Atmospheric Chemistry Cheat Sheet

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If you find an error or know of other resources that could go here, email Jose at jose.jimenez@colorado.edu (And thanks for input from many people already!)

1. Key Conversions and Parameters

Conversions between mixing ratios and molec cm^{-3}

- Values at 1 atm and 298 K (Ref: Finlayson-Pitts & Pitts, p. 34).
    - 1 atm ~ 2.46×10^{19} molec cm^{-3}
    - 1% ~ 2.46×10^{17} molec cm^{-3}
    - 1 ppm ~ 2.46×10^{13} molec cm^{-3}
    - 1 ppb ~ 2.46×10^{10} molec cm^{-3}
    - 1 ppt ~ 2.46×10^{7} molec cm^{-3}
    - 1 ppq ~ 2.46×10^{4} molec cm^{-3}
- Values under other P & T conditions
    - Multiply above by P/(1 atm) * (298 K) / (T)
    - At 1 atm & 273.15K replace 2.46 by 2.69 (known as Loschmidt Number)
    - For Boulder (P ~ 837 mbar) at room T (293 K) replace 2.46 by 2.07

Conversions between mixing ratios and mass concentrations (Finlayson-Pitts & Pitts, p. 34)

- A ($\mu g\ m^{-3}$) = A (ppb) x 0.0409 x MW (at 298 K and 1 atm)
    - N_2 ($\mu g\ m^{-3}$) = N_2 (ppb) x 1.15 (MW = 28)
    - NO_3 ($\mu g\ m^{-3}$) = NO_3 (ppb) x 2.54 (MW = 62)
    - SO_4 ($\mu g\ m^{-3}$) = SO_4 (ppb) x 3.93 (MW = 98)
    - B ($\mu g\ m^{-3}$) = B (ppb) x 10.23 (B is an organic with MW = 250)
- A ($ng\ m^{-3}$) = A (ppt) x 0.0409 x MW

Mass and Number of Molecules in one aerosol particle

- *Assumes spherical shape with material density of 1.4 g cm^{-3} and no internal voids, and MW = 150 g mol^{-1}*

Diameter (nm)	Mass (fg)	Molecules	Volume (μm^3)	Mass Concentration for 1000 particle cm^{-3} ($\mu g\ m^{-3}$)	Volume Concentration for 1000 particle cm^{-3} ($\mu m^3\ cm^{-3}$)	Surface Area Concentration for 1000 particle cm^{-3} ($m^2\ m^{-3}$) &
100	0.73	2.94×10^6	0.0005	0.73	0.52	3.1×10^{-5}
250	11.5	4.6×10^7	0.0082	11.5	8.2	1.96×10^{-4}
1	733	2.94×10^9	0.52	733	524	3.1×10^{-3}

&*Multiply by 10^6 to convert to $\mu m^2\ cm^{-3}$*

Other Conversions

- Pressure Conversions
    - 760 Torr = 1013.25 mbar = 1.013×10^5 Pa

  - 1 atm = 14.7 psi
  - psia = absolute pressure, psig = difference from 1 atm
  - 1 inch Hg = 25.40 Torr = 33.86 mbar
- Standard Flowrate = Volumetric Flowrate x (273.15 / T) x (P / 1 atm)
- SOA/ΔCO ratios: 80 μg m^{-3} ppb^{-1} = 0.0687 g/g (at 293K and 1 atm)

Typical values of important parameters:

- Vertical profile of temperature and pressure: International Standard Atmosphere
  - 11 km: -57 C, 226 mbar
  - 20 km: -57 C, 54 mbar
- Aerosol surface area in the atmosphere:
  - Mexico City ~ 2 x 10^{-3} m^2 m^{-3} = 2 x 10^3 mm^2 m^{-3} (Fig 1D in Volkamer et al. 2007)
  - Clean areas ~ 1 x 10^{-4} m^2 m^{-3}
- H_2O vapor pressure (in mbar = hPa) (Ref):
  - Over ice at 240 K: 0.273 (Review of ice P_{vap} -- includes equations)
  - over ice or water at 0^oC: 6.1
  - at 20^oC: 23.4 (= 2.3% of 1 atm, if RH = 100%, or ~1% of 1 atm if RH ~45%)
  - at 30^oC: 42.5
- Kinetic theory
  - Mean free path of air: 65 nm at 1 atm (x 1atm/P for other pressures)
  - RMS thermal speed of N_2 at 300 K: 458 m/s (Ref)
  - Time between collisions: 0.14 ns (calculated from above)
  - Collision Frequency: 7.1 x 10^9 Hz
- Gas-Phase Diffusion Coefficients
  - D = 3.5×10^{-6} m^2 s^{-1}. (approx. straight-chain C_{16} hydrocarbon (Hilal et
  - al., 2003)
- Planetary Scale (Ref: D. Fahey, S. Madronich, or calculated)
  - Radius of the Earth (mean): 6371 km
  - Total mass of the atmosphere: 5.2 x 10^{21} g
  - Number of molecules in the atmosphere: ~10^{44}
  - Surface area of all aerosols in the atmosphere ~ 1 x 10^{14} m^2
  - Surface area of all Earth / Oceans ~ 1.25 x 10^{14} m^2 / 0.87 x 10^{14} m^2
- “Standard” Conditions of P & T (there are many definitions!)
  - 1 μg sm^{-3} = 1 μg m^{-3} under 1 atm and 273.15 K (used in NASA aircraft studies)
- Air Quality Standards for Health Purposes: EPA / WHO / EU
- Important constants (Ref: NIST)
  - N_a = 6.022142E23 mol^{-1} = Avogadro constant
  - k_b = 1.38065E-23 J K^{-1} = Boltzmann constant
  - R = 8.31447 J mol^{-1} K^{-1} = molar gas constant
  - h = 6.626068E-34 J s = Planck constant
  - c = 2.99792458E8 m s^{-1} = speed of light in vacuum
  - G = 6.673E-11 m^3 kg^{-1} s^{-2} = Netwonian constant of gravitation
  - sb = 5.67040E-8 W m^{-2} K^{-4} = Stefan-Boltzmann constant
- References for other parameters or more detail:
  - Atmospheric Chemists’ Companion Book

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2. Species Lifetimes & Exposures

Oxidant and UV Exposures and Ages

- Oxidant Exposures and Ages
    - OH concentration:
        - 24-hr average for general purposes: 1.5×10^6 molec cm^{-3}
        - Global annual average for whole troposphere: 1.2×10^6 (ACC p.101 - not in preview)
        - Peak daytime concentrations: $\sim 10^7$ molec. cm^{-3}
    - OH Photochemical age = OH_{exp} (molec cm^{-3} s) / 1.5×10^6 molec cm^{-3}
    - NO_3 age: NO_{3exp} / 2.5×10^8 molec cm^{-3} (~20 ppt *for 12 nightime hrs*; Ref: A&A)
    - O_3 age: O_{3exp} / 7×10^{11} molec cm^{-3} (30 ppb; Ref: A&A)

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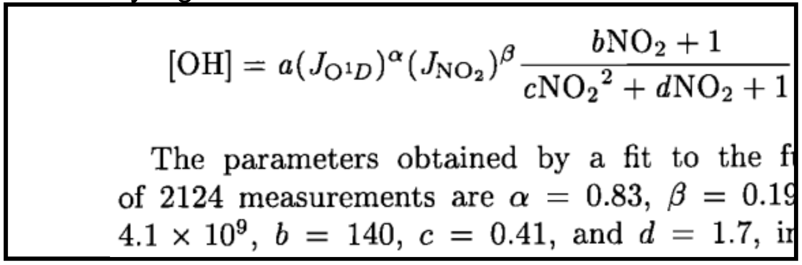
Equiv. Ages	**OH_{exp}** (molec cm^{-3} s)	**NO_{3exp}** (molec cm^{-3} s)	**O_{3exp}** (molec cm^{-3} s)
1 s	1.5×10^6	2.50×10^8	7.00×10^{11}
1 min	9×10^7	1.50×10^{10}	4.20×10^{13}
1 hr	5.4×10^9	9.00×10^{11}	2.52×10^{15}
1 day	1.3×10^{11}	2.16×10^{13}	6.05×10^{16}
1 week	9.07×10^{11}	1.51×10^{14}	4.23×10^{17}
1 month	2.76×10^{13}	4.60×10^{15}	1.29×10^{19}
1 year	3.31×10^{14}	5.52×10^{16}	1.55×10^{20}

- Estimation of OH when measurements not available (Ref: Ehhalt et al., 2000) "NO_X should be sufficiently high to be of influence"



$$[OH] = a(J_{O^1D})^{\alpha}(J_{NO_2})^{\beta}\frac{bNO_2 + 1}{cNO_2{}^2 + dNO_2 + 1}$$

The parameters obtained by a fit to the f
of 2124 measurements are $\alpha = 0.83$, $\beta = 0.19$
4.1×10^9, $b = 140$, $c = 0.41$, and $d = 1.7$, i

Photolysis Calculations

- Typical noontime values @ surface mid-latitudes
    - $j_{NO2} \sim 0.007\ s^{-1} = 0.18\ min^{-1}$
    - $j_{O1D} \sim 2 \times 10^{-5}\ s^{-1} = 0.58\ day^{-1}$
- Absorption Cross Sections & quantum yields: Mainz Database & JPL 2011
- Spectral light fluxes vs location & time:
    - TUV model
        - Also outputs j values for a number of species

    - ○ ASTM standard spectra (also includes top of atmosphere)
- UV Exposures and Ages
    - ○ Typical 24-hr avg. J values (s^{-1}), clear sky no aerosols, sea level, 10% ground albedo: (from Sasha Madronich, TUV model. Ref: Hodzic et al., 2015)

	$O_3 \rightarrow O^1D$	$NO_2 \rightarrow O^3P$	$NO_3 \rightarrow NO_2$	$CH_2O \rightarrow H$
40 N June 21 with 330 DU strat. O_3 (TOMS climatology)	1.02×10^{-5}	4.09×10^{-3}	9.11×10^{-2}	1.29×10^{-5}
40 N Dec 21 with 310 DU	1.24×10^{-6}	1.5×10^{-3}	4.64×10^{-2}	3.13×10^{-6}

    - ○ UV exposure and age (< 400 nm) = Actinic flux / 0.8×10^{16} (24-hr avg. summer solstice in Boulder) - Preliminary values
        - ■ CU blacklights: j_{NO2} ~ 0.013, UV actinic flux = 2.77×10^{16} phot. cm^{-2} s^{-1} (1.25% in UVB, rest in UVA), VIS flux = 0.85×10^{16}
        - ■ Types of UV
    - ○ j_X details coming soon

Equiv. Ages	**Total UV_{exp}** (UV phot. cm^{-2})&	**j_{NO2} Lifetimes** (unitless)	**j_{O1D} Lifetimes** (unitless)	**j_{NO3} Lifetimes** (unitless)
1 s	8.0×10^{15}			
1 min	4.8×10^{17}			
1 hr	2.88×10^{19}			
1 day	6.9×10^{20}	327		
1 week	4.8×10^{21}			
1 month	1.47×10^{23}			
1 year	1.77×10^{24}			

&: 3.04% in UVB (< 315 nm) and the rest in UVA (315-400 nm)

Important Reaction Rate Constants & Lifetimes

Reaction	**Rate Constant (2nd order)***	**1/e Lifetime under typical ambient conditions&**	**Reference**
Gas kinetic collision limit	2.5×10^{-10}	0.75 hrs	Finlayson-Pitts & Pitts, p.140. Accurate value depends on T & reacting species
OH + NO_2	1.08×10^{-11}	0.71 days	JPL 2011. (Mollner et al. 2010 is 15% lower, JPL 2011 does take it into account along with previous measurements)
OH + CO	1.5×10^{-13}	1.7 months	Seinfeld & Pandis 2006

OH + SO_2	9.56×10^{-13}	8.1 days	JPL 2011
OH + CH_4	6.3×10^{-15}	3.4 years	JPL 2011
OH + Butane	2.36×10^{-12}	3.3 days	A&A 2003
OH + Pentadecane	2.07×10^{-11}	6.5 hrs	A&A 2003
OH + Benzene	1.22×10^{-12}	6.3 days	A&A 2003
OH + Toluene	5.63×10^{-12}	1.4 days	A&A 2003
OH + xylenes	$\sim 2 \times 10^{-11}$	9.3 hrs	A&A 2003 (isomers rates vary 1.36-2.31)
OH + TMB	$\sim 4 \times 10^{-11}$	4.6 hrs	A&A 2003 (isomers rates vary 3.25-5.67)
OH + Isoprene	1.00×10^{-10}	1.9 hrs	A&A 2003
RO_2 + NO	$\sim 9 \times 10^{-12}$	1.4 s (1 ppb NO)	A&Z 2014. See Table 5 A&A 2003
RO_2 + HO_2	$\sim 1.5 \times 10^{-11}$	2.3 min (10 ppt HO_2)	A&Z 2014. See Table 6 A&A 2003
RO_2 + RO_2	10^{-13} to 10^{-17}		Depending on RO_2 identity (A&Z 2014)
NO + O_3	1.96×10^{-14}		JPL 2011

*: All rates at 298 K & 1 atm. Eff. 2nd order rates shown, if 3rd order. Units: cm^3 $molec^{-1}$ s^{-1})

&: using OH = 1.5×10^6 molec cm^{-3}. Note that clock ages will be several-fold shorter in the middle of the day.

- Where to find additional up-to-date rate constants:
  - JPL 2011 / IUPAC Evaluations / Leeds MCM / Oxygenated VOC database
- How to estimate rate constants for organics with structure-reactivity relationships
  - Review: Atkinson & Ziemann 2012
  - Primary Refs: Kwok & Atkinson 1995 / Peeters et al. 2007 / Kerdouci et al. 2010

VOC Lifetimes (Atkinson & Arey, Chem. Rev. 2003)

- *Note: while OH and O3 concentrations do not vary enormously between different locations, NO_3 concentrations do, thus you may want to scale the lifetimes here with your best estimate of NO_3 concentrations in your environment. An extensive summary of measurements is in the Atmos Chem Companion book p101-103, unfortunately those pages are not in the free preview.*

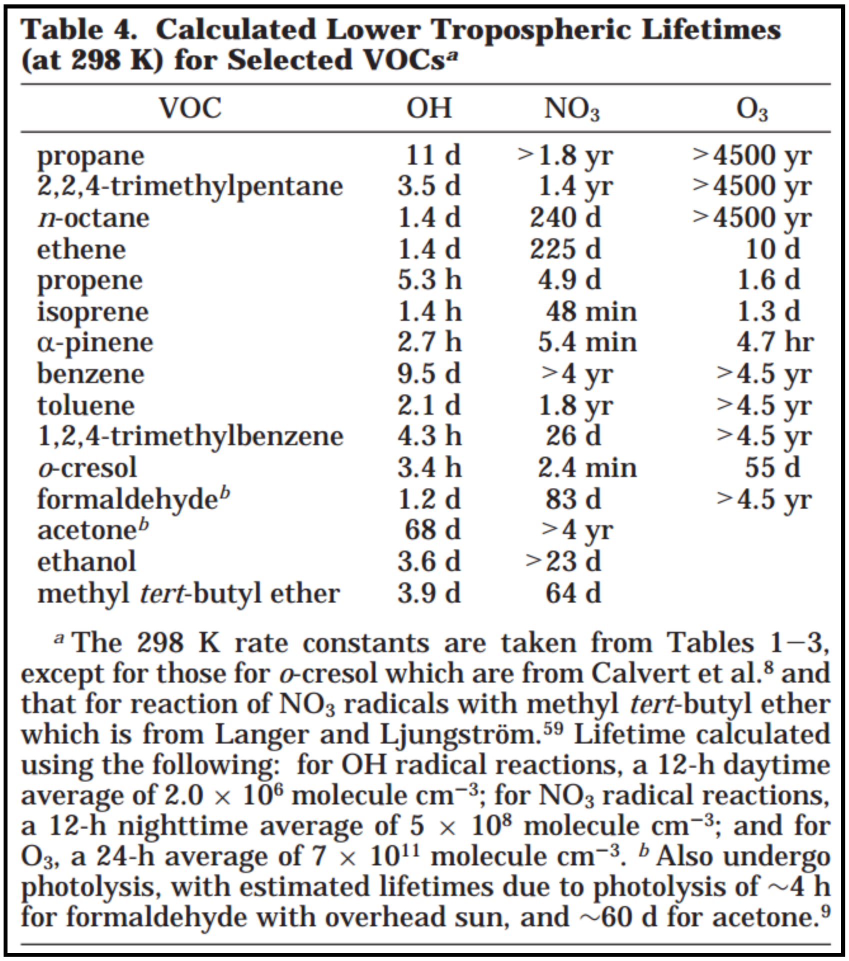


Table 4. Calculated Lower Tropospheric Lifetimes (at 298 K) for Selected VOCs[a]

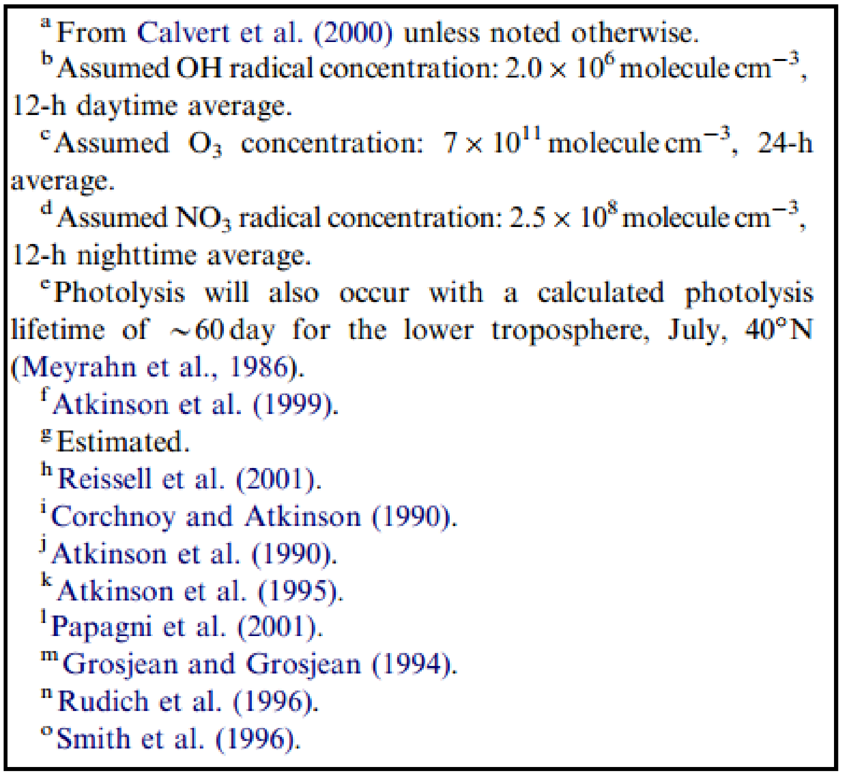
VOC	OH	NO_3	O_3
propane	11 d	>1.8 yr	>4500 yr
2,2,4-trimethylpentane	3.5 d	1.4 yr	>4500 yr
n-octane	1.4 d	240 d	>4500 yr
ethene	1.4 d	225 d	10 d
propene	5.3 h	4.9 d	1.6 d
isoprene	1.4 h	48 min	1.3 d
α-pinene	2.7 h	5.4 min	4.7 hr
benzene	9.5 d	>4 yr	>4.5 yr
toluene	2.1 d	1.8 yr	>4.5 yr
1,2,4-trimethylbenzene	4.3 h	26 d	>4.5 yr
o-cresol	3.4 h	2.4 min	55 d
formaldehyde[b]	1.2 d	83 d	>4.5 yr
acetone[b]	68 d	>4 yr	
ethanol	3.6 d	>23 d	
methyl *tert*-butyl ether	3.9 d	64 d	

[a] The 298 K rate constants are taken from Tables 1−3, except for those for *o*-cresol which are from Calvert et al.[8] and that for reaction of NO_3 radicals with methyl *tert*-butyl ether which is from Langer and Ljungström.[59] Lifetime calculated using the following: for OH radical reactions, a 12-h daytime average of 2.0×10^6 molecule cm^{-3}; for NO_3 radical reactions, a 12-h nighttime average of 5×10^8 molecule cm^{-3}; and for O_3, a 24-h average of 7×10^{11} molecule cm^{-3}. [b] Also undergo photolysis, with estimated lifetimes due to photolysis of ~4 h for formaldehyde with overhead sun, and ~60 d for acetone.[9]

Biogenic VOC Lifetimes (Atkinson & Arey, Atmos. Environ. 2003)

Calculated atmospheric lifetimes of biogenic volatile organic compounds

Biogenic VOC	Lifetime[a] for reaction with		
	OH[b]	O_3[c]	NO_3[d]
Isoprene	1.4 h	1.3 day	1.6 h
Monoterpenes			
Camphene	2.6 h	18 day	1.7 h
2-Carene	1.7 h	1.7 h	4 min
3-Carene	1.6 h	11 h	7 min
Limonene	49 min	2.0 h	5 min
Myrcene	39 min	50 min	6 min
cis-/trans-Ocimene	33 min	44 min	3 min
α-Phellandrene	27 min	8 min	0.9 min
β-Phellandrene	50 min	8.4 h	8 min
α-Pinene	2.6 h	4.6 h	11 min
β-Pinene	1.8 h	1.1 day	27 min
Sabinene	1.2 h	4.8 h	7 min
α-Terpinene	23 min	1 min	0.5 min
γ-Terpinene	47 min	2.8 h	2 min
Terpinolene	37 min	13 min	0.7 min
Sesquiterpenes			
β-Caryophyllene	42 min	2 min	3 min
α-Cedrene	2.1 h	14 h	8 min
α-Copaene	1.5 h	2.5 h	4 min
α-Humulene	28 min	2 min	2 min
Longifolene	2.9 h	> 33 day	1.6 h
Oxygenates			
Acetone[e]	61 day[f]	> 4.5 year[g]	> 8 year[f]
Camphor	2.5 day[h]	> 235 day[h]	> 300 day[h]
1,8-Cineole	1.0 day[i]	> 110 day[j]	1.5 year[i]
cis-3-Hexen-1-ol	1.3 h[k]	6.2 h[k]	4.1 h[k]
cis-3-Hexenyl acetate	1.8 h[k]	7.3 h[k]	4.5 h[k]
Linalool	52 min[k]	55 min[k]	6 min[k]
Methanol	12 day[f]	> 4.5 year[g]	2.0 year[f]
2-Methyl-3-buten-2-ol	2.4 h[l]	1.7 day[m]	7.7 day[n]
6-Methyl-5-hepten-2-one	53 min[o]	1.0 h[o]	9 min[o]



[a] From Calvert et al. (2000) unless noted otherwise.

[b] Assumed OH radical concentration: 2.0×10^6 molecule cm^{-3}, 12-h daytime average.

[c] Assumed O_3 concentration: 7×10^{11} molecule cm^{-3}, 24-h average.

[d] Assumed NO_3 radical concentration: 2.5×10^8 molecule cm^{-3}, 12-h nighttime average.

[e] Photolysis will also occur with a calculated photolysis lifetime of ~60 day for the lower troposphere, July, 40°N (Meyrahn et al., 1986).

[f] Atkinson et al. (1999).

[g] Estimated.

[h] Reissell et al. (2001).

[i] Corchnoy and Atkinson (1990).

[j] Atkinson et al. (1990).

[k] Atkinson et al. (1995).

[l] Papagni et al. (2001).

[m] Grosjean and Grosjean (1994).

[n] Rudich et al. (1996).

[o] Smith et al. (1996).

- VOC Lifetimes (Atkinson & Ziemann, CSR 2012)

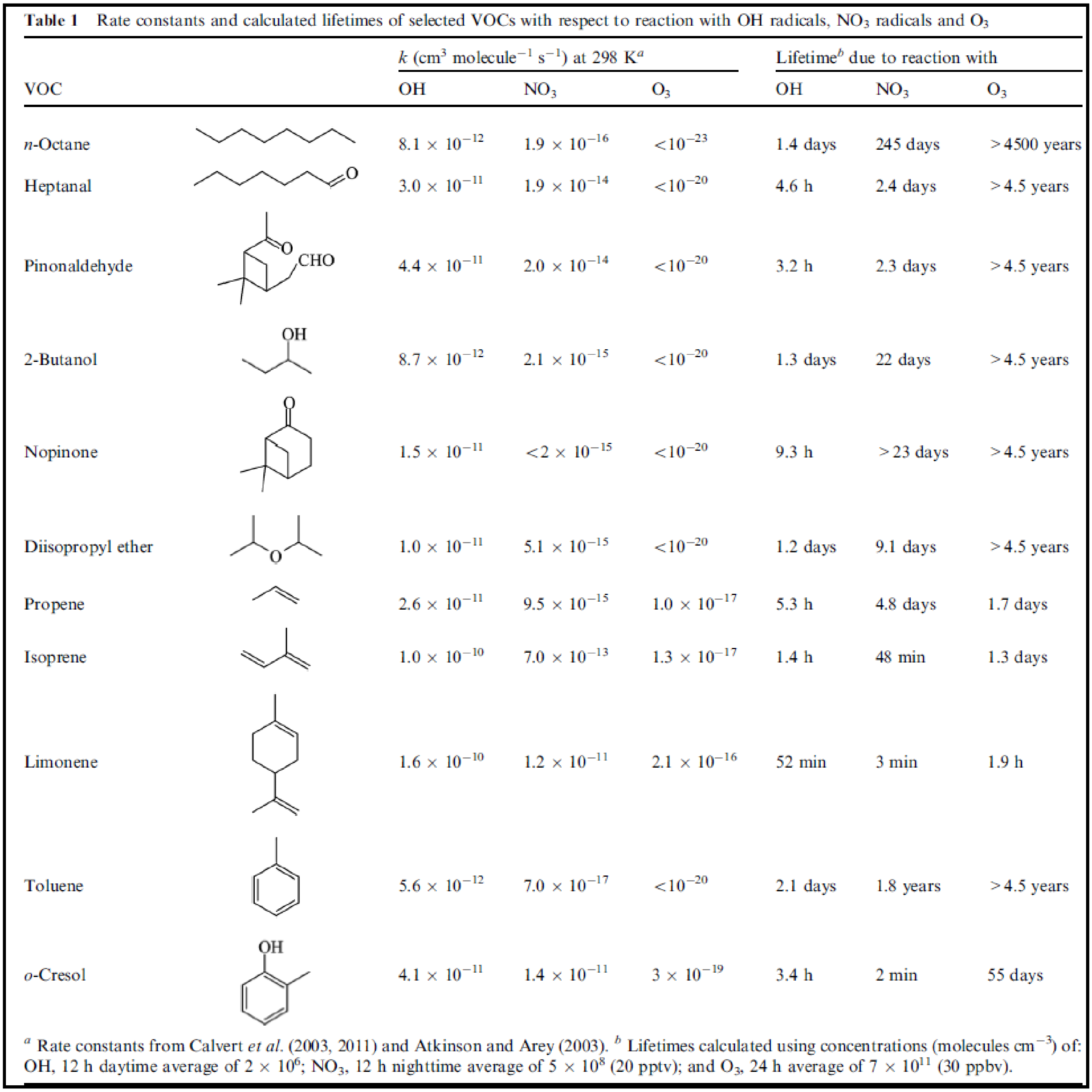
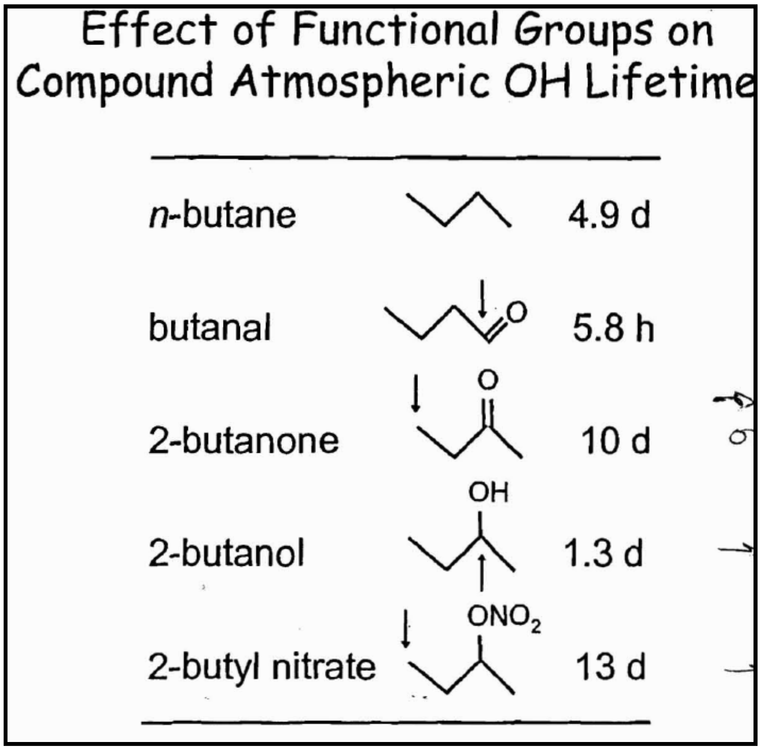


Table 1 Rate constants and calculated lifetimes of selected VOCs with respect to reaction with OH radicals, NO_3 radicals and O_3

	k (cm^3 $molecule^{-1}$ s^{-1}) at 298 K[a]			Lifetime[b] due to reaction with		
VOC	OH	NO_3	O_3	OH	NO_3	O_3
n-Octane	8.1×10^{-12}	1.9×10^{-16}	$<10^{-23}$	1.4 days	245 days	> 4500 years
Heptanal	3.0×10^{-11}	1.9×10^{-14}	$<10^{-20}$	4.6 h	2.4 days	> 4.5 years
Pinonaldehyde	4.4×10^{-11}	2.0×10^{-14}	$<10^{-20}$	3.2 h	2.3 days	> 4.5 years
2-Butanol	8.7×10^{-12}	2.1×10^{-15}	$<10^{-20}$	1.3 days	22 days	> 4.5 years
Nopinone	1.5×10^{-11}	$<2 \times 10^{-15}$	$<10^{-20}$	9.3 h	> 23 days	> 4.5 years
Diisopropyl ether	1.0×10^{-11}	5.1×10^{-15}	$<10^{-20}$	1.2 days	9.1 days	> 4.5 years
Propene	2.6×10^{-11}	9.5×10^{-15}	1.0×10^{-17}	5.3 h	4.8 days	1.7 days
Isoprene	1.0×10^{-10}	7.0×10^{-13}	1.3×10^{-17}	1.4 h	48 min	1.3 days
Limonene	1.6×10^{-10}	1.2×10^{-11}	2.1×10^{-16}	52 min	3 min	1.9 h
Toluene	5.6×10^{-12}	7.0×10^{-17}	$<10^{-20}$	2.1 days	1.8 years	> 4.5 years
o-Cresol	4.1×10^{-11}	1.4×10^{-11}	3×10^{-19}	3.4 h	2 min	55 days

[a] Rate constants from Calvert *et al.* (2003, 2011) and Atkinson and Arey (2003). [b] Lifetimes calculated using concentrations (molecules cm^{-3}) of: OH, 12 h daytime average of 2×10^6; NO_3, 12 h nighttime average of 5×10^8 (20 pptv); and O_3, 24 h average of 7×10^{11} (30 ppbv).

- Effects of Functional Groups on OH Lifetimes (P.J. Ziemann, 2006 Tutorial AAAR)



Effect of Functional Groups on Compound Atmospheric OH Lifetime

n-butane	4.9 d
butanal	5.8 h
2-butanone	10 d
2-butanol	1.3 d
2-butyl nitrate	13 d

- Approximate k_{OH} rate constants vs c*, OS_C (Donahue et al., Env. Chem., 2013)

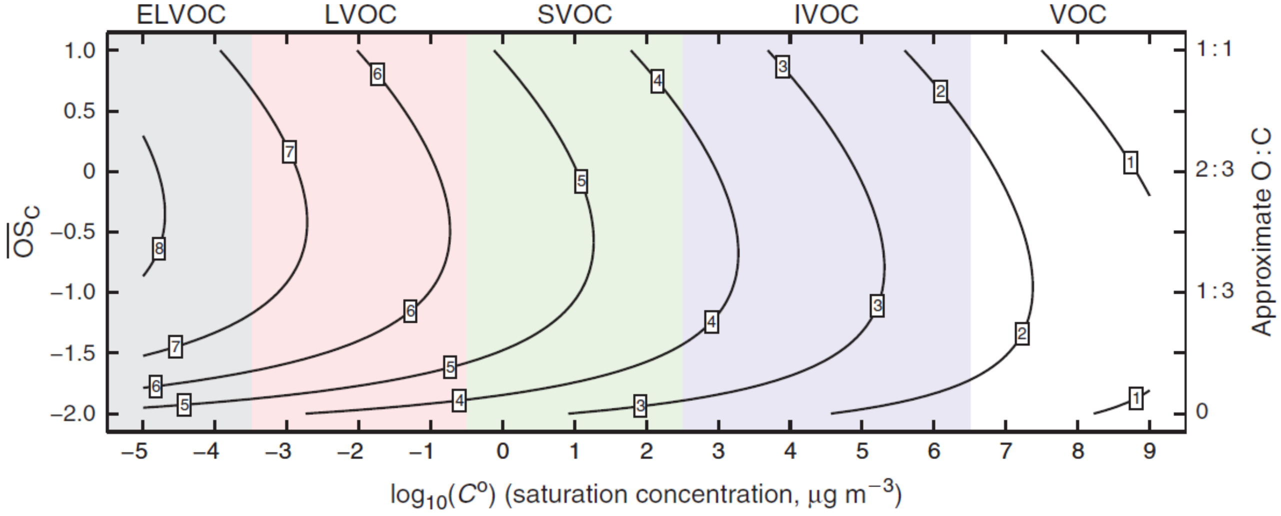


Fig. 1. Gas-phase $OH^{\bullet}$ oxidation rate constants for organic species *v.* volatility and oxidation state ($\overline{OS}_C$) (contours are $k \times 10^{11}$ cm^3 molecule^{-1} s^{-1}). Rate constants are estimated based on extrapolated group contribution methods, as described in the text. The $OH^{\bullet}$ oxidation rate constant increases with increasing carbon number, rapidly with increasing oxygen number, but decreases quadratically as O : C increases due to the loss of abstractable hydrogens. (ELVOC, extremely low volatility organic compounds; LVOC, low volatility organic compounds; SVOC, semivolatile organic compounds; IVOC, intermediate volatility organic compounds; VOC, volatile organic compounds.)

- Lifetimes against NO_3 Oxidation

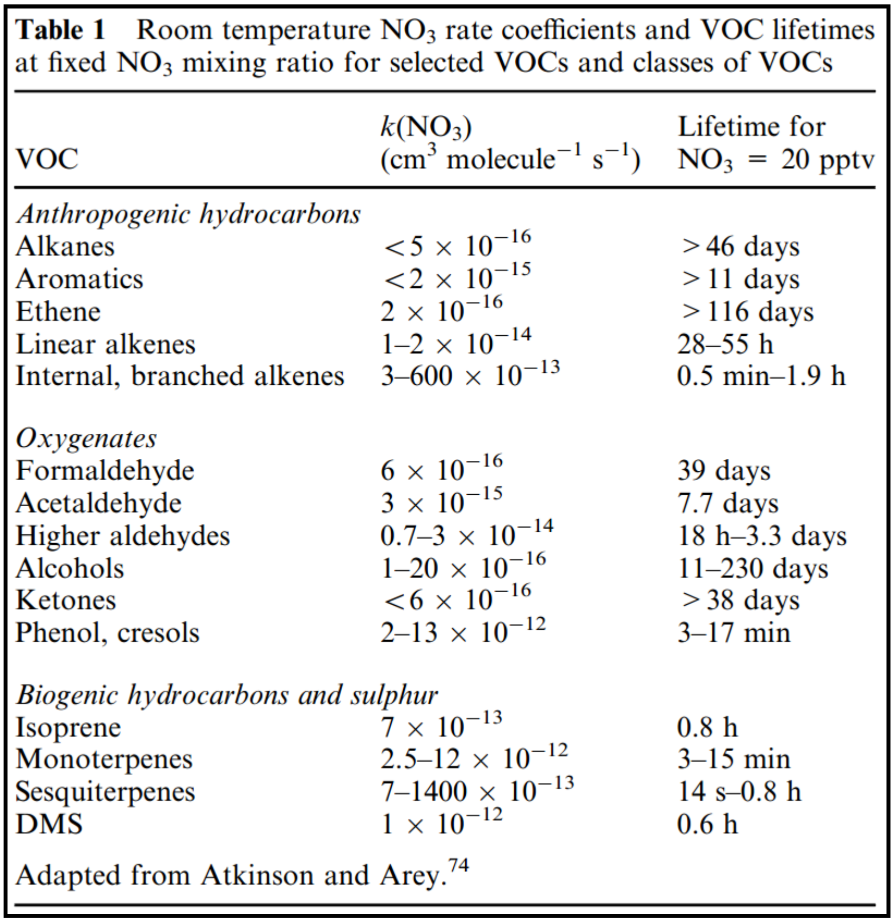


Table 1 Room temperature NO_3 rate coefficients and VOC lifetimes at fixed NO_3 mixing ratio for selected VOCs and classes of VOCs

VOC	$k(NO_3)$ (cm^3 $molecule^{-1}$ s^{-1})	Lifetime for NO_3 = 20 pptv
Anthropogenic hydrocarbons		
Alkanes	$< 5 \times 10^{-16}$	> 46 days
Aromatics	$< 2 \times 10^{-15}$	> 11 days
Ethene	2×10^{-16}	> 116 days
Linear alkenes	$1–2 \times 10^{-14}$	28–55 h
Internal, branched alkenes	$3–600 \times 10^{-13}$	0.5 min–1.9 h
Oxygenates		
Formaldehyde	6×10^{-16}	39 days
Acetaldehyde	3×10^{-15}	7.7 days
Higher aldehydes	$0.7–3 \times 10^{-14}$	18 h–3.3 days
Alcohols	$1–20 \times 10^{-16}$	11–230 days
Ketones	$< 6 \times 10^{-16}$	> 38 days
Phenol, cresols	$2–13 \times 10^{-12}$	3–17 min
Biogenic hydrocarbons and sulphur		
Isoprene	7×10^{-13}	0.8 h
Monoterpenes	$2.5–12 \times 10^{-12}$	3–15 min
Sesquiterpenes	$7–1400 \times 10^{-13}$	14 s–0.8 h
DMS	1×10^{-12}	0.6 h

Adapted from Atkinson and Arey.[74]

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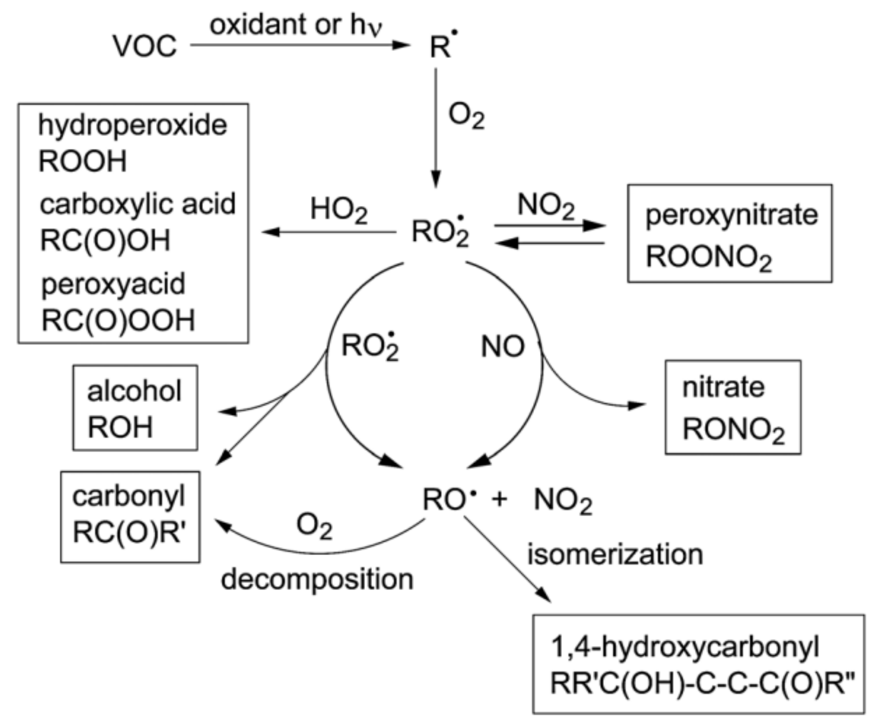
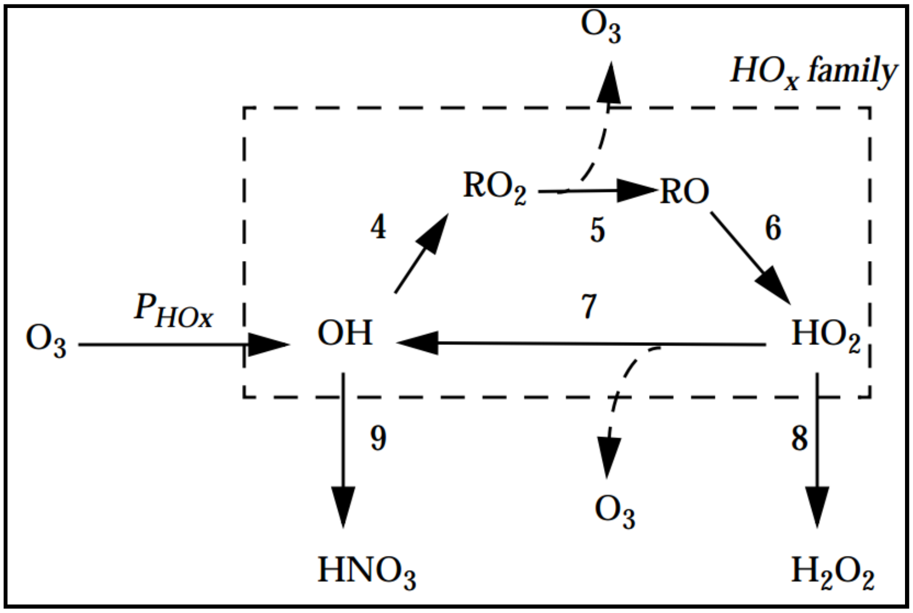
3. Reaction Mechanisms

- Initial steps of VOC oxidation by OH, Cl, or hv (Atkinson & Ziemann CSR 2012)



Scheme 1 VOC atmospheric degradation reactions proceeding through formation of an alkyl or substituted alkyl radical (see text). Product classes are shown in boxes. The carboxylic acid, $RC(O)OH$, and peroxyacid, $RC(O)OOH$, are formed from reactions of acyl peroxy ($RC(O)O_2^•$) radicals with HO_2 radicals.

- Simplified HOx-ROx Cycle and O_3 Formation (Jacob Fig 12-3)



- HOx Mechanism (Mao et al. Atm. Env. 2009)
- HOx Mechanism (Jackson et al. 2009)

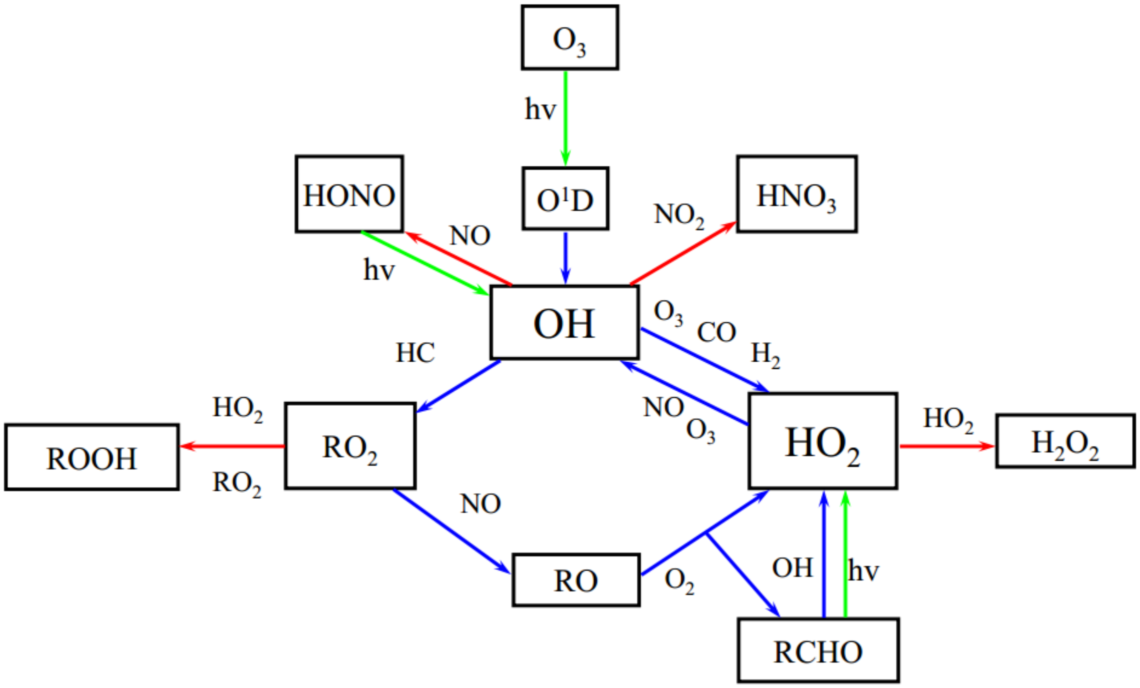
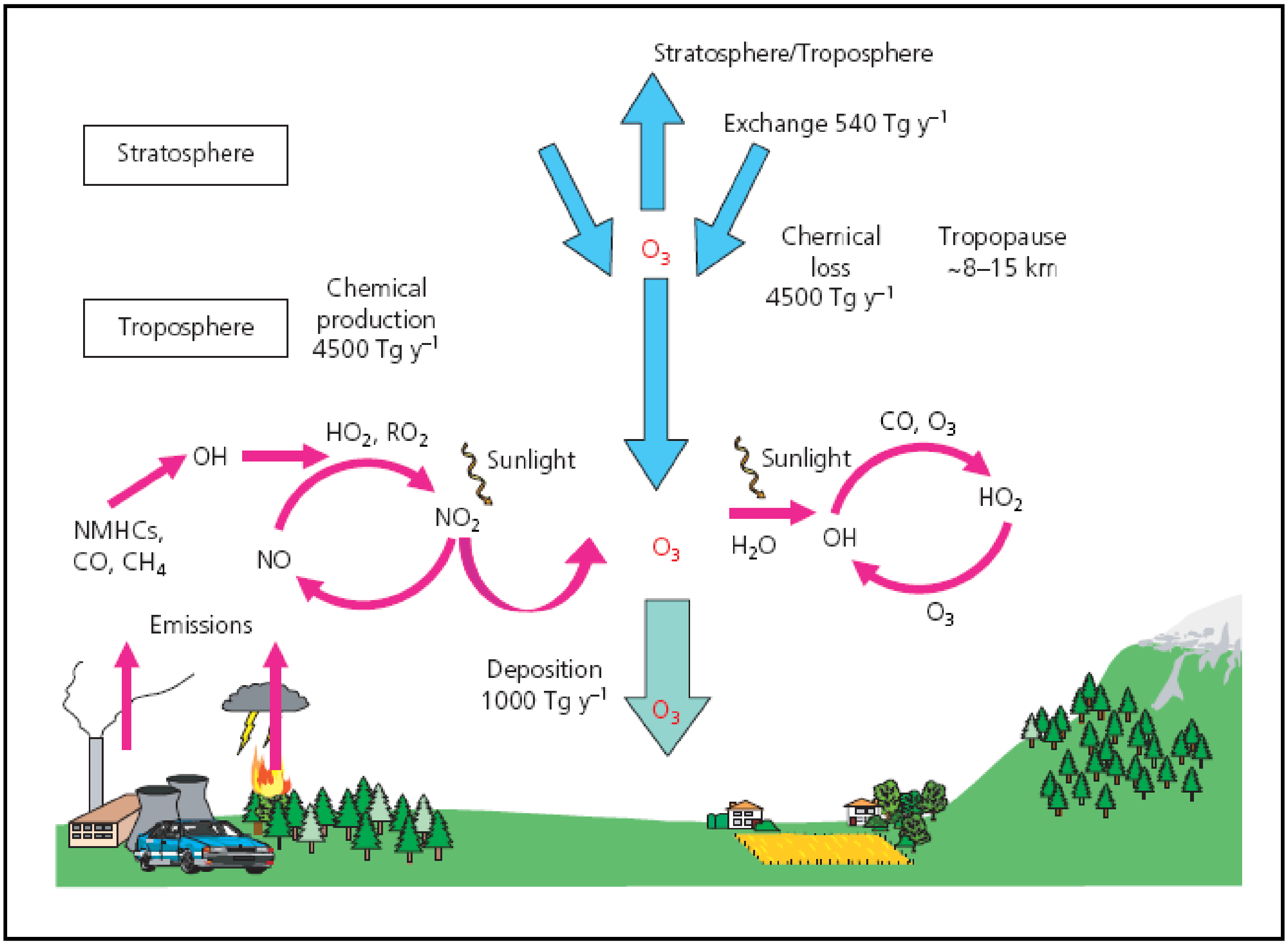
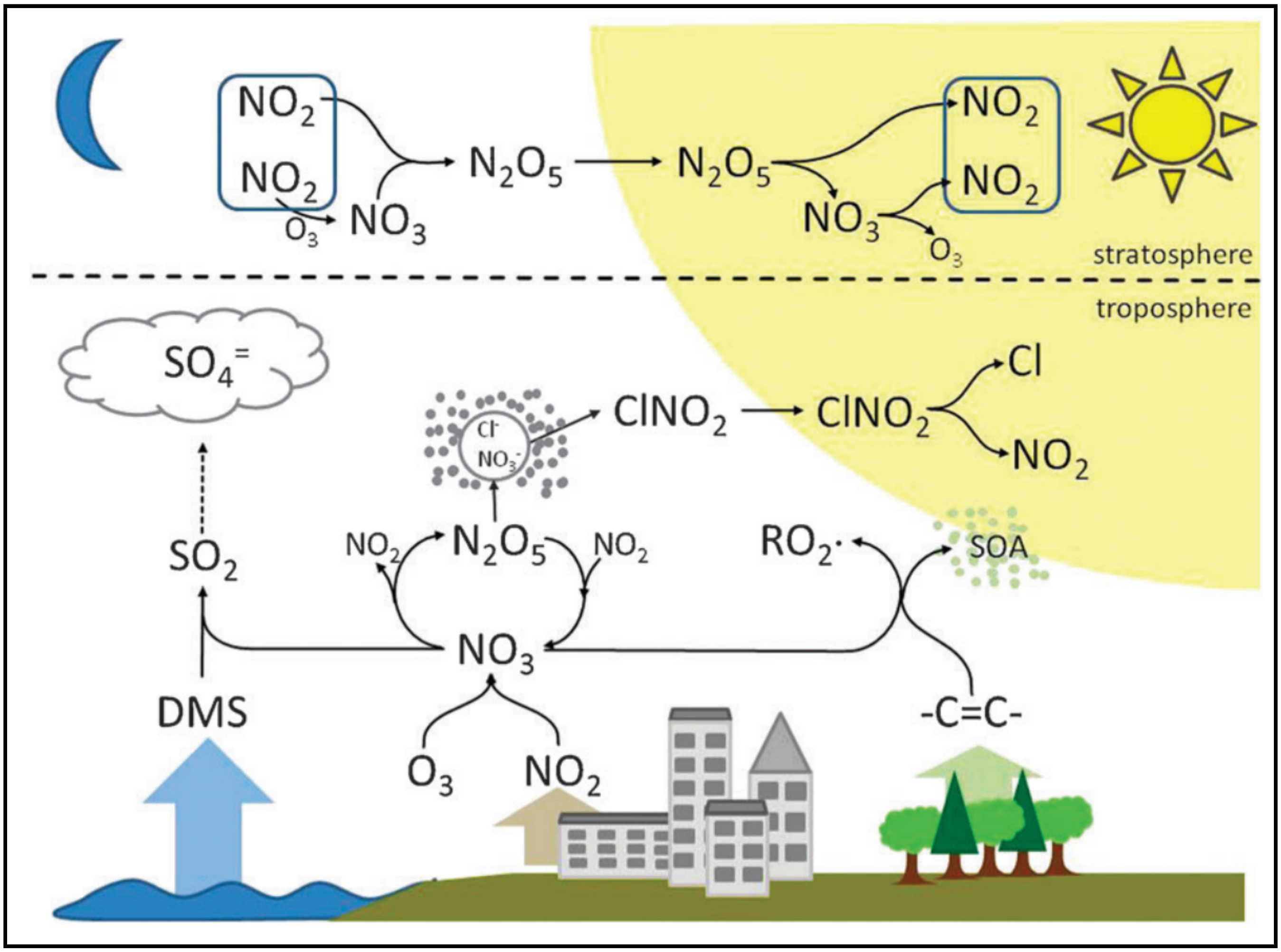


Fig. 1. Schematic of the key reactions of the OH radical in the atmosphere. The green lines show radical initiation, the red lines radical termination and the blue lines represent propagation reactions between radical species. RO_2 represents a generic peroxy radical, RO an oxy radical, ROOH an organic peroxide species and RCHO an aldehyde species.

- Processes Controlling O_3 in the troposphere (RSC, 2008)



- NO_3 and N_2O_5 Chemistry (Brown & Stutz, CSR 2012)
    - Note NO_2 arrows are reversed on N_2O_5 cycle



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4. Species and Aerosol Properties

Spectral Databases

- Multiple Types of Spectra
  - NIST Chemistry Webbook
  - REAXYS Database
  - ACS SciFinder (click here to create account - CU only)
  - Spectral Database of Organic Compounds
- IR
  - NIST database of IR spectra
- UV-Vis
  - Mainz Database
  - JPL 2011
  - SoftCon Database (A brief description here)

Key Species Properties

- Multiple properties
  - CHEMID Plus database
  - EPA EPI Suite
  - CRC Handbook of Chemistry and Physics
- Atomic weights and isotopic compositions: NIST database
- Thermochemical properties:
  - JANAF tables

    - Standard enthalpies of formation
- Vapor Pressures & Phase partitioning
    - Univ of Manchester Structure-Activity Interface
    - REAXYS Database
    - Evaporation
    - Extended AIM Aerosol Thermod Model
    - ISORROPIA
- Henry's Law Constants
    - JPL 2011
    - Sander's compilation: 2014 ACPD paper & website (latter has only errata)
    - HenryWin Database
- Solubilities: IUPAC-NIST database
- PAH structures: NIST database

Aerosol Calculations

- Aerosol Calculator (Excel) (Ref: Aerosol Measurements Book)
- Aerosol Inlets and Transmission Losses:
    - Particle Loss Calculator (Igor) (Ref: von der Weiden et al. 2009)
    - Brockman: 2006 AAAR Tutorial & Explanations
    -

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5. SOA Modeling

- Partitioning theory (Donahue et al., 2006):

$$\xi_i = \left(1+\frac{C_i^*}{[OA]}\right)^{-1} \;;\; [OA] = \sum_i [SV$$

$$C_i^* = C_{i,o}^* \frac{T_0}{T} \exp\left[\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_o}\right.\right.$$

- Near room temperature ΔH_{vap} can be estimated as (Epstein & Donahue, 2010), with where ΔH_{vap} in kJ mol^{-1} and C^* in µg m^{-3}:

$$\Delta H^{VAP} = -11 \log_{10} C^*_{300} +$$

- Typical SOA yields (Tsimpidi et al., 2010). If "aging" is used, a rate constant of 1 x 10^{-11} cm^3 molec^{-1} s^{-1} should be used (the rate constant in the paper is x4 larger due to an error, per pers. comm. from S. Pandis).

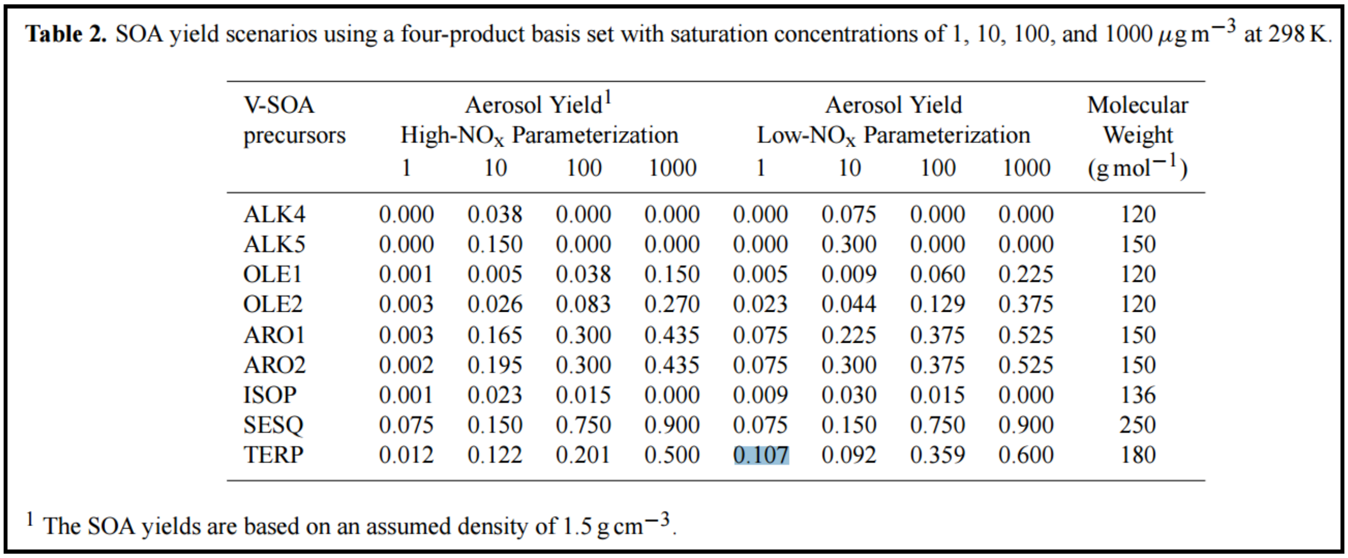


Table 2. SOA yield scenarios using a four-product basis set with saturation concentrations of 1, 10, 100, and 1000 $\mu g\,m^{-3}$ at 298 K.

V-SOA precursors	Aerosol Yield[1] High-NO_x Parameterization 1	10	100	1000	Aerosol Yield Low-NO_x Parameterization 1	10	100	1000	Molecular Weight ($g\,mol^{-1}$)
ALK4	0.000	0.038	0.000	0.000	0.000	0.075	0.000	0.000	120
ALK5	0.000	0.150	0.000	0.000	0.000	0.300	0.000	0.000	150
OLE1	0.001	0.005	0.038	0.150	0.005	0.009	0.060	0.225	120
OLE2	0.003	0.026	0.083	0.270	0.023	0.044	0.129	0.375	120
ARO1	0.003	0.165	0.300	0.435	0.075	0.225	0.375	0.525	150
ARO2	0.002	0.195	0.300	0.435	0.075	0.300	0.375	0.525	150
ISOP	0.001	0.023	0.015	0.000	0.009	0.030	0.015	0.000	136
SESQ	0.075	0.150	0.750	0.900	0.075	0.150	0.750	0.900	250
TERP	0.012	0.122	0.201	0.500	0.107	0.092	0.359	0.600	180

[1] The SOA yields are based on an assumed density of 1.5 $g\,cm^{-3}$.

- SIMPOL: Vapor Pressure Estimation by Group Contribution Theory, from Pankow & Asher (2008)
    - E.g. for a C_{15} Hydroxynitrate:
    - $\log_{10}(P_{vap}\,(\mathrm{Atm})) = 1.79 - N_C * 0.438 - (N_{OH} + N_{ONO2}) * 2.23 = -9.24$

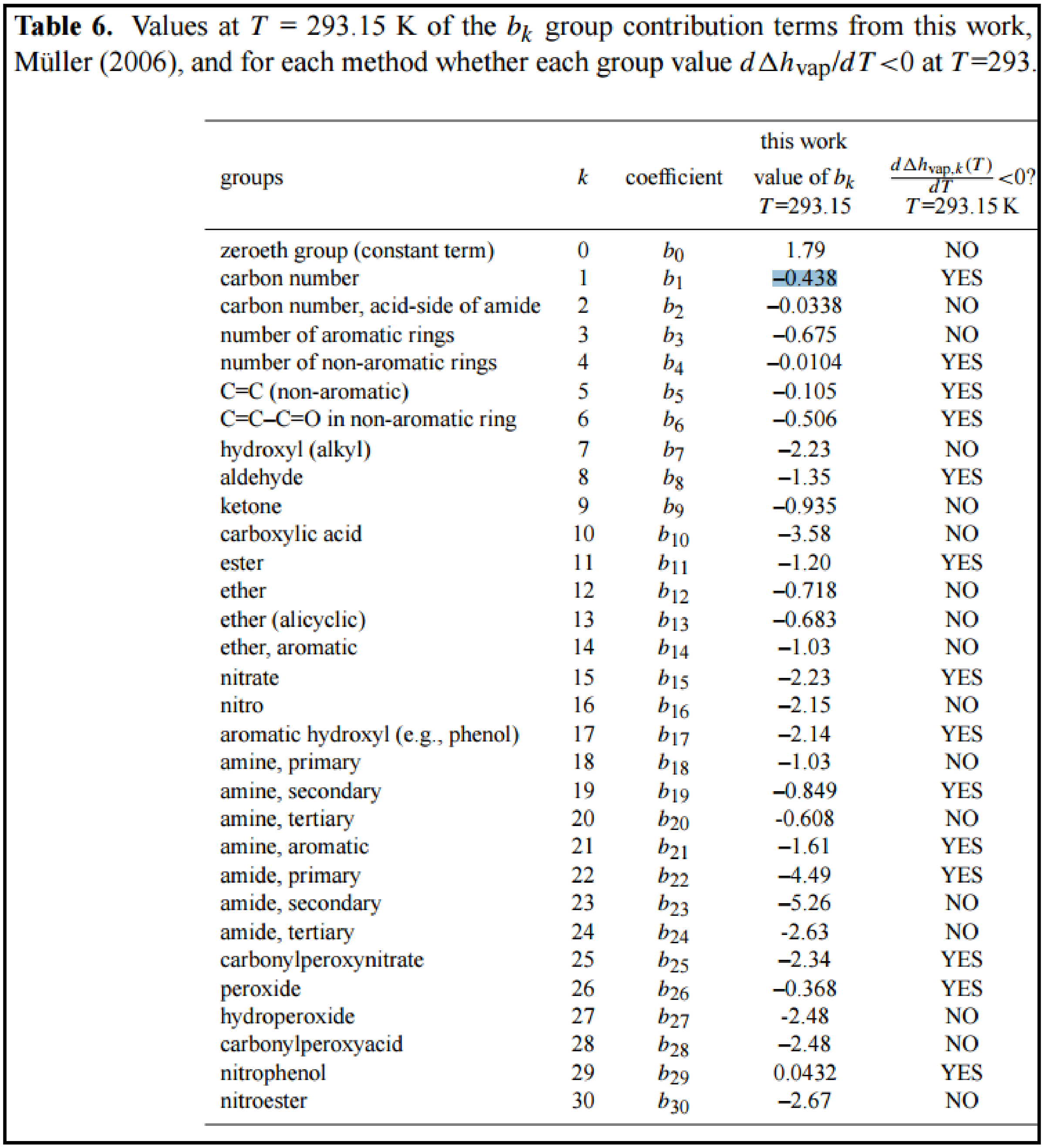
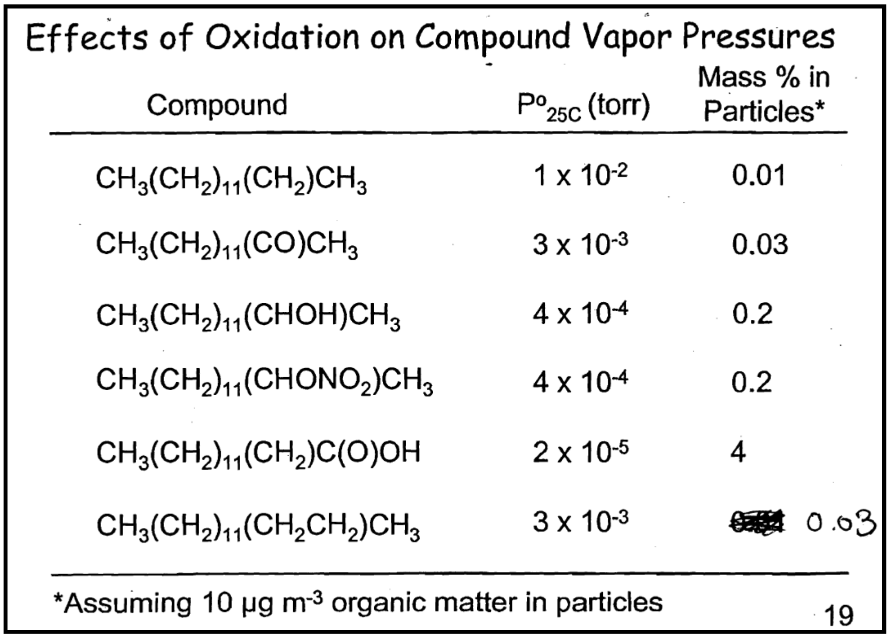


Table 6. Values at T = 293.15 K of the b_k group contribution terms from this work, Müller (2006), and for each method whether each group value $d\Delta h_{vap}/dT < 0$ at T=293.

groups	k	coefficient	this work value of b_k T=293.15	$\frac{d\Delta h_{vap,k}(T)}{dT} < 0?$ T=293.15 K
zeroeth group (constant term)	0	b_0	1.79	NO
carbon number	1	b_1	–0.438	YES
carbon number, acid-side of amide	2	b_2	–0.0338	NO
number of aromatic rings	3	b_3	–0.675	NO
number of non-aromatic rings	4	b_4	–0.0104	YES
C=C (non-aromatic)	5	b_5	–0.105	YES
C=C–C=O in non-aromatic ring	6	b_6	–0.506	YES
hydroxyl (alkyl)	7	b_7	–2.23	NO
aldehyde	8	b_8	–1.35	YES
ketone	9	b_9	–0.935	NO
carboxylic acid	10	b_{10}	–3.58	NO
ester	11	b_{11}	–1.20	YES
ether	12	b_{12}	–0.718	NO
ether (alicyclic)	13	b_{13}	–0.683	NO
ether, aromatic	14	b_{14}	–1.03	NO
nitrate	15	b_{15}	–2.23	YES
nitro	16	b_{16}	–2.15	NO
aromatic hydroxyl (e.g., phenol)	17	b_{17}	–2.14	YES
amine, primary	18	b_{18}	–1.03	NO
amine, secondary	19	b_{19}	–0.849	YES
amine, tertiary	20	b_{20}	-0.608	NO
amine, aromatic	21	b_{21}	–1.61	YES
amide, primary	22	b_{22}	–4.49	YES
amide, secondary	23	b_{23}	–5.26	NO
amide, tertiary	24	b_{24}	-2.63	NO
carbonylperoxynitrate	25	b_{25}	–2.34	YES
peroxide	26	b_{26}	–0.368	YES
hydroperoxide	27	b_{27}	-2.48	NO
carbonylperoxyacid	28	b_{28}	–2.48	NO
nitrophenol	29	b_{29}	0.0432	YES
nitroester	30	b_{30}	–2.67	NO

- Effects of Functional Groups on vapor pressures (P.J. Ziemann, 2006 Tutorial AAAR)

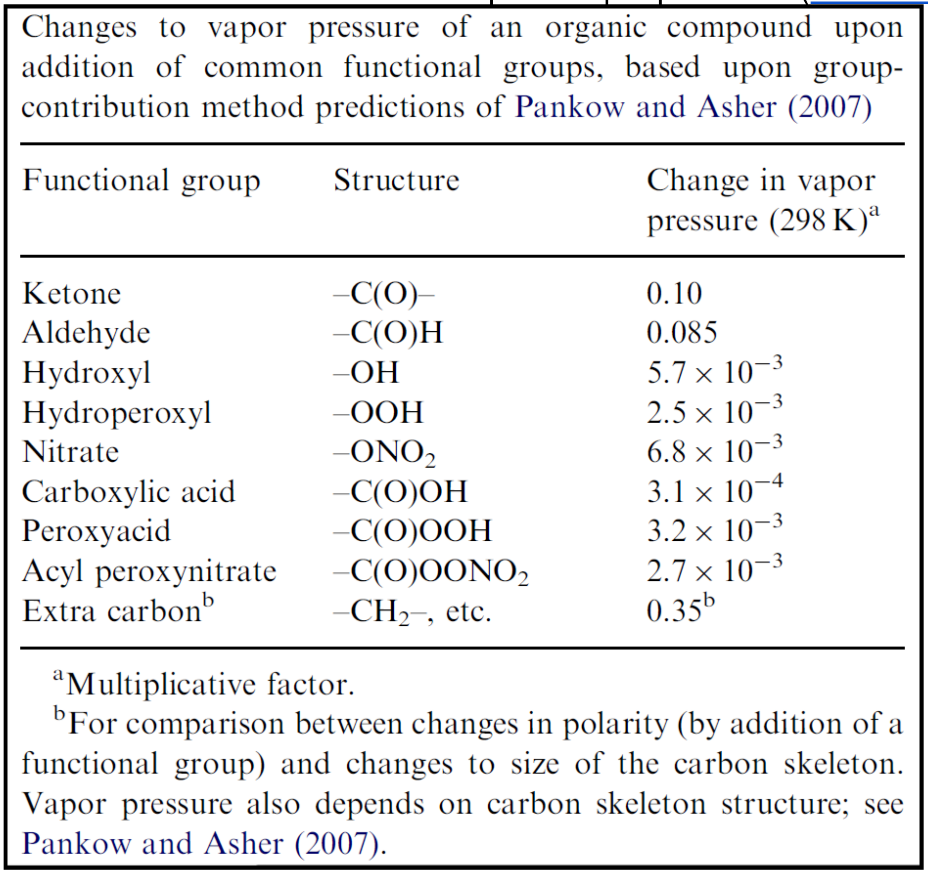


Effects of Oxidation on Compound Vapor Pressures

Compound	P^o_{25C} (torr)	Mass % in Particles*
$CH_3(CH_2)_{11}(CH_2)CH_3$	1×10^{-2}	0.01
$CH_3(CH_2)_{11}(CO)CH_3$	3×10^{-3}	0.03
$CH_3(CH_2)_{11}(CHOH)CH_3$	4×10^{-4}	0.2
$CH_3(CH_2)_{11}(CHONO_2)CH_3$	4×10^{-4}	0.2
$CH_3(CH_2)_{11}(CH_2)C(O)OH$	2×10^{-5}	4
$CH_3(CH_2)_{11}(CH_2CH_2)CH_3$	3×10^{-3}	0.03

*Assuming 10 μg m^{-3} organic matter in particles

- Effects of Functional Groups on vapor pressures (Kroll & Seinfeld, 2008)



Changes to vapor pressure of an organic compound upon addition of common functional groups, based upon group-contribution method predictions of Pankow and Asher (2007)

Functional group	Structure	Change in vapor pressure (298 K)[a]
Ketone	–C(O)–	0.10
Aldehyde	–C(O)H	0.085
Hydroxyl	–OH	5.7×10^{-3}
Hydroperoxyl	–OOH	2.5×10^{-3}
Nitrate	$–ONO_2$	6.8×10^{-3}
Carboxylic acid	–C(O)OH	3.1×10^{-4}
Peroxyacid	–C(O)OOH	3.2×10^{-3}
Acyl peroxynitrate	$–C(O)OONO_2$	2.7×10^{-3}
Extra carbon[b]	$–CH_2–$, etc.	0.35[b]

[a] Multiplicative factor.

[b] For comparison between changes in polarity (by addition of a functional group) and changes to size of the carbon skeleton. Vapor pressure also depends on carbon skeleton structure; see Pankow and Asher (2007).

- Approx. relationship between C*, O/C, N_C & N_O (Murphy et al., 2011 & Pandis et al. 2013)

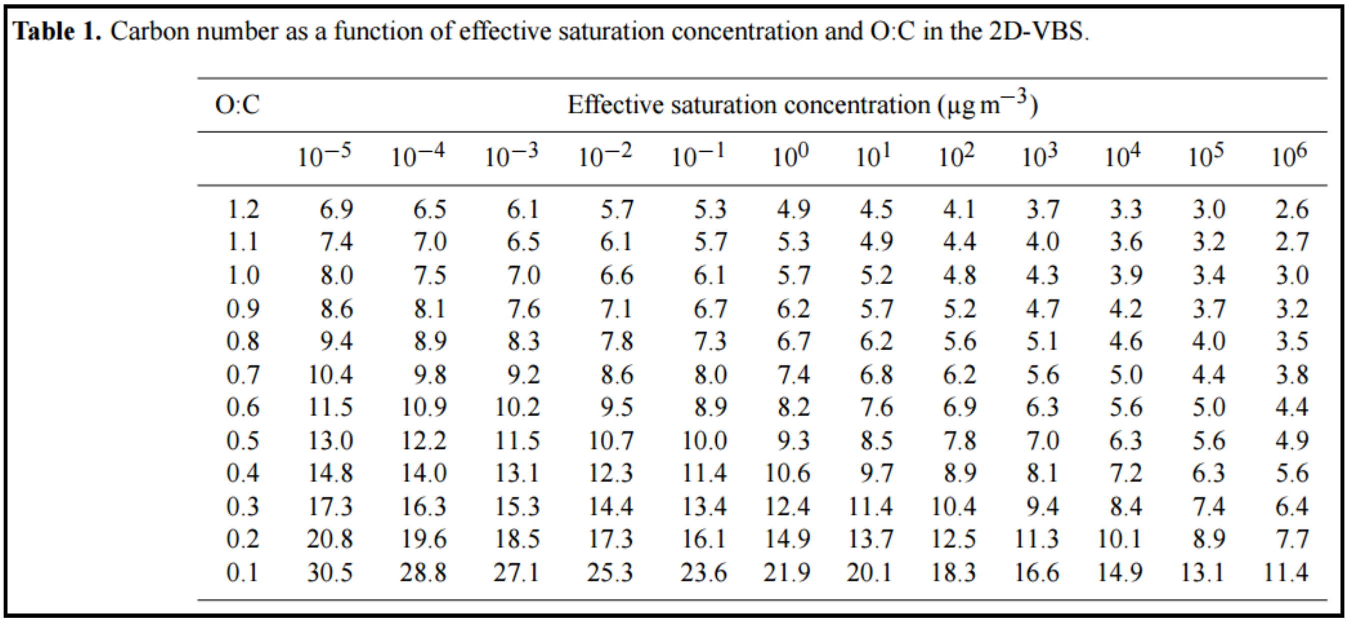


Table 1. Carbon number as a function of effective saturation concentration and O:C in the 2D-VBS.

O:C	Effective saturation concentration (μg m^{-3})											
	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	10^{0}	10^{1}	10^{2}	10^{3}	10^{4}	10^{5}	10^{6}
1.2	6.9	6.5	6.1	5.7	5.3	4.9	4.5	4.1	3.7	3.3	3.0	2.6
1.1	7.4	7.0	6.5	6.1	5.7	5.3	4.9	4.4	4.0	3.6	3.2	2.7
1.0	8.0	7.5	7.0	6.6	6.1	5.7	5.2	4.8	4.3	3.9	3.4	3.0
0.9	8.6	8.1	7.6	7.1	6.7	6.2	5.7	5.2	4.7	4.2	3.7	3.2
0.8	9.4	8.9	8.3	7.8	7.3	6.7	6.2	5.6	5.1	4.6	4.0	3.5
0.7	10.4	9.8	9.2	8.6	8.0	7.4	6.8	6.2	5.6	5.0	4.4	3.8
0.6	11.5	10.9	10.2	9.5	8.9	8.2	7.6	6.9	6.3	5.6	5.0	4.4
0.5	13.0	12.2	11.5	10.7	10.0	9.3	8.5	7.8	7.0	6.3	5.6	4.9
0.4	14.8	14.0	13.1	12.3	11.4	10.6	9.7	8.9	8.1	7.2	6.3	5.6
0.3	17.3	16.3	15.3	14.4	13.4	12.4	11.4	10.4	9.4	8.4	7.4	6.4
0.2	20.8	19.6	18.5	17.3	16.1	14.9	13.7	12.5	11.3	10.1	8.9	7.7
0.1	30.5	28.8	27.1	25.3	23.6	21.9	20.1	18.3	16.6	14.9	13.1	11.4

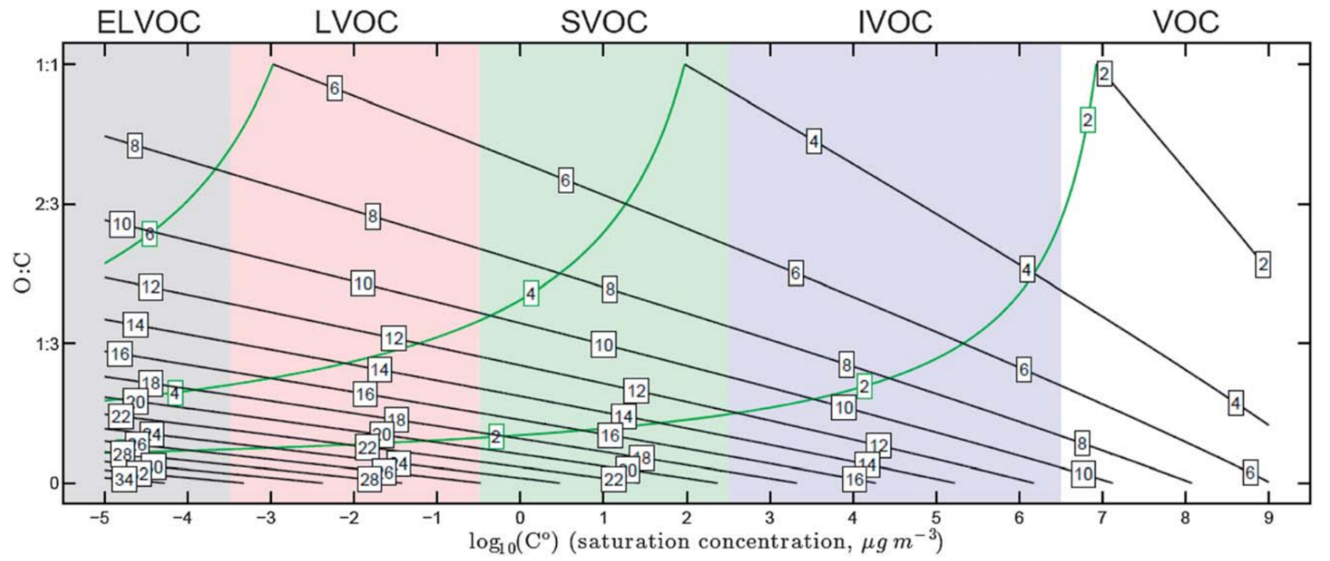


Fig. 1 The 2D Volatility Basis Set space with the volatility (expressed as the logarithm of the saturation concentration) as the *x*-axis and the O : C ratio as the *y*-axis (based on Fig. 4 of Donahue *et al.*[21]). The black isopleths are the number of carbon atoms and the green isopleths the number of oxygen atoms.

- SIMPLE SOA Model (Hodzic & Jimenez, 2011; Cubison et al., 2011; Hayes et al., 2014)
  - Introduce a tracer VOC ("VOC*") proportional to CO emissions as:
    E_{VOC^*} / E_{CO} (gram/gram) = 0.069 for urban emissions
    E_{VOC^*} / E_{CO} (gram/gram) = 0.013 for biomass burning emissions
  - The urban values are quite similar between locations (see Hayes et al., 2014). The BB values are an average over multiple campaigns and there is a lot of variability in BB (see Cubison et al., 2011 & Jolleys et al., 2012), so for a specific campaign it may be 0 or 0.020, but should average around that ratio.
  - VOC* is oxidized as:

$$VOC^* + OH \rightarrow SOA_{nv} \qquad (k = 1.25 \times 10^{-11}\ cm^3\ molec^{-1}\ s^{-1})$$

where SOA_{nv} is non-volatile SOA

The evolution of the atomic O/C ratio of urban SOA vs photochemical age (OH_{exp}) can be estimated as:

$O/C = 1.28(1-0.6\exp(-A/1.5))$

where A is the OH photochemical age (OH_{exp}), in days, using a typical OH concentration of 1.5×10^6 molec cm^{-3}.

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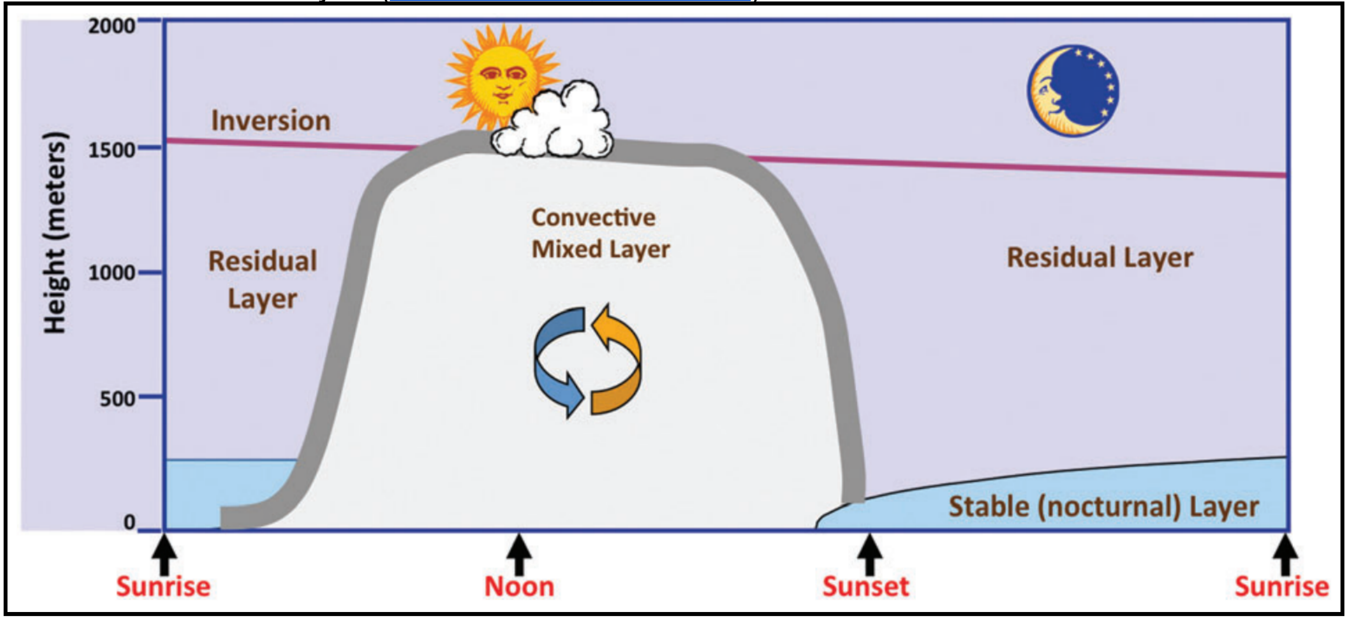
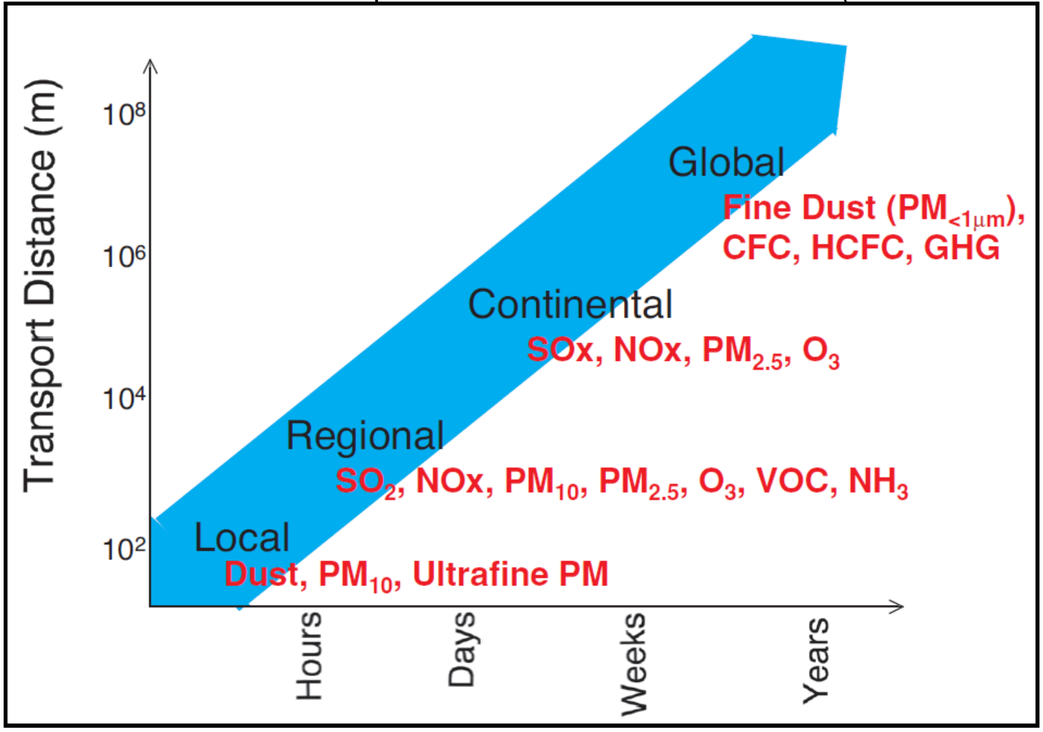
6. Atmospheric Dynamics & Micrometeorology

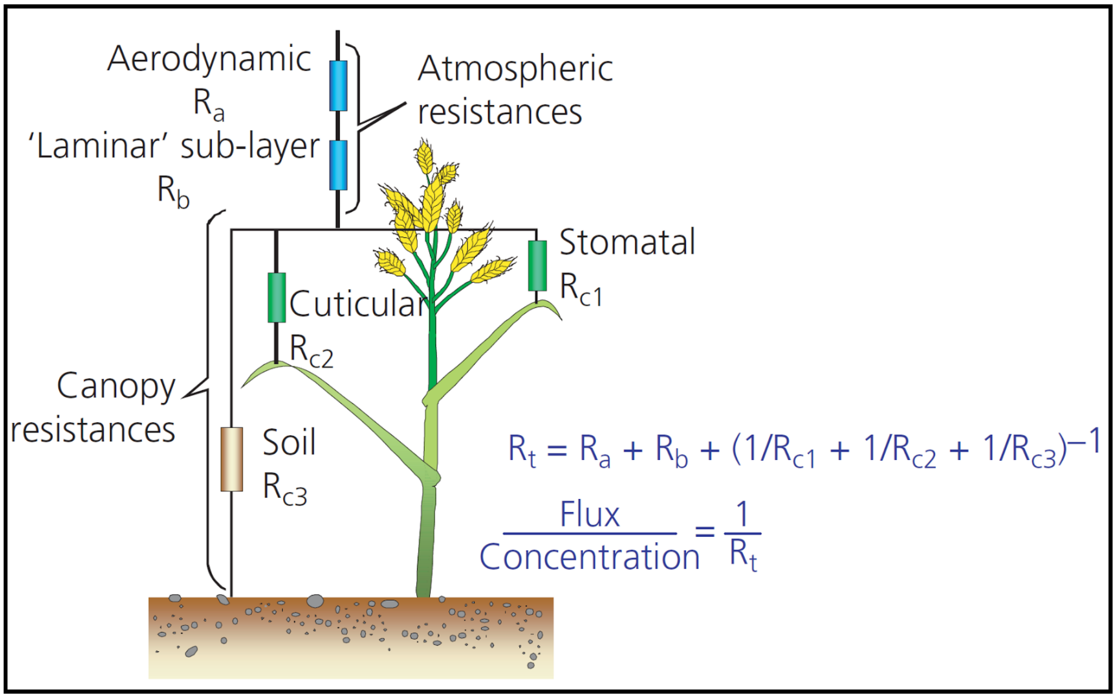
- HYSPLIT synoptic back-trajectory model
- FLEXPART lagrangian trajectory model
- PBL diurnal cycle (Brown & Stutz, CSR 2012)



- Lifetimes & Transport Scales of Different Pollutants (2003 NARSTO PM Assessment)



- Parameterization of Dry Deposition in Atmospheric Models (RSC, 2008)


Aerodynamic
R_a
'Laminar' sub-layer
R_b
Atmospheric resistances
Stomatal
R_{c1}
Cuticular
R_{c2}
Canopy resistances
Soil
R_{c3}
$R_t = R_a + R_b + (1/R_{c1} + 1/R_{c2} + 1/R_{c3})^{-1}$
$\frac{\text{Flux}}{\text{Concentration}} = \frac{1}{R_t}$