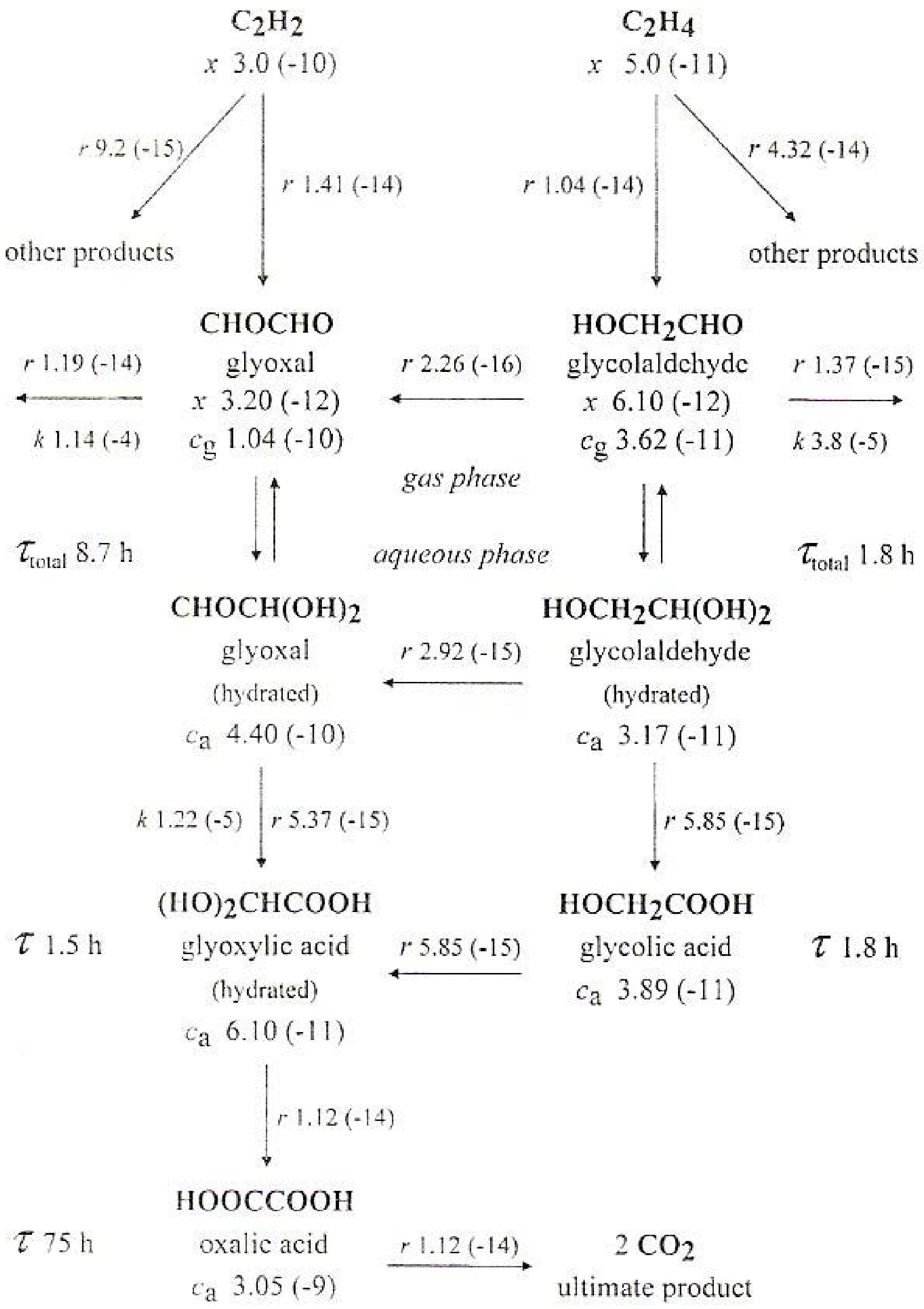
$HCHO*H_2O_{(aqu)} = HOCH_2OH_{(aqu.)}$

$NO_{3\,aqu}^{\cdot} + HOCH_2OH_{(aqu)} \rightarrow H_{4\,aqu}^{+} + NO_{3\,aqu}^{-} + HOCH_2O^{\cdot}_{aqu}$

$HOCH_2O^{\cdot}_{aqu} \rightarrow HO_{2\,(aqu)}^{\cdot} + HCOOH_{aqu}$

$2\ HO_{2\,aqu}^{\cdot} \rightarrow H_2O_{2\,aqu} + O_{2\,aqu}$

Acidity formation in the troposphere: Example oxalic acid



$r = k$ [mol m^{-3} s^{-1}] (Warneck, 2003)

Reactivity of organics in the aqueous phase: Overview OH reactions

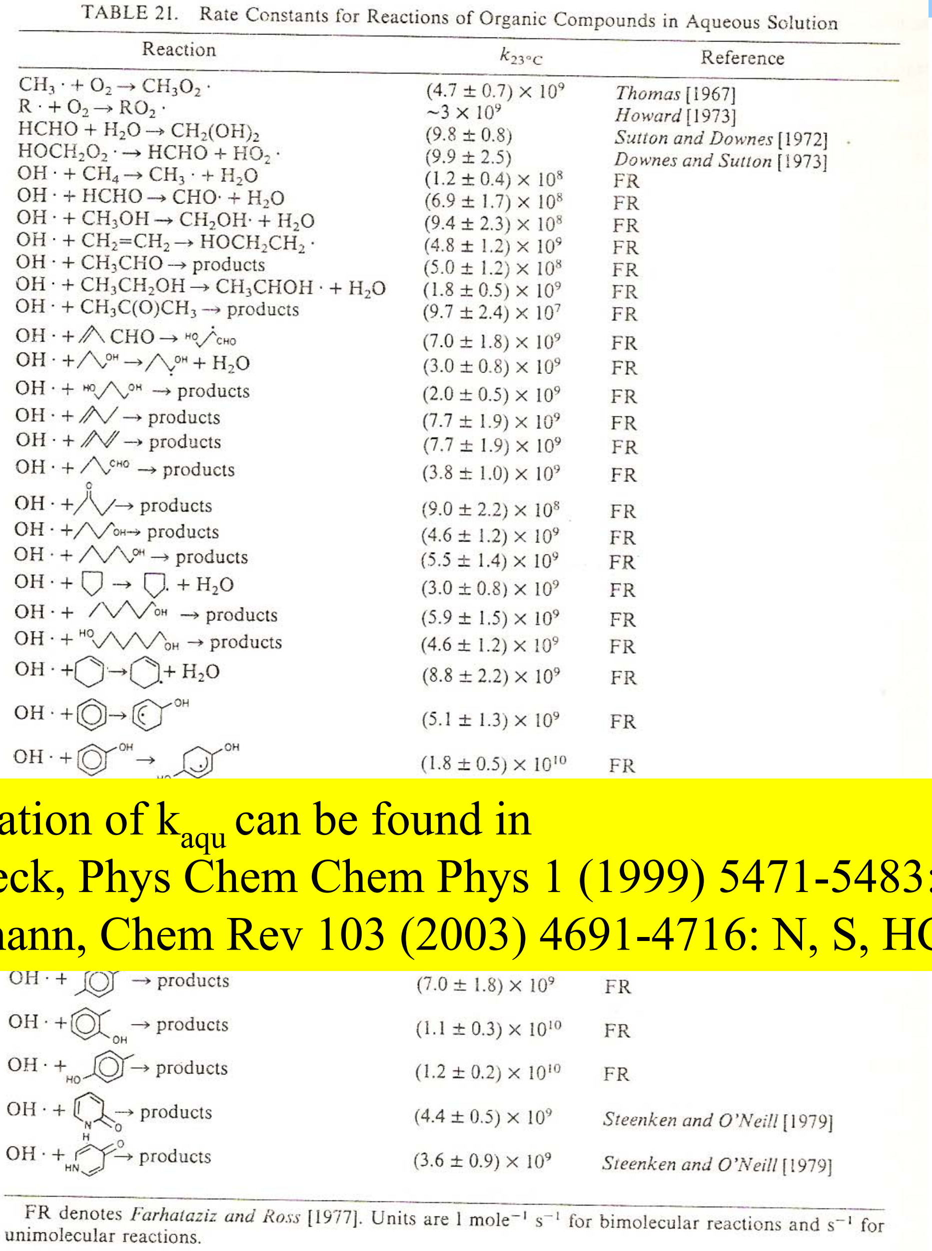


TABLE 21. Rate Constants for Reactions of Organic Compounds in Aqueous Solution

Reaction	$k_{23°C}$	Reference
$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot$	$(4.7 \pm 0.7) \times 10^9$	*Thomas* [1967]
$R\cdot + O_2 \rightarrow RO_2\cdot$	$\sim 3 \times 10^9$	*Howard* [1973]
$HCHO + H_2O \rightarrow CH_2(OH)_2$	(9.8 ± 0.8)	*Sutton and Downes* [1972]
$HOCH_2O_2\cdot \rightarrow HCHO + HO_2\cdot$	(9.9 ± 2.5)	*Downes and Sutton* [1973]
$OH\cdot + CH_4 \rightarrow CH_3\cdot + H_2O$	$(1.2 \pm 0.4) \times 10^8$	FR
$OH\cdot + HCHO \rightarrow CHO\cdot + H_2O$	$(6.9 \pm 1.7) \times 10^8$	FR
$OH\cdot + CH_3OH \rightarrow CH_2OH\cdot + H_2O$	$(9.4 \pm 2.3) \times 10^8$	FR
$OH\cdot + CH_2{=}CH_2 \rightarrow HOCH_2CH_2\cdot$	$(4.8 \pm 1.2) \times 10^9$	FR
$OH\cdot + CH_3CHO \rightarrow$ products	$(5.0 \pm 1.2) \times 10^8$	FR
$OH\cdot + CH_3CH_2OH \rightarrow CH_3CHOH\cdot + H_2O$	$(1.8 \pm 0.5) \times 10^9$	FR
$OH\cdot + CH_3C(O)CH_3 \rightarrow$ products	$(9.7 \pm 2.4) \times 10^7$	FR
OH · + CHO → HO CHO	$(7.0 \pm 1.8) \times 10^9$	FR
OH · + OH → OH + H_2O	$(3.0 \pm 0.8) \times 10^9$	FR
OH · + HO OH → products	$(2.0 \pm 0.5) \times 10^9$	FR
OH · + → products	$(7.7 \pm 1.9) \times 10^9$	FR
OH · + → products	$(7.7 \pm 1.9) \times 10^9$	FR
OH · + CHO → products	$(3.8 \pm 1.0) \times 10^9$	FR
OH · + O → products	$(9.0 \pm 2.2) \times 10^8$	FR
OH · + OH → products	$(4.6 \pm 1.2) \times 10^9$	FR
OH · + OH → products	$(5.5 \pm 1.4) \times 10^9$	FR
OH · + → . + H_2O	$(3.0 \pm 0.8) \times 10^9$	FR
OH · + OH → products	$(5.9 \pm 1.5) \times 10^9$	FR
OH · + HO OH → products	$(4.6 \pm 1.2) \times 10^9$	FR
OH · + → . + H_2O	$(8.8 \pm 2.2) \times 10^9$	FR
OH · + → OH	$(5.1 \pm 1.3) \times 10^9$	FR
OH · + OH → OH	$(1.8 \pm 0.5) \times 10^{10}$	FR
OH · + → products	$(7.0 \pm 1.8) \times 10^9$	FR
OH · + OH → products	$(1.1 \pm 0.3) \times 10^{10}$	FR
OH · + HO → products	$(1.2 \pm 0.2) \times 10^{10}$	FR
OH · + N H O → products	$(4.4 \pm 0.5) \times 10^9$	*Steenken and O'Neill* [1979]
OH · + HN O → products	$(3.6 \pm 0.9) \times 10^9$	*Steenken and O'Neill* [1979]

FR denotes *Farhataziz and Ross* [1977]. Units are l $mole^{-1}$ s^{-1} for bimolecular reactions and s^{-1} for unimolecular reactions.

Compilation of k_{aqu} can be found in

- Warneck, Phys Chem Chem Phys 1 (1999) 5471-5483: N, S chemistry
- Herrmann, Chem Rev 103 (2003) 4691-4716: N, S, HC_x chemistry

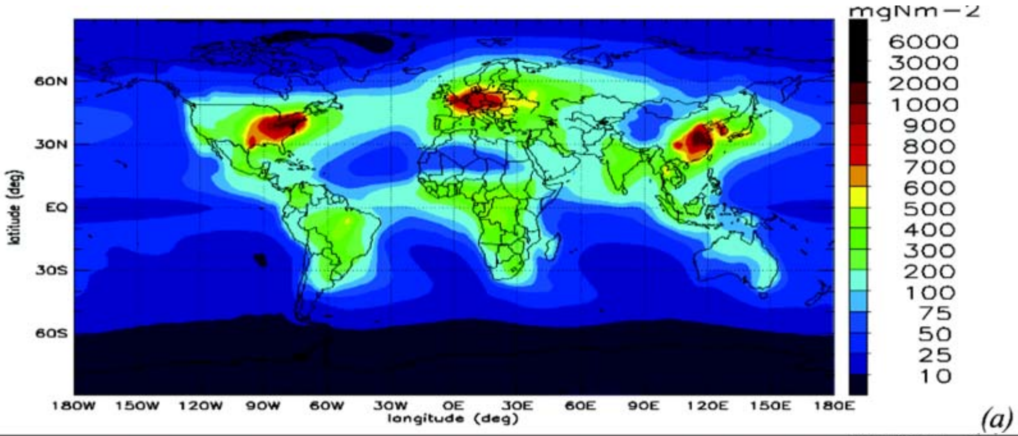
[L/M/s]

(Graedel & Weschler, 1981)

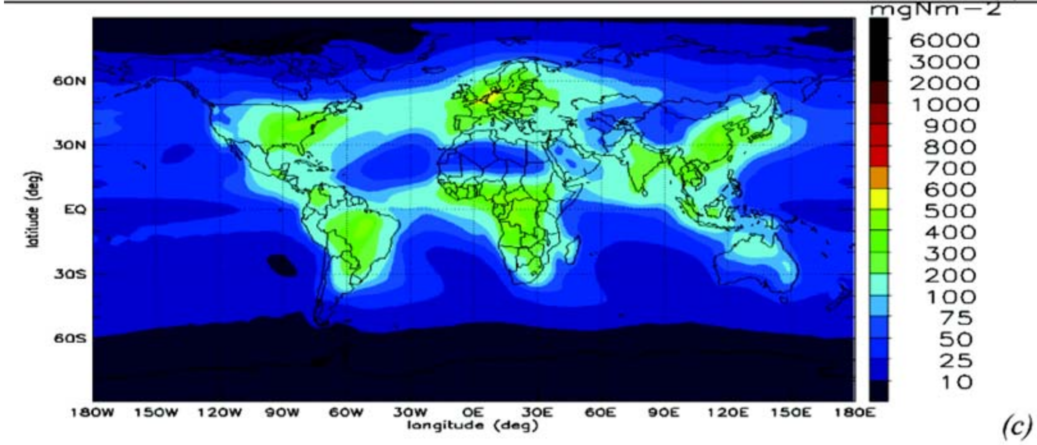
3.3.9 Impacts of atmospheric acidity in ecosystems

acid deposition,
example NO_y trends

2000



2030 under MFR



[mg N/m²/a]
(Dentener et al., 2006)

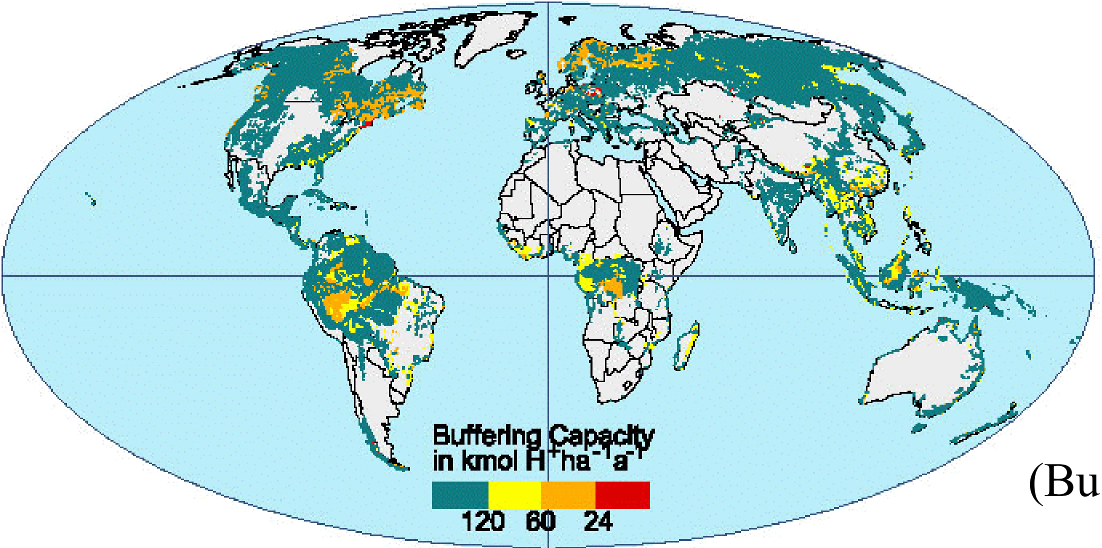
TABLE 1. Overview of Simulations, Prescribed Methane Volume Mixing Ratios, and Global Anthropogenic Emissions of CO, NMVOC, NO_x, SO_2, and NH_3[a]

simulation	meteorology	description	CH_4 [ppb]	CO	NMVOC	NO_x (NO_2)	SO_2	NH_3
S1-B2000	CTM 2000 GCM SSTs 1990s	baseline	1760	977.0	147.1	124.8	111.1	64.8
S2-CLE/CLEc	CTM 2000 GCM SSTs 1990s	IIASA CLE 2030, current legislation scenario	2088	904.1	145.5	141.1	117.6	84.8
S3-MFR	CTM 2000 GCM SSTs 1990s	IIASA MFR 2030, maximum feasible reduction scenario	1760	728.7	104.4	76.0	35.8	84.8
S4-A2	CTM 2000 GCM SSTs 1990s	SRES A2 2030, the most 'pessimistic' IPCC SRES scenario	2163	1268.2	206.7	206.7	202.3	89.2

Impacts of atmospheric acidity: acidification of soils

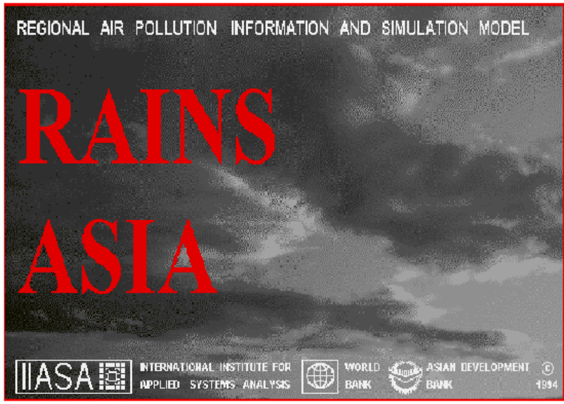
Deposition of nitrogen and sulphur compounds and their corresponding production of acidity in a nitrogen unsaturated plant-soil-system

Deposited individual ion	**H^+-Production [mol/mol]**	**Deposited species**	**H^+-Production [mol/mol]**
H^+	+1	$[NH_4]_2SO_4$/ NH_4NO_3	+2 / 0
NH_4^+	+1	H_2SO_4/HNO_3	+2 / 0
NO_3^-	-1	H_2SO_4/ NH_4NO_3	+2 / 0
SO			



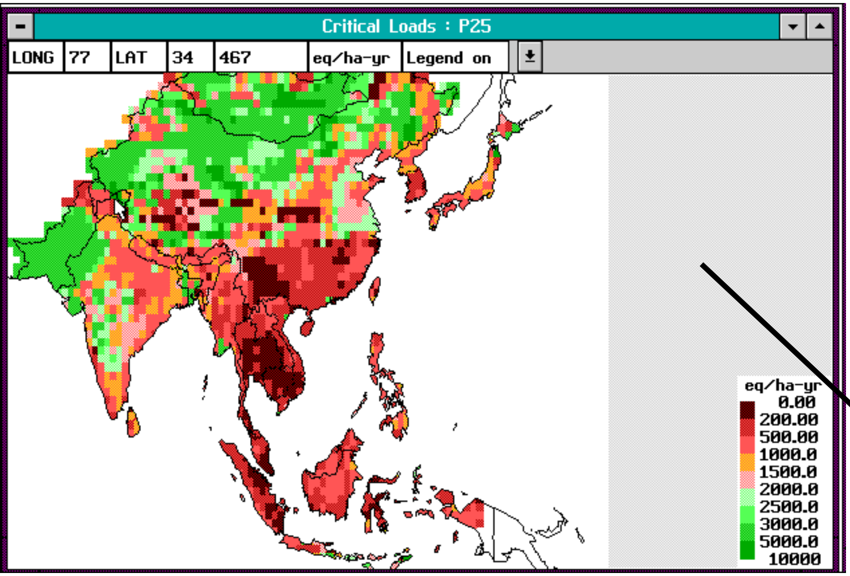
(Busch et al., 2001)

Deposition of acid: Effects in soils



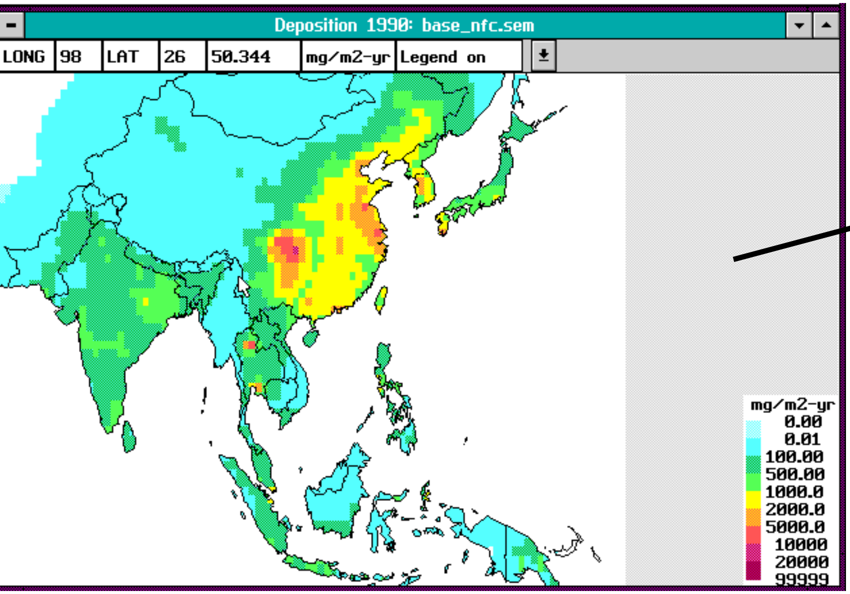
REGIONAL AIR POLLUTION INFORMATION AND SIMULATION MODEL

RAINS
ASIA



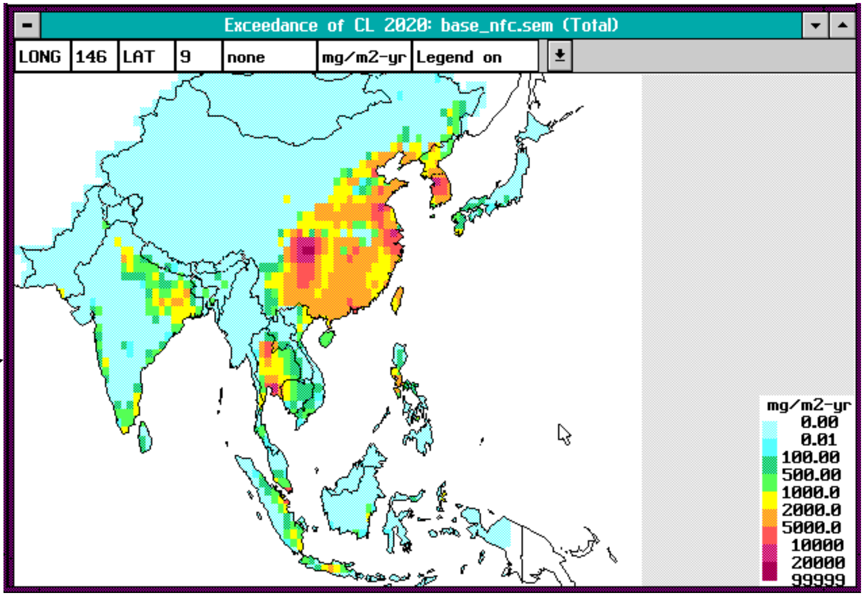
Critical Loads : P25

LONG 77 LAT 34 467 eq/ha-yr Legend on



Deposition 1990: base_nfc.sem

LONG 98 LAT 26 50.344 mg/m2-yr Legend on



Exceedance of CL 2020: base_nfc.sem (Total)

LONG 146 LAT 9 none mg/m2-yr Legend on

Critical loads concept to protect ecosystems

- Mapping of critical loads „...below which harmful effects in ecosystem structure and function do not occur according to present knowledge“
- which loads of pollutants and combinations thereof will not cause adverse effects, do not exceed ecosystem resilience (*PNEC*) ?
- \+ Protection of vulnerable areas is possible (protection of 95% of the area is common)
- \+ Accounts for dynamics (→ *Sustainability*), mostly however based on steady state-assumption and therefore neglecting the very slow dynamics of the soils
- \- Scale problems when matching exposure (deposition model output) and vulnerabilities (mapped ecosystems)
- \- normative steps are not transparent

•Integrated Assessment Modelling (IAM) under the auspices of the Convention on Long-range Transboundary Air Pollution (CLRTAP): Study various scenarios comprising emissions and related abatement costs + depositions and related exceedances of thresholds (Alcamo et al., 1987, besides others)