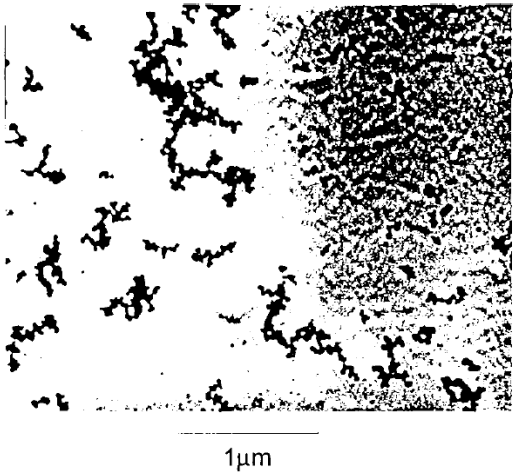
Lecture 22. Carbonaceous Aerosols

Elemental carbon (EC): also called black carbon or graphitic carbon, has a chemical structure similar to impure graphite and is emitted directly into the atmosphere predominantly during combustion

Organic carbon (OC): is either emitted directly by sources (primary OC) or can be formed in situ by condensation of low-volatility products of the photooxidation of hydrocarbons (secondary OC). Note that OC refers to only a fraction of the mass of the organic material (the rest is hydrogen, oxygen, nitrogen, etc.), but because the carbon fraction is measured directly the designation is used routinely.

Carbonaceous particles: are a byproduct of the combustion of liquid or gaseous fuels. Particles formed this way consist of both EC and OC and are known as **soot**. Soot particles are agglomerates of small roughly spherical elementary carbonaceous particles.

Soot



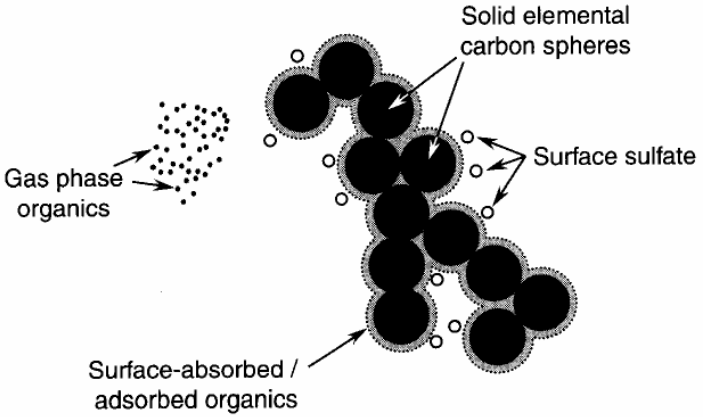


FIGURE 10.1 Schematic of a diesel soot particle consisting of an agglomeration of elemental carbon spheres (0.01- to 0.08-μm diameter). Its surface is covered with absorbed/adsorbed particle-phase organics, including 5-ring (e.g., BaP) and 6-ring PAHs. Gas-phase organics include all of the highly volatile 2-ring PAHs (e.g., naphthalene and methylnapthalenes). Semivolatile 3-ring (e.g., phenanthrene and anthracene) and 4-ring PAHs (e.g., pyrene (**II**) and fluoranthene (**V**)) are distributed between both phases. Sulfate is also associated with diesel particles. (Adapted with permission from Johnson *et al.*, 1994, SAE Paper 940233 © 940233 Society of Automotive Engineers, Inc.; see also Schauer *et al.*, 1999.) *Finlayson-Pitts & Pitts*

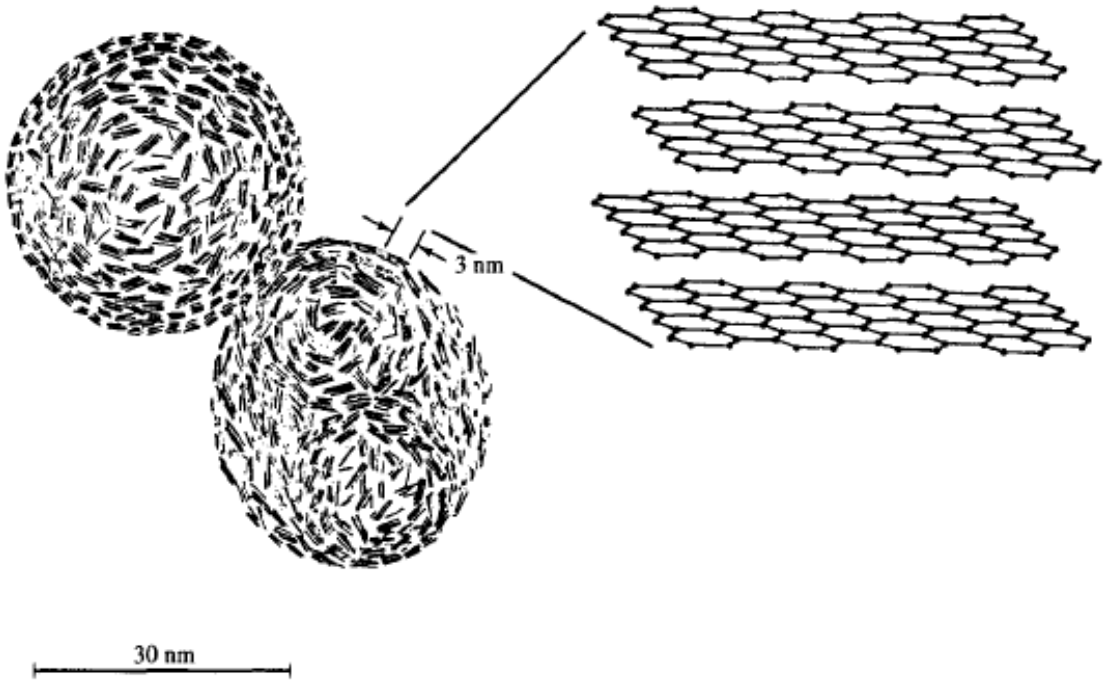
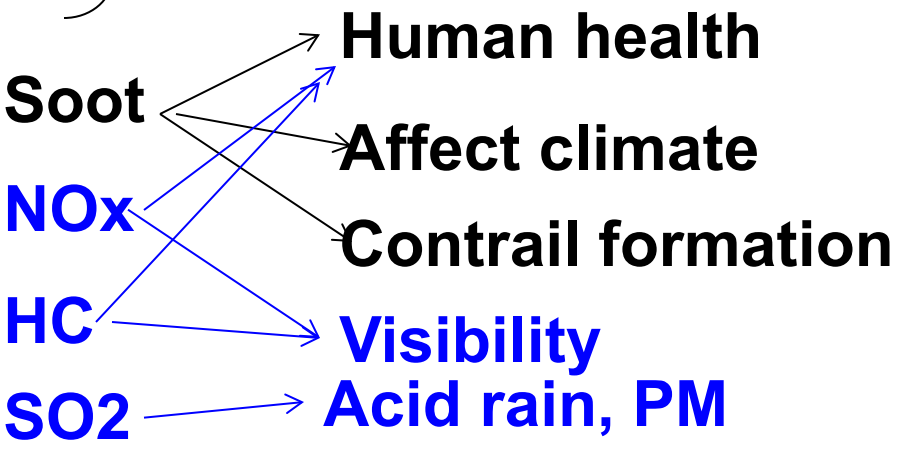


FIGURE 14.1 Schematic of soot microstructure.

Soot

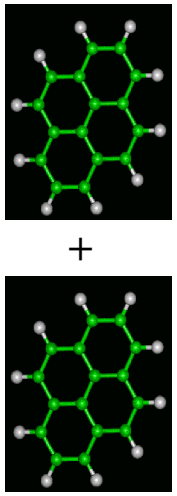
- HC combustion is the source of 79 % of world's energy consumption

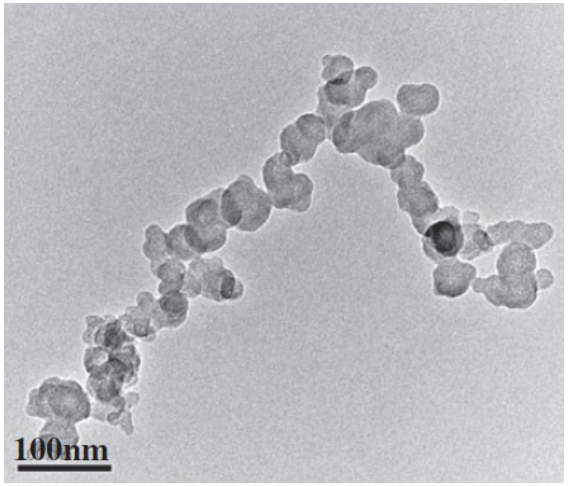
Combustion has undesirable byproducts

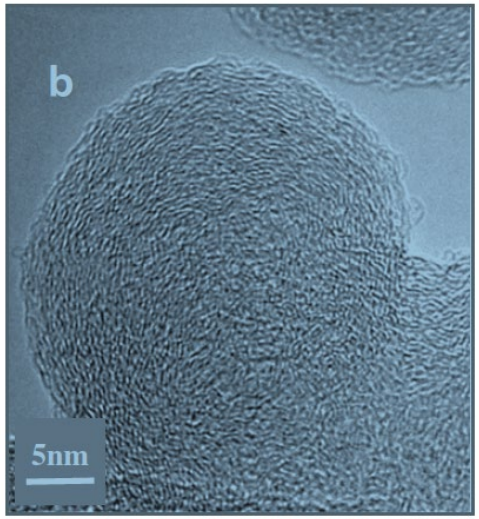


Soot

- A combustion product composed mainly of carbon
- Soot is produced from incomplete combustion of fuel
- Diesel engine generates most soot
- Soot is nucleated from polycyclic aromatic hydrocarbon (PAH)







TEM image of soot

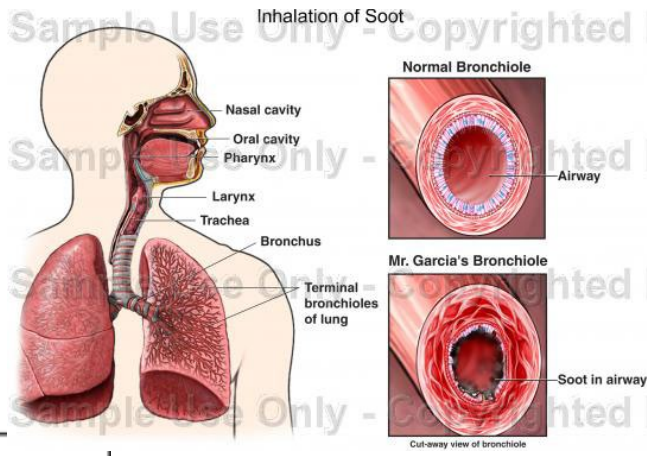
Li et al., 2011, CF

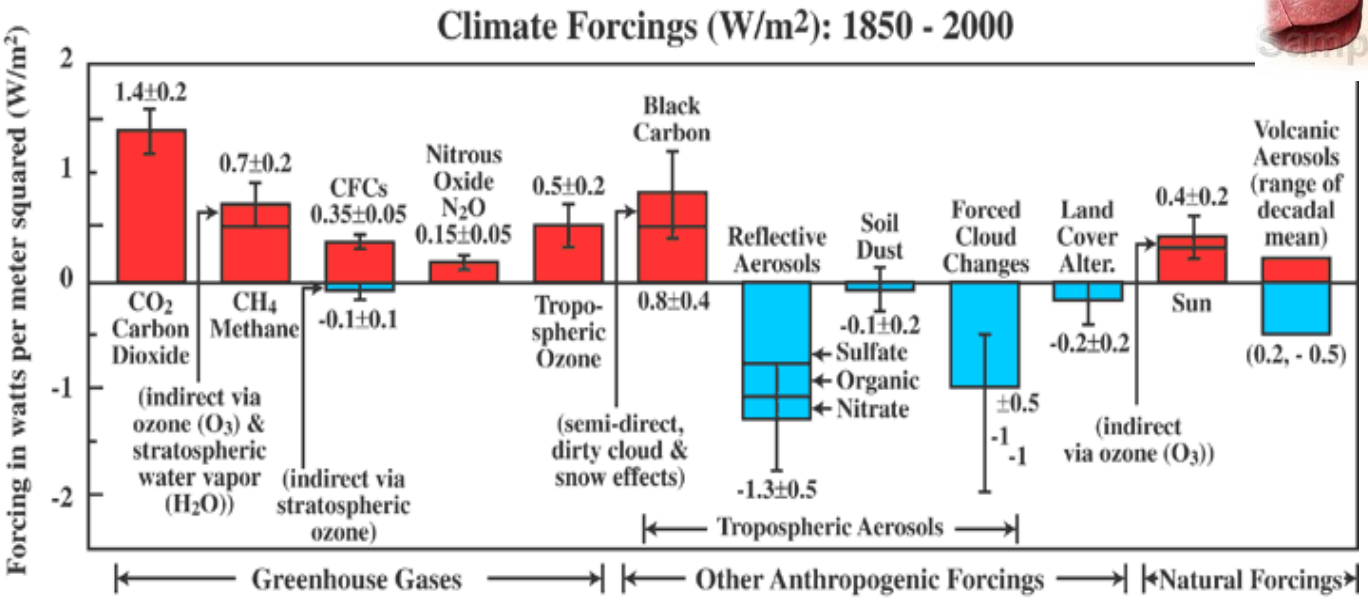
Importance of Soot Study

Soot (PM) inhalation kills

60,000 people a year in US.

Wilson, and Spengler, 1999

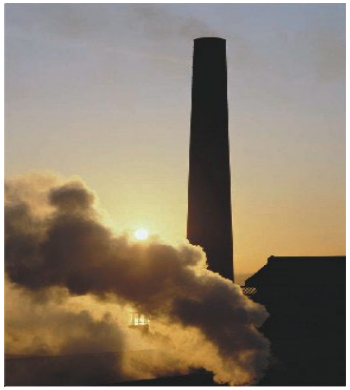
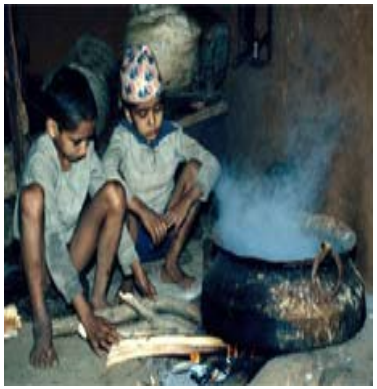


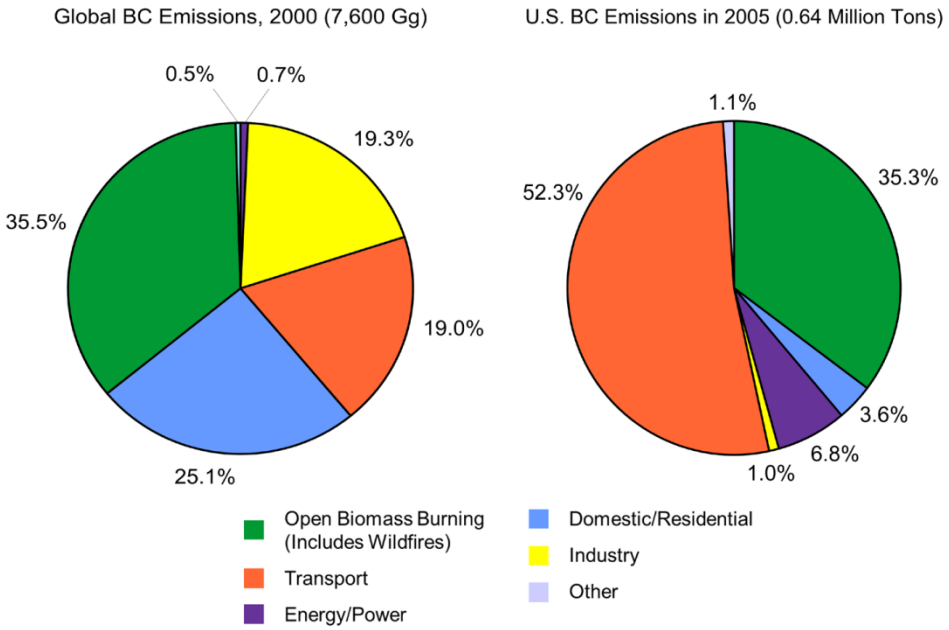


- black carbon is the 2nd most important heating agent after CO_2 , (Jacobson 2001 ,NATURE)
- Soot formation reduces combustion efficiency
- Hence, it is important to study soot

Source of Soot Emission



US EPA, 2012

Although main soot source are biomass and forest-fire in the world, diesel soot is the main source IN USA (52 %).

$$C_mH_n + a\ O_2 \longrightarrow 2\,a\ CO + 0.5\,n\ H_2 + (m - 2a)\ C_s$$

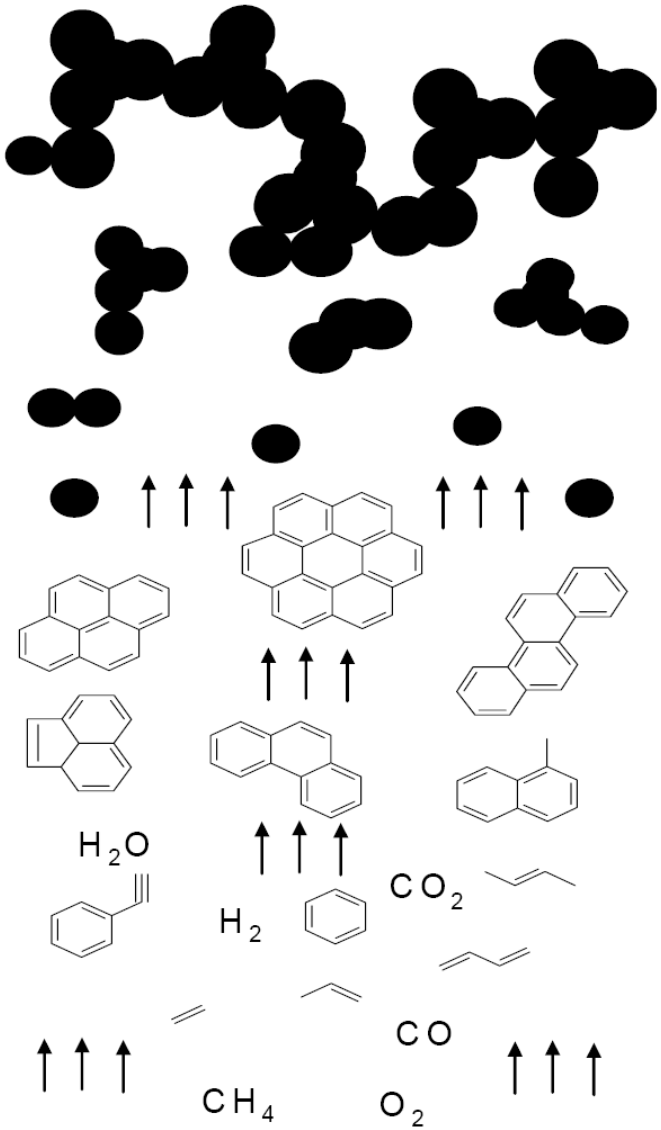


Figure 2: *A schematic picture of soot formation in homogenous mixtures.*

Table 2: Chemical processes and the rates of reactions used in original Fusco et al's model [7]

No.	Chemical processes	Reaction rates	Refs.
1	$Fuel \xrightarrow{\dot{R}_1} \frac{m}{2} R$	$\dot{R}_1 = \frac{m}{2} k_1 [Fuel]$ $k_1 = 0.7 \times 10^{12} \exp\left(-1.2 \times 10^5 / RT\right)$	[7]
2	$Fuel \xrightarrow{\dot{R}_2} \frac{m}{2} C_2 H_2$	$\dot{R}_2 = \frac{m}{2} k_2 [Fuel]$ $k_2 = 2.0 \times 10^8 \exp\left(-4.9 \times 10^4 / RT\right)$	[7]
3	$R + O_2 \xrightarrow{\dot{R}_3} \text{Pr}\, oduct$	$\dot{R}_3 = \frac{m}{2} k_3 [R][O_2]$ $k_3 = 1.0 \times 10^{12} \exp\left(-4.0 \times 10^4 / RT\right)$	[7]
4	$C_2 H_2 + O_2 \xrightarrow{\dot{R}_4} 2CO + H_2$	$\dot{R}_4 = \frac{m}{2} k_4 [C_2 H_2][O_2]$ $k_4 = 6.0 \times 10^{13} \exp\left(-5.0 \times 10^4 / RT\right)$	[7]
5	$R \xrightarrow{\dot{R}_5} C_{soot}$	$\dot{R}_5 = k_5 [R]$ $k_5 = 1.0 \times 10^{10} \exp\left(-5.0 \times 10^4 / RT\right)$	[7]
6	$C_{soot} + C_2 H_2 \xrightarrow{\dot{R}_5} C_{soot+2} + H_2$	$\dot{R}_6 = k_6 [C_2 H_2] (A_{\text{Soot}})^{1/2}$ $k_6 = 4.2 \times 10^4 \exp\left(-1.2 \times 10^4 / RT\right)$ $A_{Soot} = \pi (d_{Soot})^2 N$, $d_{Soot} = 25$ nm	[7]
7	$C_{soot} + O_2 \xrightarrow{\dot{R}_7} C_{soot-2} + 2CO$	Nagle and Strckland-Constable model	[6]
8	$xC_{soot} \xrightarrow{\dot{R}_8} C_{soot}$	$\dot{R}_8 = k_{coag} T^{1/2} (f_v)^{1/6} (f_{\text{N}})^{11/6}$ $k_{coag} = 1.05 \times 10^{-7}$	[7]

Soot forms in a flame as the result of a chain of events starting with the oxidation and/or pyrolysis of the fuel into small molecules. Acetylene, C_2H_2, and polycyclic aromatic hydrocarbons (PAHs) are considered the main molecular intermediates for soot formation and growth (McKinnon and Howard, 1990). The growth of soot particles involves first the formation of soot nuclei and then their rapid growth due to surface reactions (Harris and Weiner, 1983a,b).

The soot nuclei themselves represent only a small fraction of the overall soot mass produced. However, the final soot mass depends critically on the number of nuclei formed, since the growth rate of soot particles is not a strong function of the fuel composition (Harris and Weiner, 1983a,b). Unfortunately, despite numerous studies, this crucial nuclei formation step remains poorly understood.

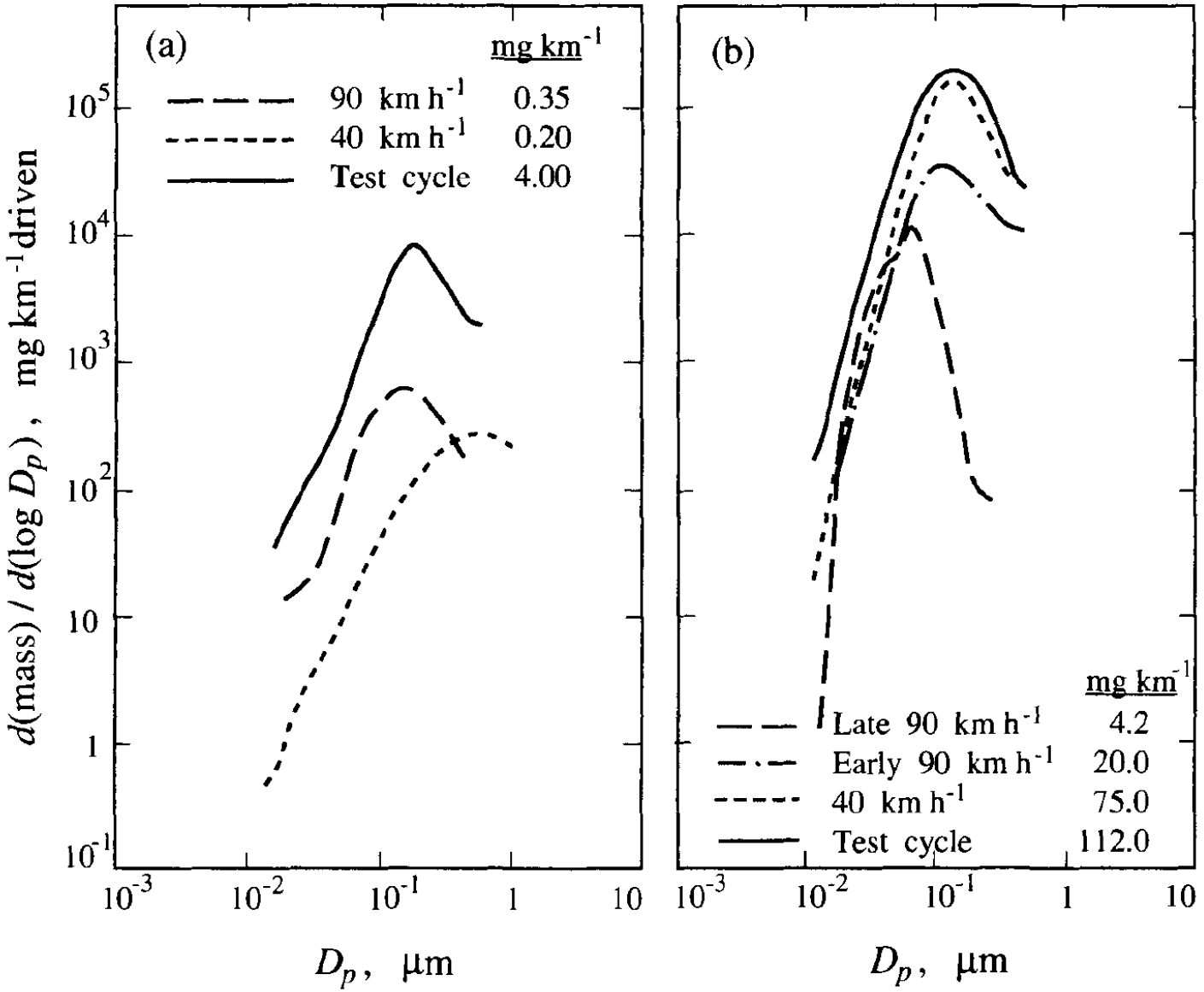


FIGURE 14.2 Mass distributions of primary automobile exhaust produced under cruise conditions as a function of speed during combustion of (a) unleaded gasoline and (b) leaded gasoline as reported by Hildemann et al. (1991b). (Reprinted from *Aerosol Sci. Technol.* **14**, Hildemann et al., 138–152, Copyright 1991, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.)

TABLE 14.1 Estimates of Fuel-Specific Particulate Carbon Emission Rates, g(C) (kg fuel)$^{-1}$

Source	Organic Carbon	Elemental Carbon
Fireplace		
Hardwood	4.7	0.4
Softwood	2.8	1.3
Motor vehicles		
Noncatalytic	0.04–0.24	0.01–0.13
Catalytic	0.01–0.03	0.01–0.03
Diesel	0.7–1.0	2.1–3.4
Furnace (natural gas)		
Normal	0.0004	0.0002
Rich	0.007	0.12

Sources: Muhlbaier and Williams (1982) and Muhlbaier and Cadle (1989).

TABLE 14.2 Elemental and Organic Carbon Percentages in Emissions by Different Sources

Fuel	Elemental Carbon	Organic Carbon	References
Diesel	74 ± 21^a	23 ± 8^a	Watson et al. (1990)
	52 ± 5^a	36 ± 3^a	Cooper et al. (1987)
	43 ± 8^b	49 ± 13^b	Houck et al. (1989)
Unleaded gasoline	18 ± 11^a	76 ± 29^a	Watson et al. (1990)
	5 ± 7^c	93 ± 52^c	Cooper et al. (1987)
	39 ± 10^a	49 ± 10^a	Cooper et al. (1987)
Leaded gasoline	16 ± 7^a	67 ± 23^a	Watson et al. (1990)
	13 ± 1^c	52 ± 4^c	Cooper et al. (1987)
	15 ± 2^a	51 ± 20^a	Cooper et al. (1987)
Mixed vehicles	28 ± 19	50 ± 24	Watson et al. (1990)
(tunnel and roadside)	38 ± 5	38 ± 6	Cooper et al. (1987)
	36 ± 11	39 ± 19	Watson et al. (1990)
Dust ($< 2.5\,\mu m$)	2	12	Watson and Chow (1994)
Woodburning	15	70	Watson and Chow (1994)
Coal-fired power plant	2	—	Olmez et al. (1988)

[a]Measured during dynamometer tests following the modified Federal Test Procedure (FTP).
[b]Roof monitoring at inspection station.
[c]Steady-speed ($55\,km\,h^{-1}$) tests.

Ambient Elemental Carbon Concentrations

TABLE 14.3 Measured Daily Average Elemental and Organic Carbon Concentration in a Series of U.S. Studies

Location	Date	Samples	EC		OC	
			$\mu g\ m^{-3}$	%	$\mu g(C)\ m^{-3}$	%
Eastern USA						
Philadelphia	August 1994	21	0.76	2.4	4.51	14
Roanoke	Winter 1988/1989	—[a]	1.5	7.5	7.3	36.7
Western USA						
Los Angeles	Summer 1987	44	2.37	5.8	8.27	20.1
Los Angeles	Fall 1987	24	7.28	8.1	18.46	20.5
San Joaquin	1988–1989	35	3.24	10.8	4.87	16.3
Phoenix	Winter 1989/1990	200	7.47	25.4	10.10	34.4
Central USA						
Albuquerque	Winter 1984/1985	—[a]	2.1	10.2	13.2	64.6
Denver	Winter 1987/1988	136	4.41	22.4	7.25	36.9
Chicago	July 1994	16	1.31	9.6	5.39	43.5

[a]Not reported.

Source: U.S. EPA (1996).

Primary and Secondary Organic Aerosols

Primary Organic Aerosol (POA)

Anthropogenic
- Gasoline
- Diesel
- Wood smoke
- Meat Cooking …

Biogenic
- *Plant debris*
- *Pollen*
- *Bacteria …*

Secondary Organic Aerosol (SOA)

Particulate products of anthropogenic & biogenic VOCs (volatile organic compounds)

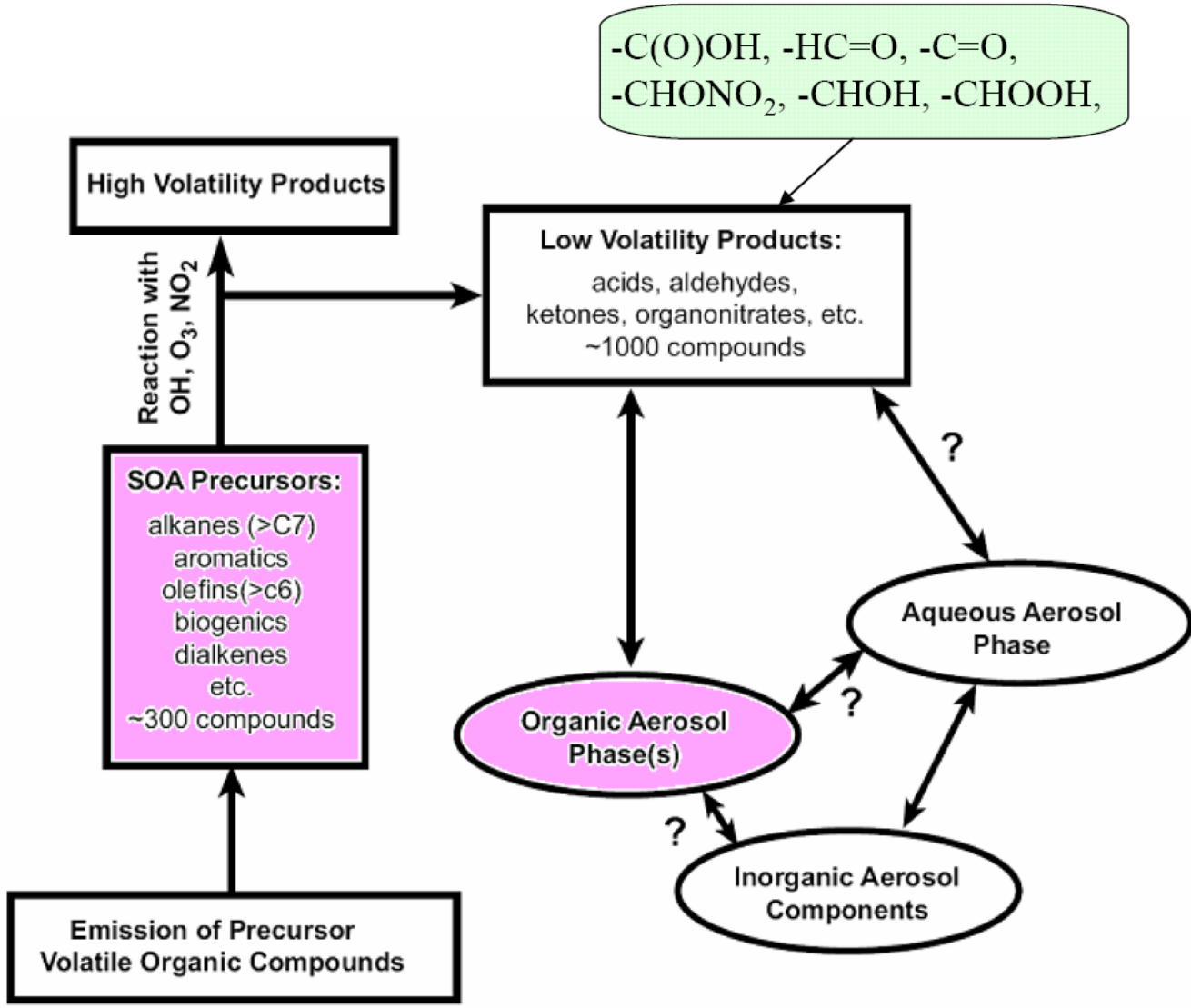


Figure 3.9. Schematic of the formation of secondary organic aerosol in the atmosphere. *2003 NARSTO Assessment*

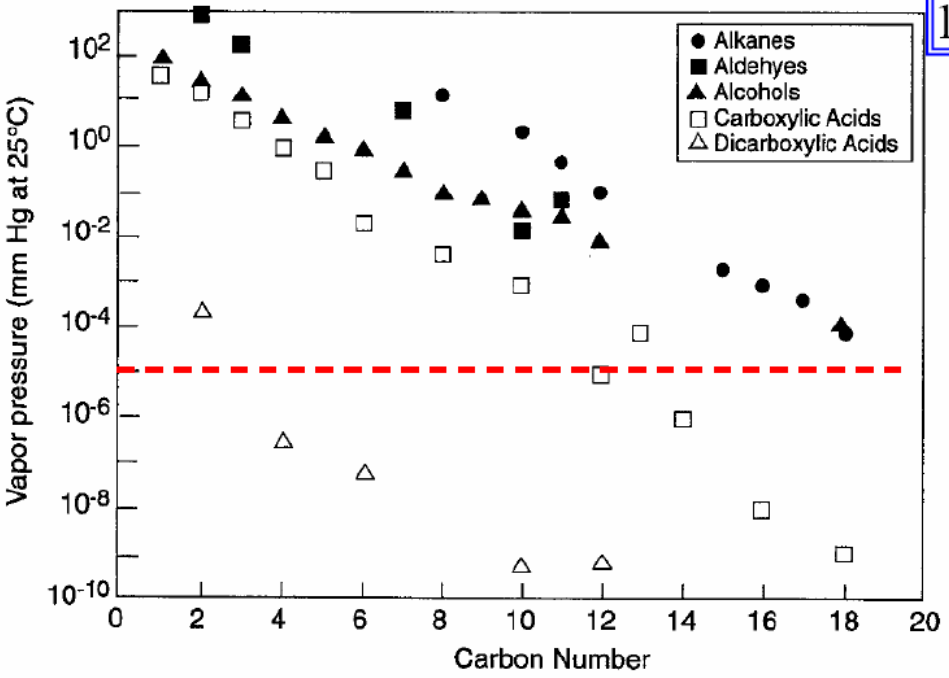
Secondary Organic Aerosol Formation

Mechanisms:

Volatility is the key!

VOC $\xrightarrow{\text{rxn}}$ higher polarity, lower volatility products $\xrightarrow[\text{conversion}]{\text{G-P}}$ SOA material

- Typically VOC ≥ C_{6-7} are effective SOA precursors
  - aromatic hydrocarbons (*e.g.* toluene, ethylbenzene, xylenes)
  - terpenic biogenic hydrocarbons (*e.g.* α-pinene, β-pinene)
- Oxidation mechanisms for large VOCs are very complex



1 mmHg = 1 torr = 133 Pa = (1/760) atm

Vapor pressure depends on:

1) the number of carbon atoms in the molecule.
2) the number and type of polar functional groups.
3) Adding O and/or N atoms reduce volatility.

Figure 1. Vapor pressures of organic compounds as a function of carbon number and functionality. Data from *Grosjean* [1978]. *Jacobson, M.C., H.C. Hansson, K.J. Noone, and R.J. Charlson, Organic atmospheric aerosols: Review and state of the science, Reviews of Geophysics, 38 (2), 267-294, 2000.*

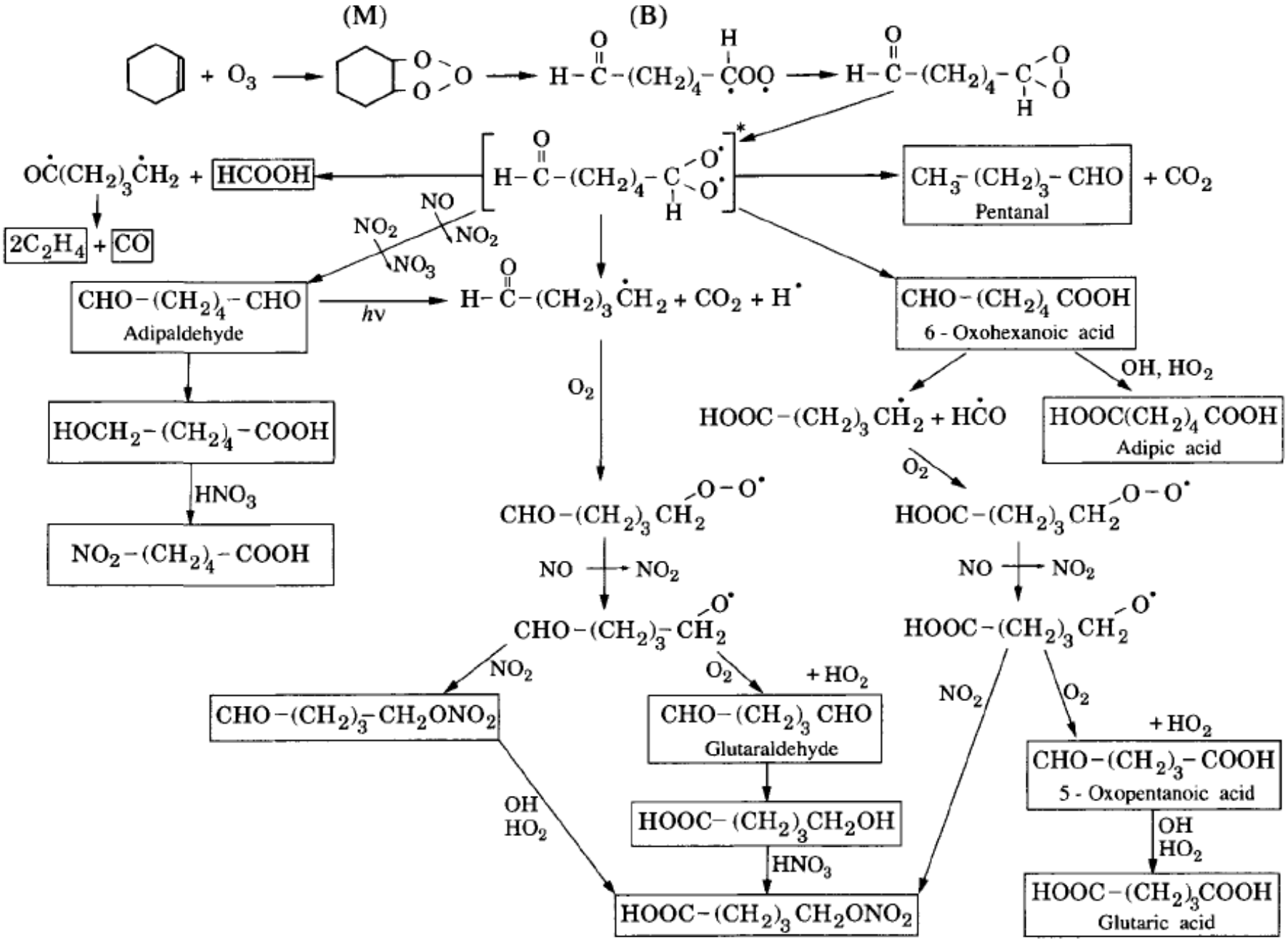


FIGURE 14.11 Proposed gas-phase reaction mechanism for the cyclohexene-ozone reaction.

TABLE 13.10 Products of the Cyclohexene–Ozone Gas–Phase Reaction (Seinfeld and Pandis, 1998 edition)

Compound	Formula	Molar Yield	Vapor Pressure (10^{-9} atm)
Pentanal	$CH_3(CH_2)_3CHO$	0.17	$>10^6$
Adipaldehyde	$CHO(CH_2)_4CHO$	0.09	
Glutaraldehyde	$CHO(CH_2)_3CHO$	0.22	
Formic acid	$HCOOH$	0.12	$>10^6$
6-Oxohexanoic acid	$CHO(CH_2)_4COOH$	0.02–0.05	
Adipic acid	$COOH(CH_2)_4COOH$	0.004–0.05	0.08
5-Oxopentanoic acid	$CHO(CH_2)_3COOH$	0.007–0.05	0.3
Glutaric acid	$COOH(CH_2)_3COOH$	0–0.05	6
6-Nitrohexanoic acid	$COOH(CH_2)_4CH_2ONO_2$	—	—
6-Hydrohexanoic acid	$COOH(CH_2)_4CH_2OH$	—	—
5-Nitratopentanoic acid	$COOH(CH_2)_3CH_2ONO_2$	—	—
5-Hydroxypentanoic acid	$COOH(CH_2)_3CH_2OH$	—	—
Carbon monoxide	CO	0.42	$>10^6$
Carbon dioxide	CO_2	0.18	$>10^6$

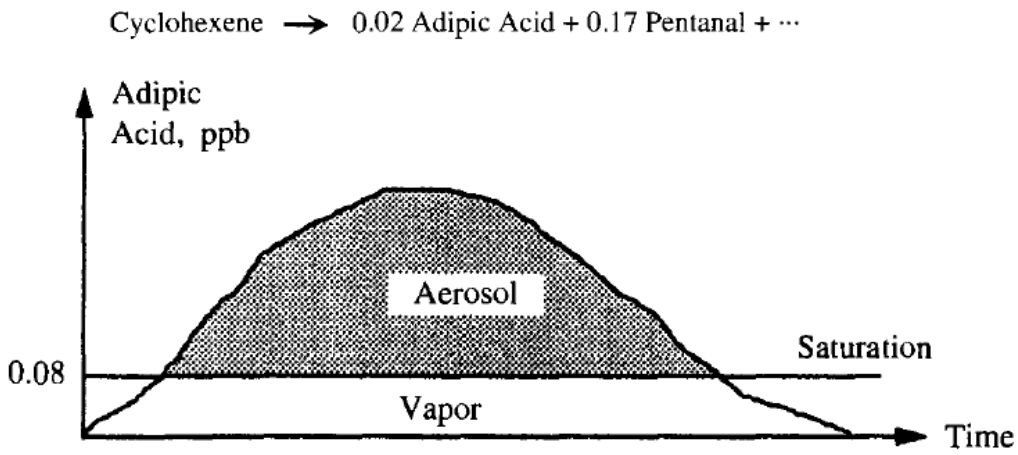


FIGURE 14.12 Schematic of the formation of secondary organic aerosol during the cyclohexene oxidation by mass transfer of adipic acid to the aerosol phase. This case corresponds to a single-component secondary organic aerosol phase without any interactions with the rest of the aerosol species.

Organic Aerosol Analysis

- Organic aerosols are composed of thousands of compounds.
- Chemical analysis is a significant challenge.
- Compound specific study can only explain a small fraction of total organic mass. Large fraction unidentified.
- A number of analytical methods are available, they are complementary.

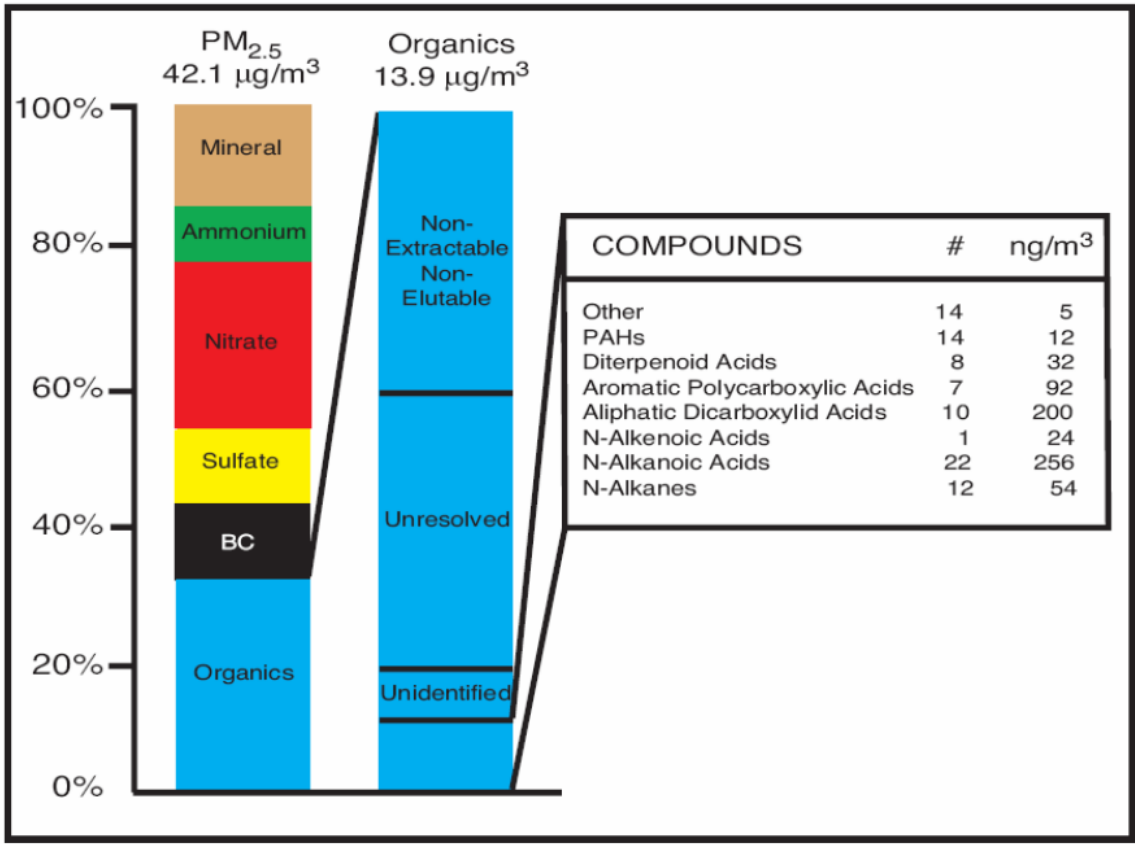
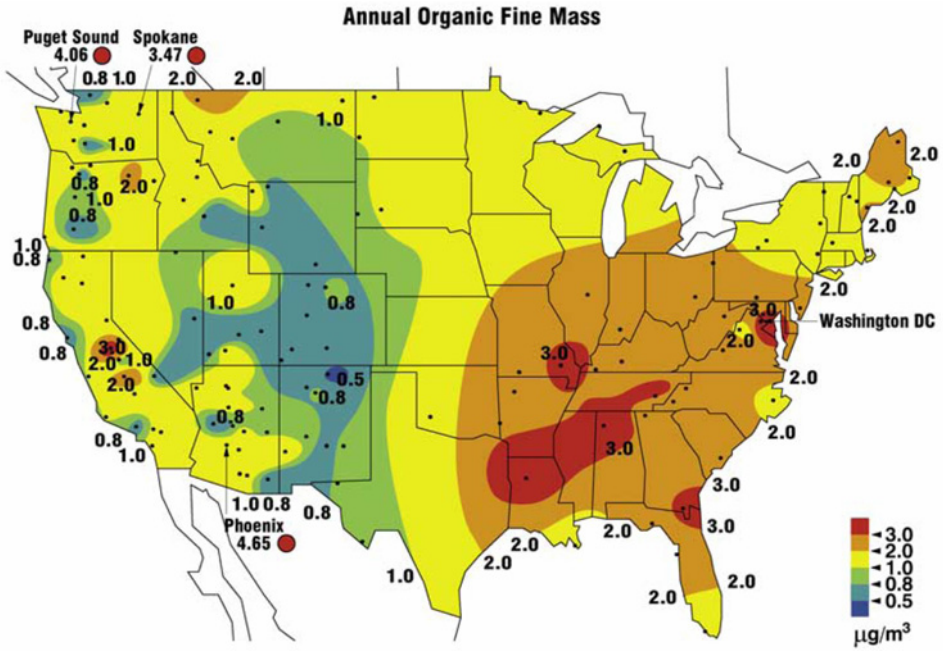


Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds were identified and quantified they represented only 15 percent or so of the total organic mass. *2003 NARSTO Assessment*



- Estimated mass concentrations of OA:
  - Typical ~ 2.0 and 3.0 µg/m³
  - Highest in the eastern US.
    (emissions of biogenic VOC are 2–10 times greater in the Southeast than much of the Northeast)
- Org% of total $PM_{2.5}$ mass:
  - Highest in the Northwest, typically > 40%.
  - ~ 30% in the Southeast.
  - Only a few sites < 20%

Figure 4a. Isopleth map of organic mass concentrations. Phoenix, Seattle, and Spokane are shown as numerical insets and were not used for creating the contours.

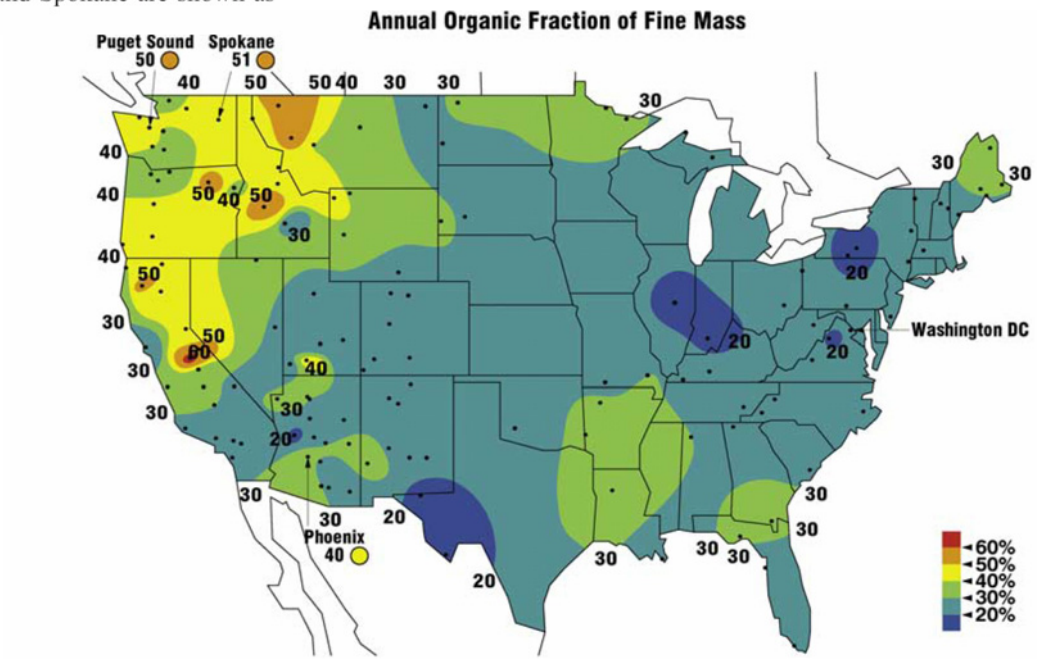


Figure 4b. Isopleth map of the percent that organic mass contributes to reconstructed fine mass Phoenix, Seattle, and Spokane are shown as numerical insets and were not used for creating the contours

Data from 143 EPA IMPROVE (Interagency Monitoring of Protected Visual Environments) network sites in 2004.

Organic mass concentration = OC × 1.4

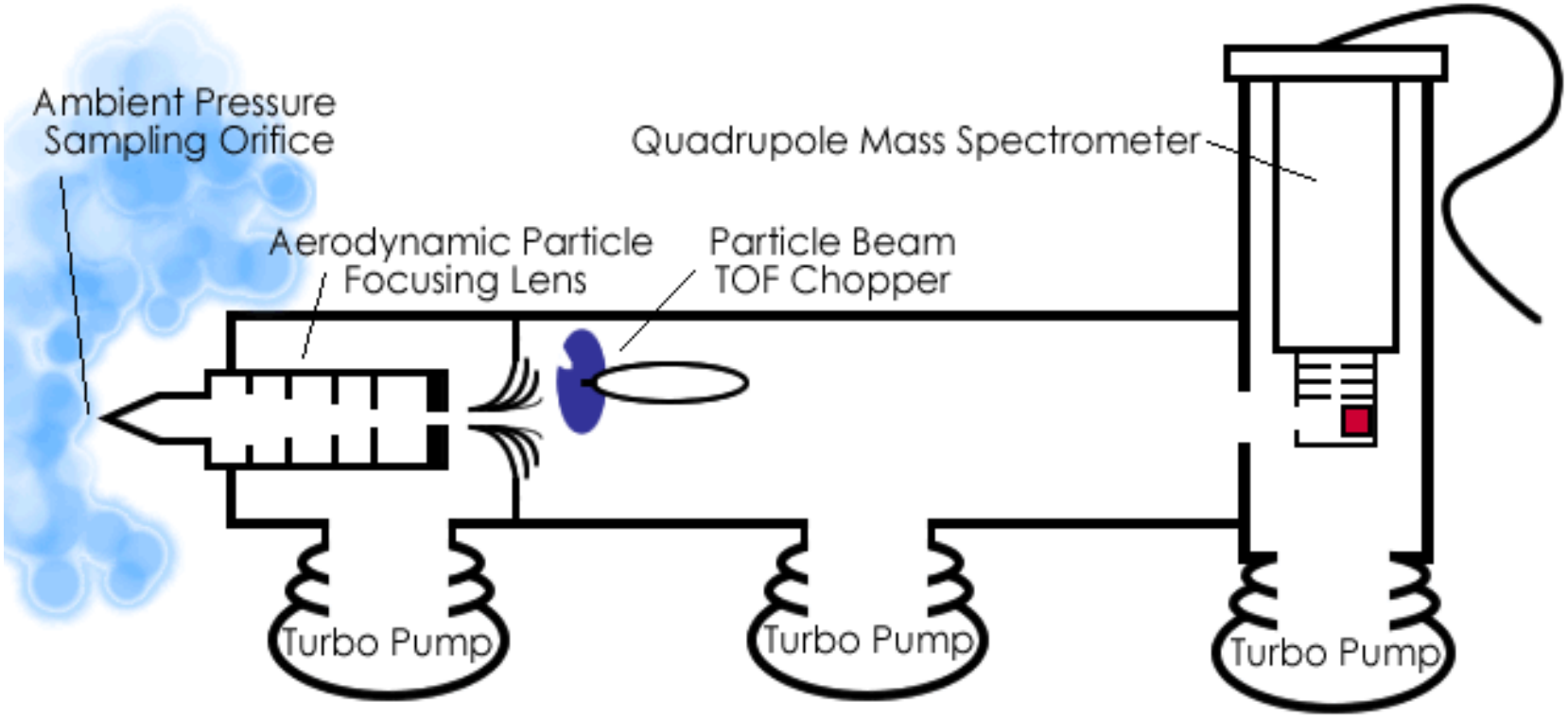
Malm, W.C., B.A. Schichtel, M.L. Pitchford, L.L. Ashbaugh, and R.A. Eldred, Spatial and monthly trends in speciated fine particle concentration in the United States, Journal of Geophysical Research-Atmospheres, 109, D03306, doi:10.1029/2003JD003739, 2004.

Aerodyne Aerosol Mass Spectrometer (AMS)

Particle Beam Generation

Aerodynamic Sizing

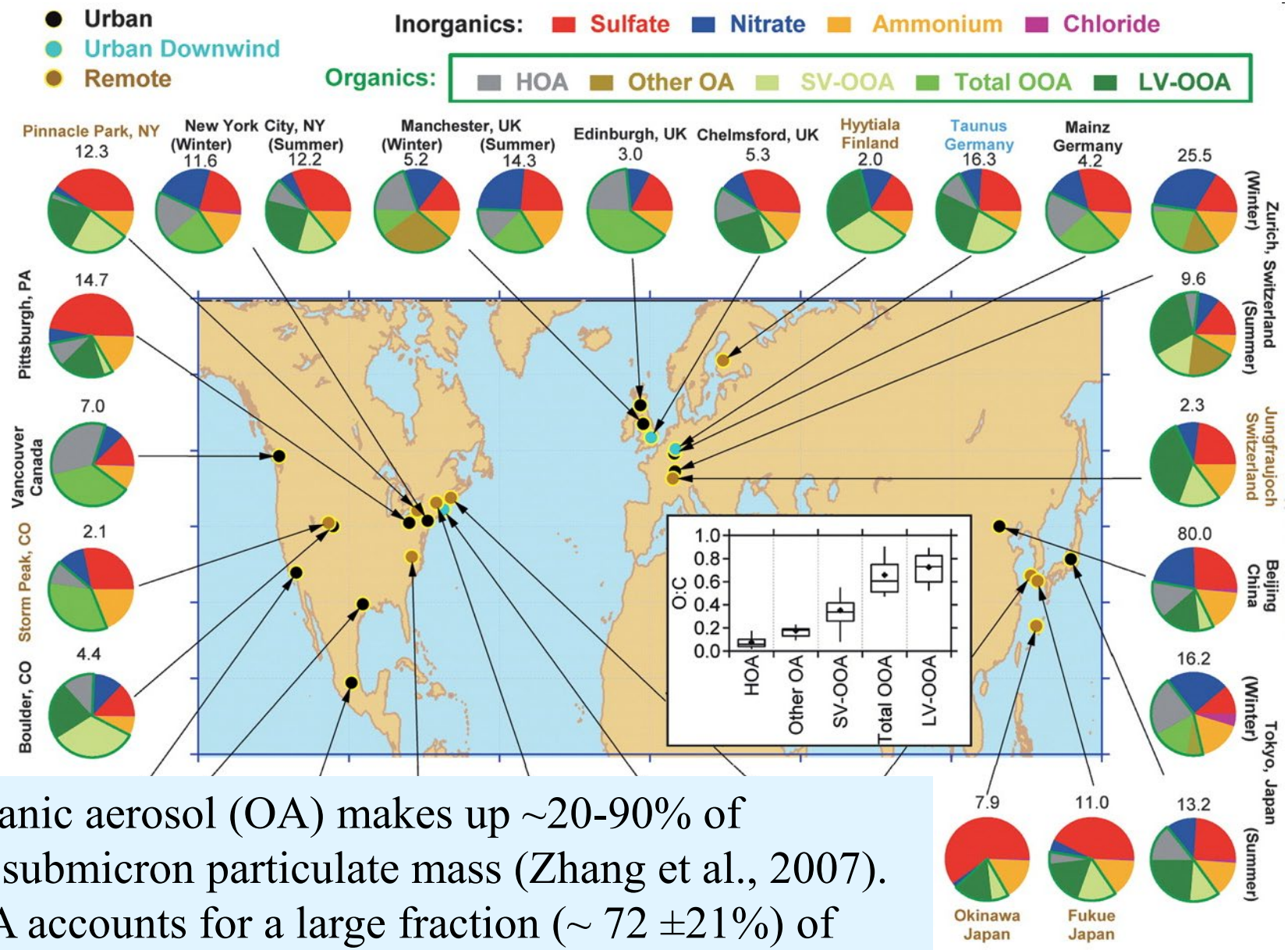
Particle Composition



100% transmission (60-600 nm), aerodynamic sizing, linear mass signal, time resolution = minutes

Jayne et al., ***AS&T****, 33:1-2(49-70), 2000.*
Jimenez et al., ***JGR****, 108(D7), 8425, 2003*

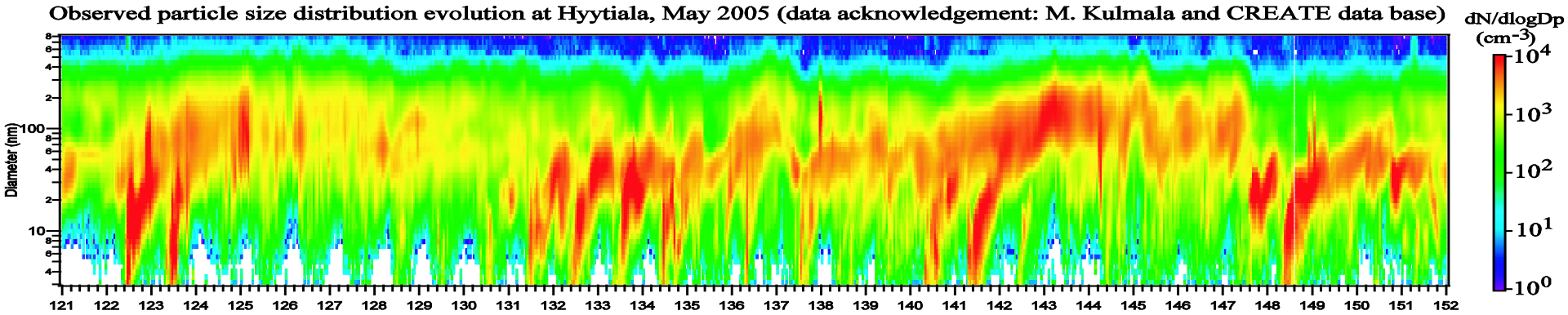
Organic Aerosol Components Worldwide



Organic aerosol (OA) makes up ~20-90% of submicron particulate mass (Zhang et al., 2007).

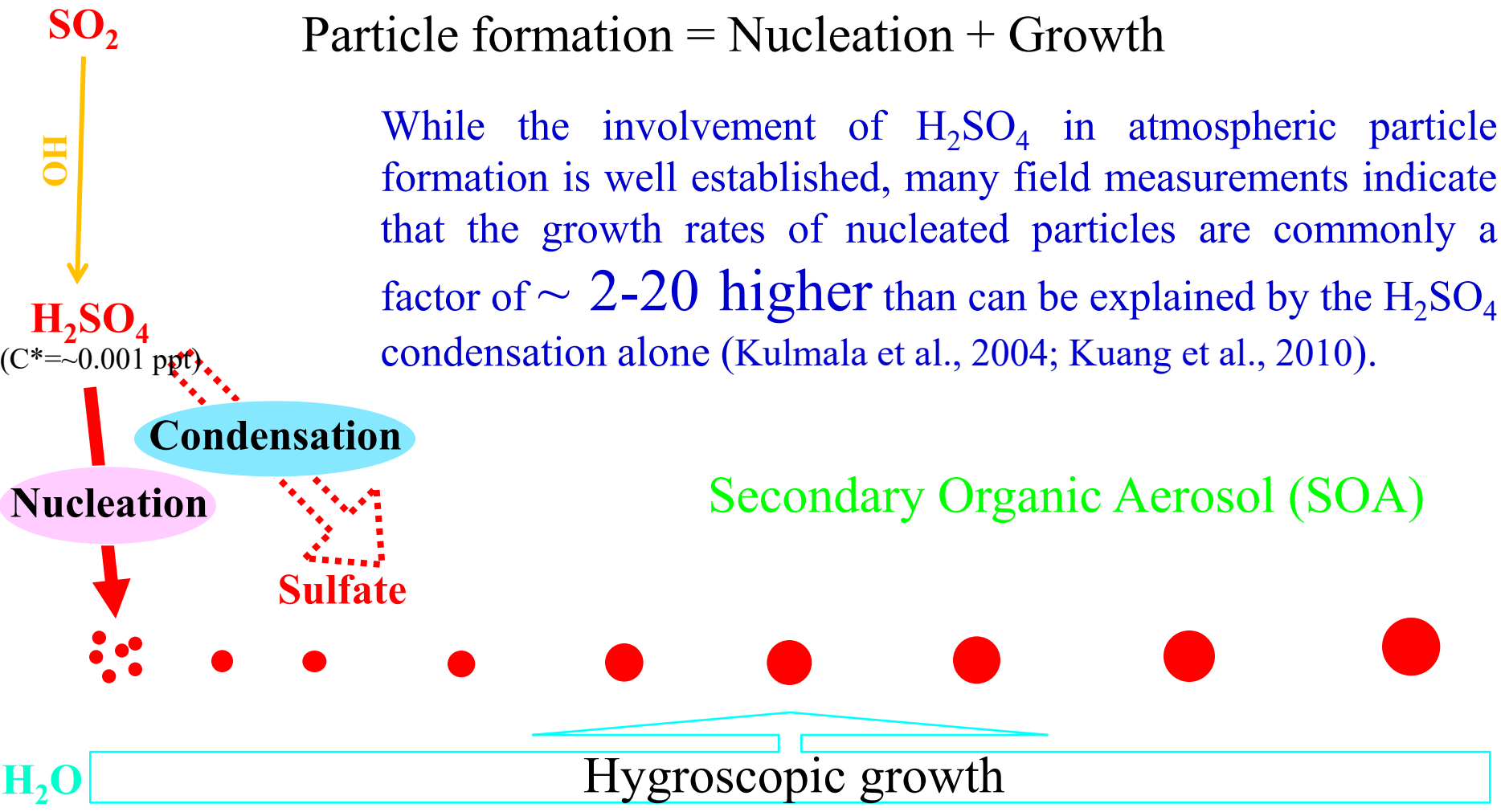
SOA accounts for a large fraction (~ 72 ±21%) of these OA mass (Jimenez et al., 2009).

Donahue, et al., Science 326, 1525 (2009)



Particle formation = Nucleation + Growth

While the involvement of H_2SO_4 in atmospheric particle formation is well established, many field measurements indicate that the growth rates of nucleated particles are commonly a factor of ~ 2-20 higher than can be explained by the H_2SO_4 condensation alone (Kulmala et al., 2004; Kuang et al., 2010).



Environ. Sci. Technol. **2004**, *38,* 4797−4809

Insights into the Chemistry of New Particle Formation and Growth Events in Pittsburgh Based on Aerosol Mass Spectrometry

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particles and contributed the least to the new particle growth.

1. Introduction

New particle formation and growth events have be observed in many locations including forested (*2*, *3*), coast (*4*−*6*), rural/remote (*7*−*11*), arctic (*12*, *13*), and urban (*1*, *14*−*19*) areas. These events are one of the major sources ultrafine particles in both clean and polluted atmospher and an important mechanism for sustaining the ambie aerosol population. Given the increased toxicity of ultrafi particles (*20*) and the role of ultrafine particles in partic related premature deaths and morbidity (*21*−*24*), the abu dance of these particles after nucleation is considered as potential human health hazard. In addition, the growth nuclei from a detectable size of a few nanometers in particles that are optically active and efficient cloud co densation nuclei has important implications for visibili and climate (*4*, *25*, *26*).

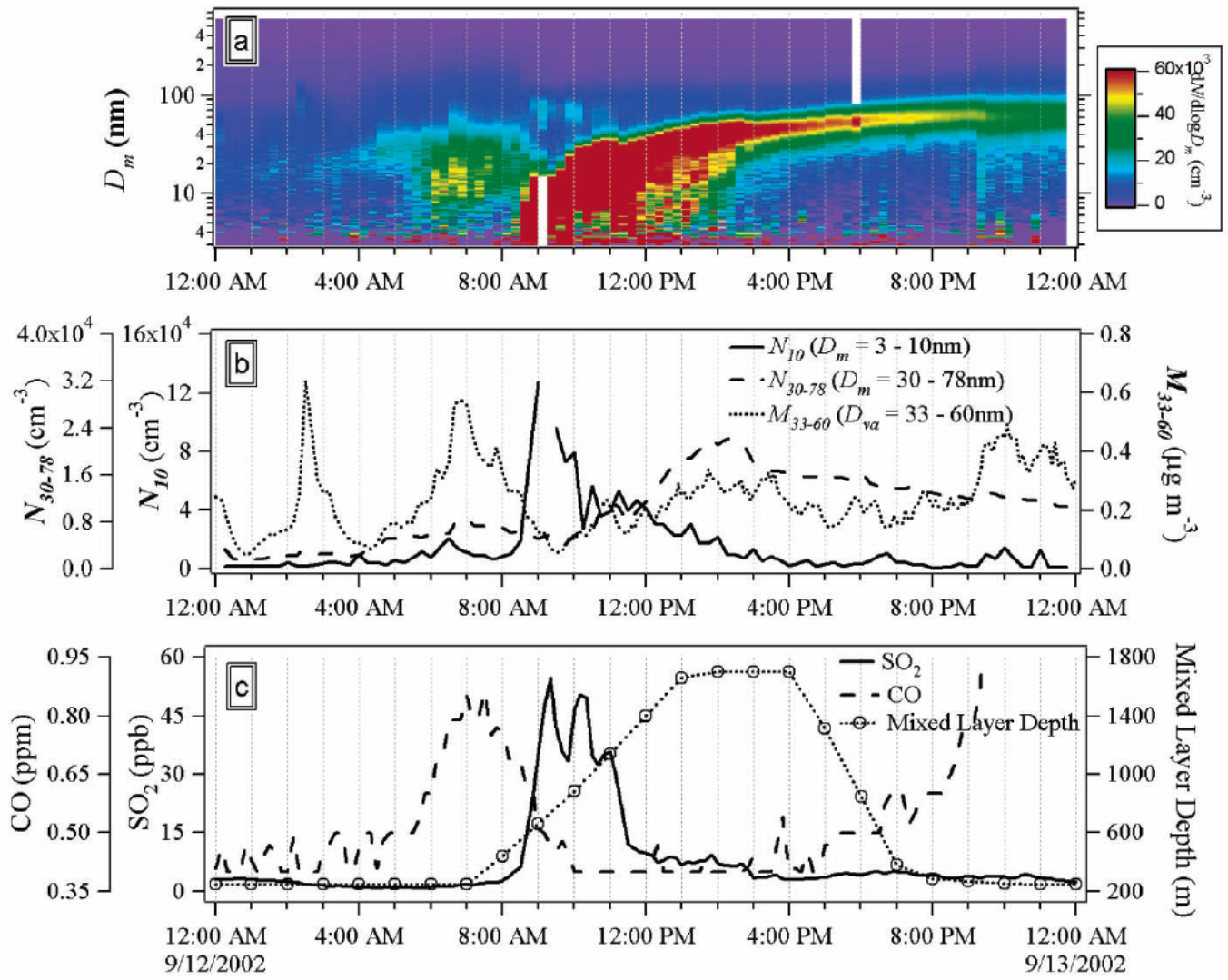
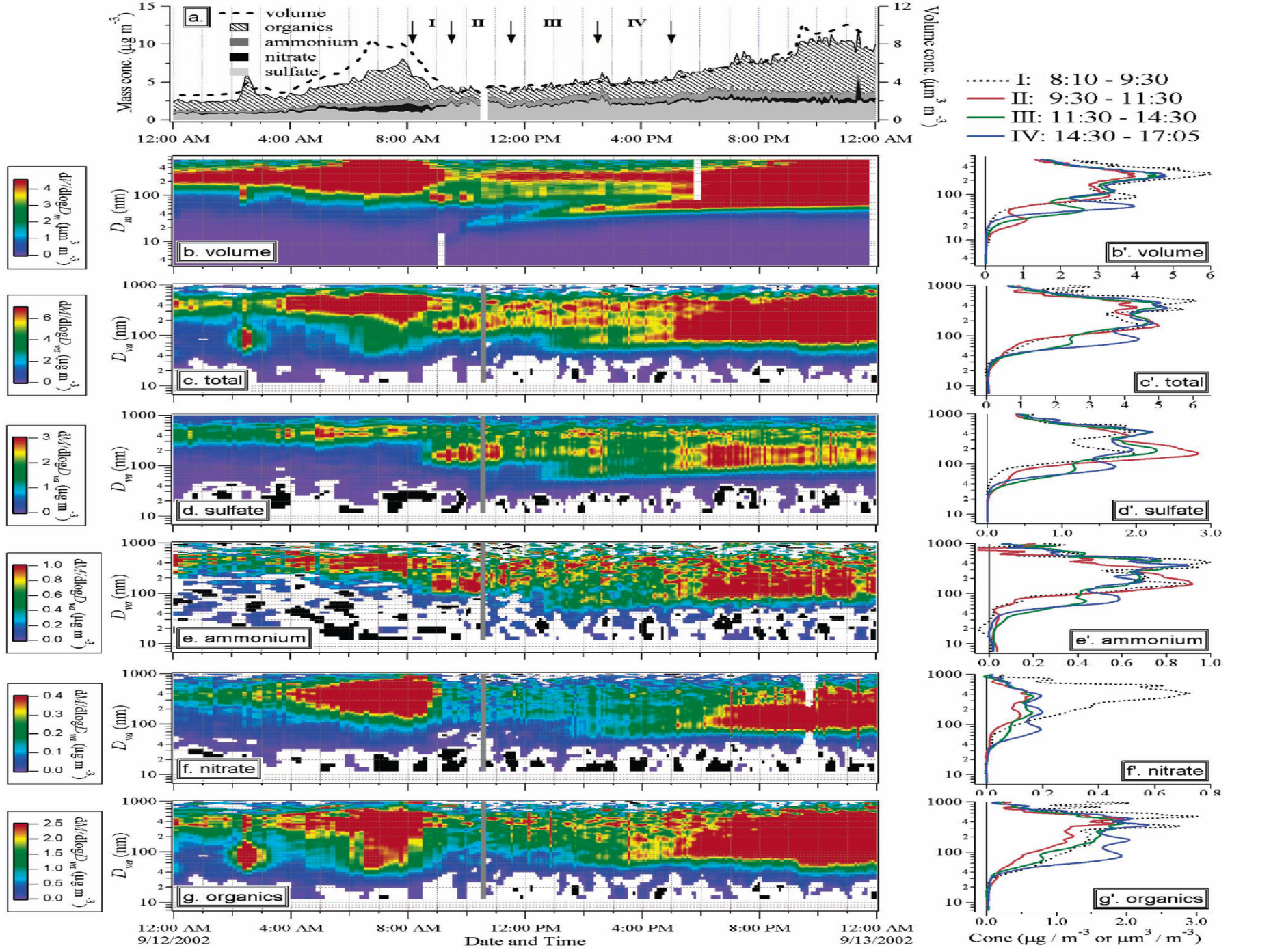


FIGURE 1. Change of (a) particle size distribution; (b) number concentration and total mass loading; and (c) SO_2, CO, and mixing layer depth as a function of time on September 12, 2002, a day with a well-defined and intense nucleation event. Mixing layer depth was calculated with the HYSPLIT4 trajectory model using EDAS wind field data.


a.
volume
organics
ammonium
nitrate
sulfate
I
II
III
IV
Mass conc. (μg m-3)
Volume conc. (μm3 m-3)
12:00 AM
4:00 AM
8:00 AM
12:00 PM
4:00 PM
8:00 PM
12:00 AM
I: 8:10 - 9:30
II: 9:30 - 11:30
III: 11:30 - 14:30
IV: 14:30 - 17:05
b. volume
c. total
d. sulfate
e. ammonium
f. nitrate
g. organics
b'. volume
c'. total
d'. sulfate
e'. ammonium
f'. nitrate
g'. organics
Dm (nm)
Dva (nm)
dV/dlogDm (μm3 m-3)
dM/dlogDva (μg m-3)
9/12/2002
Date and Time
9/13/2002
Conc (μg / m-3 or μm3 / m-3)

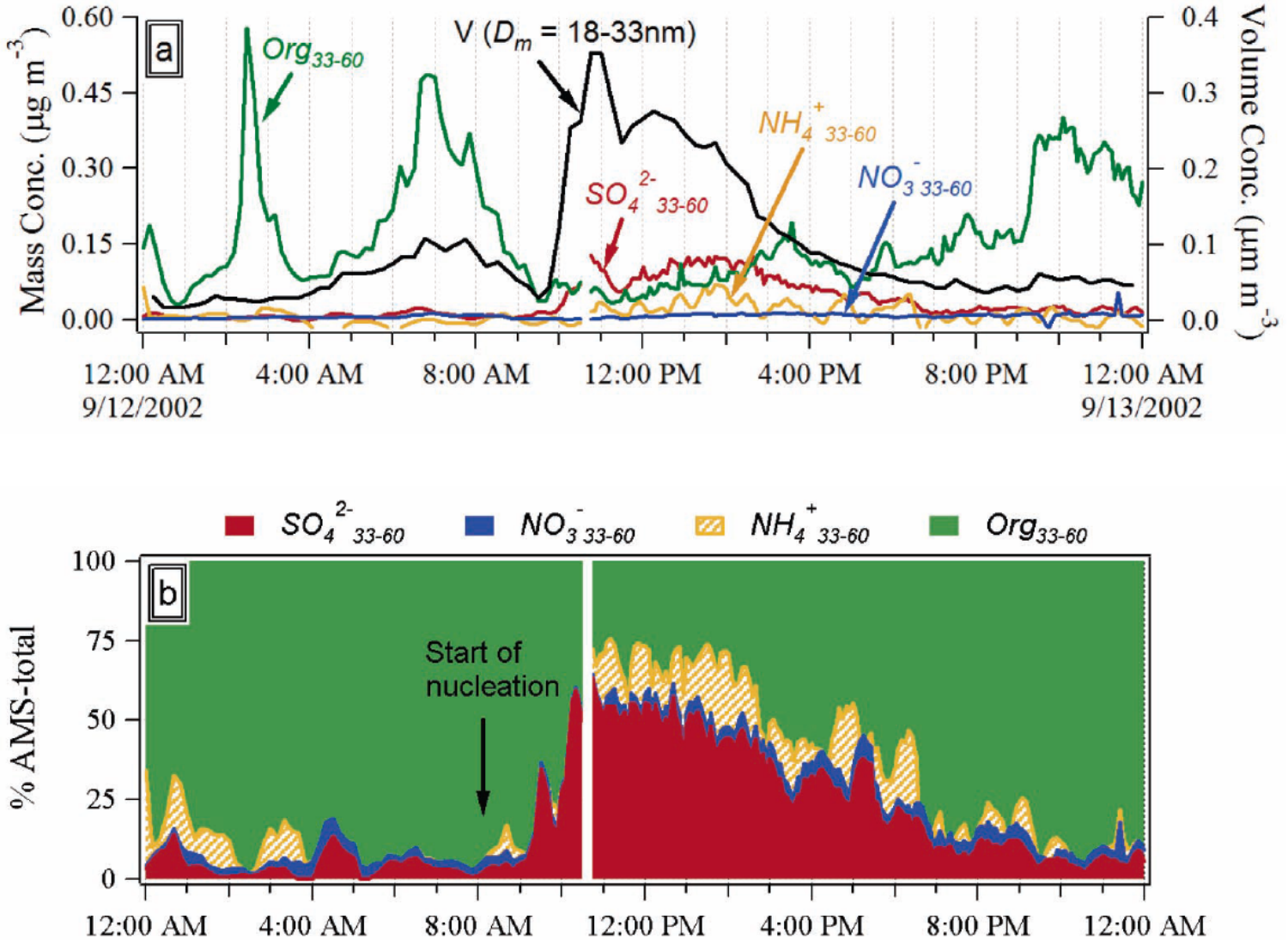


FIGURE 5. (a) Concentrations of SO_4^{2-}, NH_4^+, NO_3^-, organics, and particle volume in the 33−60 nm (D_{va}) particles on September 12, 2002. Particle volume was calculated using SMPS data in the D_m range of 18−33 nm by assuming spherical particles with density of 1.8 g cm^3. (b) Percent fraction of each species vs total (= sulfate + nitrate + ammonium + organics) in the 33−60 nm (D_{va}) particles. Missing data are due to either occasional instrumental malfunction or maintenance/calibration.

SOA formation

The chemical and physical processes associated with SOA formation are very complex (Kroll and Seinfeld, 2008; Hallquist et al., 2009) .

Present model predictions of atmospheric SOA formation are largely built upon the theoretical foundations on organic gas/particle partitioning developed by Pankow in the 1990s (Pankow, 1994) and extended by Odum et al. to SOA formation (Odum et al., 1996)

$$VOC_i + OX_j \rightarrow \alpha_{i,j,1}\, SOG_{i,j,1} + \alpha_{i,j,2}\, SOG_{i,j,2} + \ldots + \alpha_{i,j,m}\, SOG_{i,j,m} \leftrightarrow SOAs$$

where $\alpha_{i,j,k}$ is the mass-based Stoichiometric yield

Because of the large number of products formed in a given HC oxidation reaction and the difficulty in measuring individual semi-volatile compounds, two surrogate products (i.e., $m = 2$) have been widely used to express the volatility distribution of the oxidation products (Odum et al., 1996) and are considered as the standard means of representing laboratory SOA yield data in many experimental studies (Seinfeld and Pankow, 2003).

Secondary Organic Aerosol Formation

Once a multicomponent system contains enough condensable material to form aerosol, equilibrium G/P partitioning is governed by the equation for absorptive gas/liquid partitioning in a potentially nonideal system:

1) $p_i = X_i \zeta_i p^o_{L,i}$

2) $K_{p,i} = \frac{(ng/\mu g)_{ParticlePhase}}{(ng/m^3)_{GasPhase}} = \frac{F_i / TSP}{A_i} = \frac{760 RT f_{om}}{10^6 \mathbf{MW_{om}} \zeta_i p^o_{L,i}}$

p_i (torr): the gas-phase partial pressure of species i

X_i: the mole fraction of i in the particle phase

ζ_i: the activity coefficient of species i in the particle phase typically lie in the range 0.3~ 3.

$p^o_{L,i}$ (torr): the compound's vapor pressure as a pure liquid (subcooled if necessary) at the temperature of interest.

A_i (ng m^{-3}): gas phase conc.

F_i (ng m^{-3}): OM phase conc.

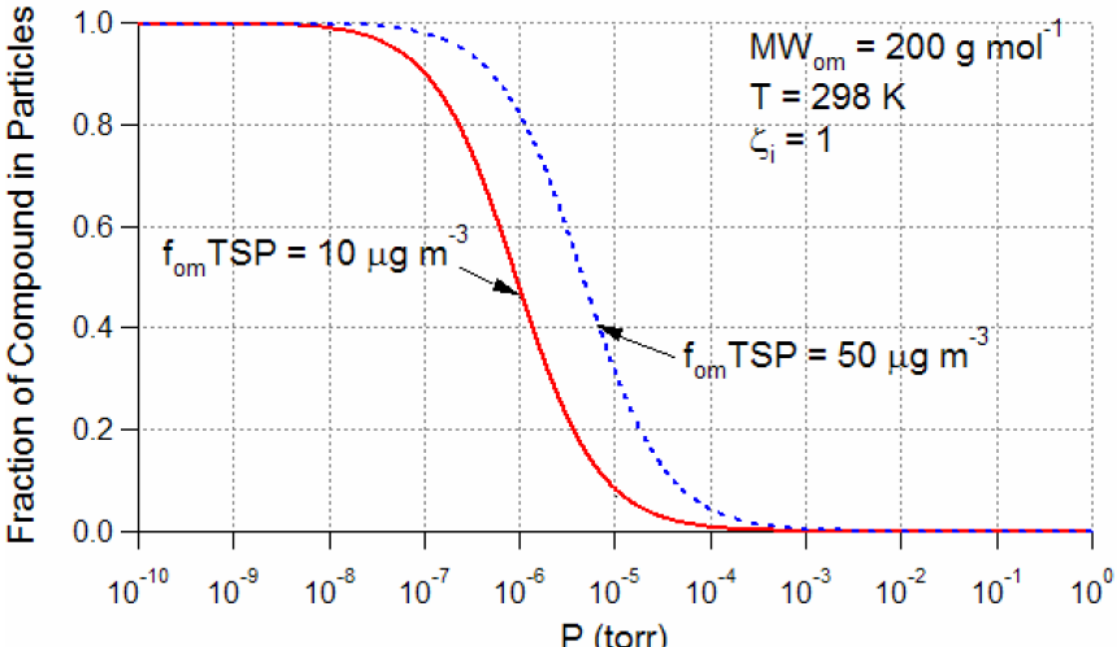
TSP (μg m^{-3}): total suspended PM conc.

R : the ideal gas constant (8.2E-5 m^3 atm mol^{-1} K^{-1})

T (K): temperature

f_{om}: the weight fraction of the TSP that comprises the absorbing OM phase

MW_{om} (g mol^{-1}): the number-average molecular weight of the absorbing OM phase.



The 2-product model of SOA formation has been employed in a number of regional and global models such as CMAQ (Schell et al., 2001), CMAQ-MADRID (Zhang et al., 2004), GEOS-Chem (Chung and Seinfeld, 2002; Liao et al., 2007); GISS GCM II-prime (Chung and Seinfeld, 2002), and TM-3 with CBM-4 (Tsigaridis and Kanakidou, 2003).

One limitation of the 2-product SOA formation model is the lack of consideration of the SOG aging process which has been observed in the atmosphere and in the laboratory (Donahue et al., 2006; Rudich et al., 2007; Kroll and Seinfeld, 2008; Hallquist et al., 2009; Jimenez et al., 2009).

Kroll and Seinfeld (2008) pointed out that, in order to gain a quantitative and predictive understanding of SOA formation, the volatility changes arising from the aging process must be parameterized and included in models.

Another limitation of the 2-product model is the lack of information about the condensable portion of oxidation products which is important for the growth of freshly nucleated particles

In GEOS-Chem, reactive biogenic volatile organic compounds (VOCs) are grouped into six categories (Liao et al., 2007):

VOC_1= α-pinene + β-pinene + sabinene + careen + terpenoid ketones;
VOC_2 = limonene;
VOC_3 = α -terpinene + γ-terpinene + terpinolene;
VOC_4 = myrcene + terpenoid alcohols + ocimene;
VOC_5 = sesquiterpenes;
VOC_6 = isoprene.

The oxidation reactions of VOC_i with O_3+OH (OX_1) and NO_3 (OX_2) produce 16 groups of SOGs which then lead to the formation of 16 groups of SOAs through equilibrium partitioning (Chung and Seinfeld, 2002; Liao et al., 2007),

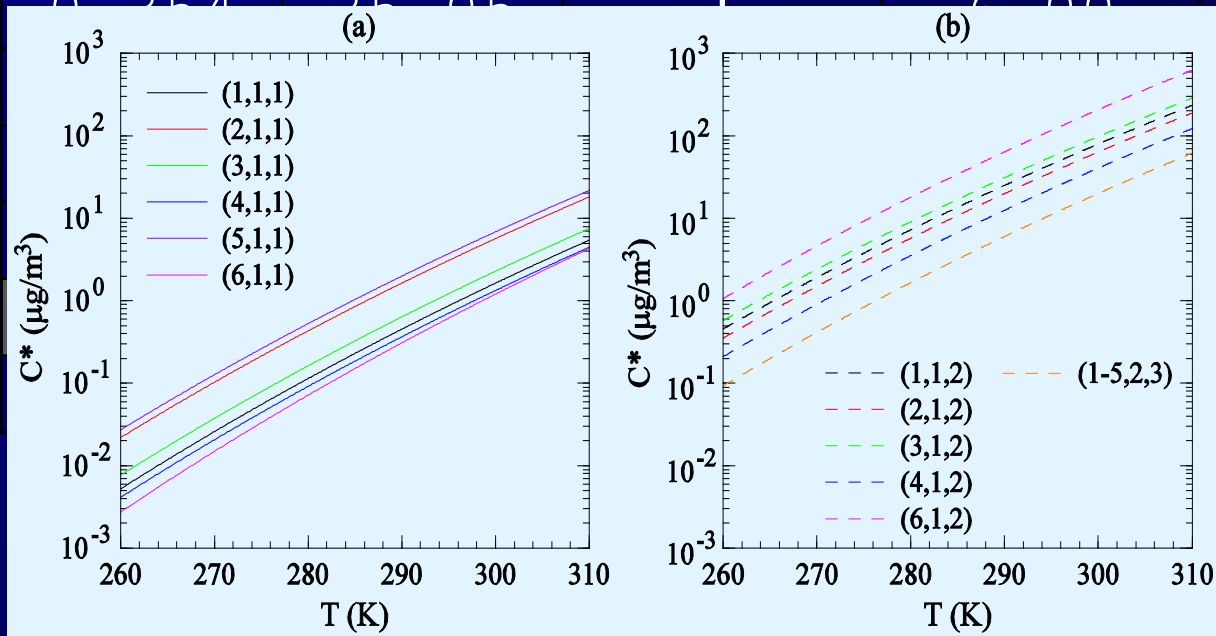
$$VOC_i + OX_1 \rightarrow \alpha_{i,1,1}\, SOG_{i,1,1} + \alpha_{i,1,2}\, SOG_{i,1,2} \quad \leftrightarrow \text{SOAs}$$
$$VOC_i + OX_2 \rightarrow \alpha_{i,2,3}\, SOG_{i,2,3} \quad \leftrightarrow \text{SOAs}$$

Table 1. Mass-based Stoichiometric yield for semi-volatile products from the oxidation of various VOC_i and C^* (in $\mu g/m^3$) of these products at T=290 K. $\alpha_{i,j,k}$ and $K_{i,j,k}$ values based on Griffin et al. (1999a, 1999b) and Kroll et al. (2006).

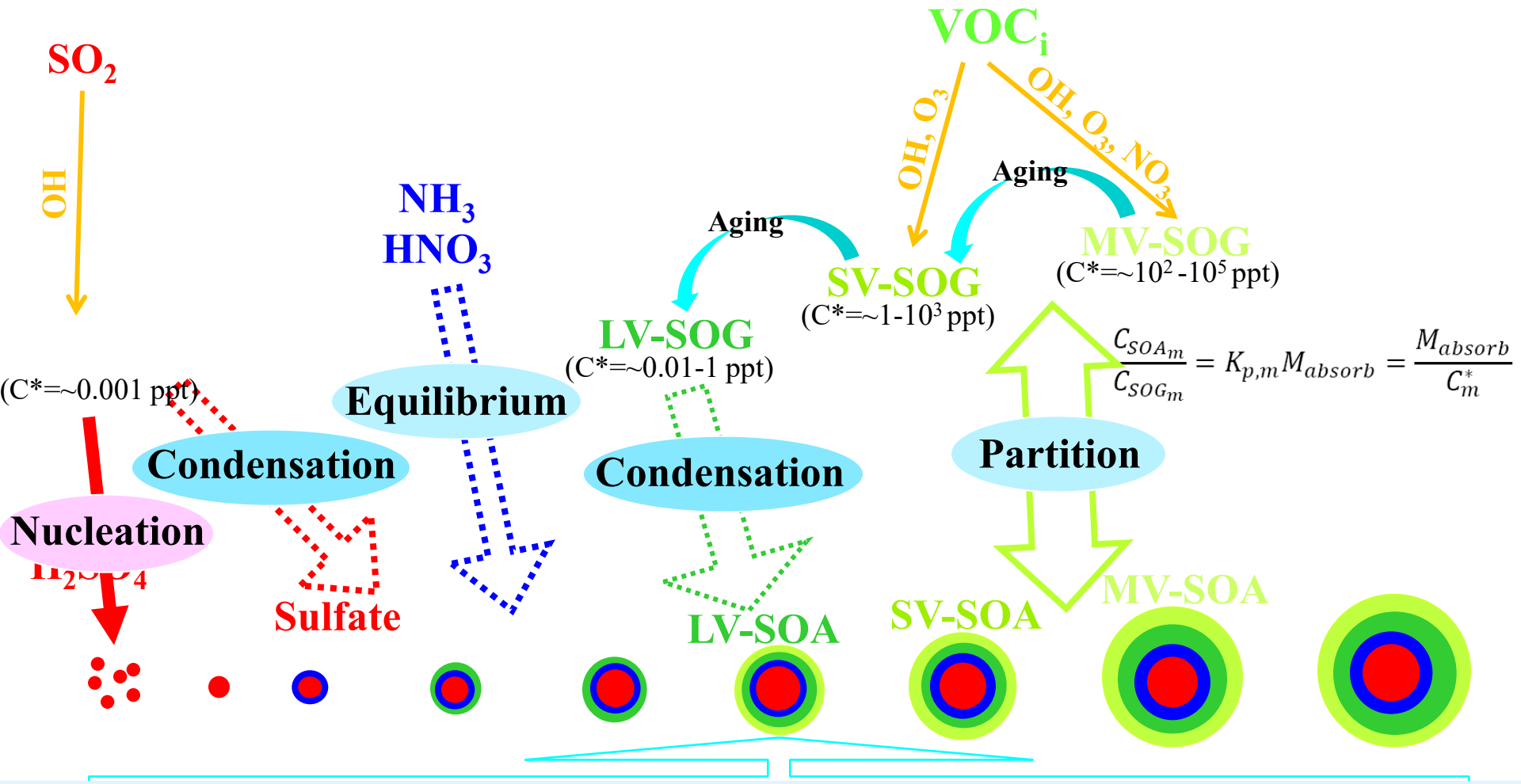
VOC_i	O_3+OH oxidation (OX_1)				NO_3 oxidation (OX_2)	
	Product type 1 (SV-SOG)		Product type 2 (MV-SOG)		Product type 3 (MV-SOG)	
	$\alpha_{i,1,1}$	$C_{i,1,1}^*$	$\alpha_{i,1,2}$	$C_{i,1,2}^*$	$\alpha_{i,2,3}$	$C_{i,2,3}^*$
$i=1$	0.067	0.45	0.354	25.05	1	6.00
$i=2$	0.239	1.64	0.363	19.92	1	6.00
$i=3$	0.069	0.64	0.201	31.02	1	6.00
$i=4$	0.067	0.37	0.135	12.50	1	6.00
$i=5$	1	1.99			1	6.00
$i=6$	0.029	0.31	0.232	63.68		

Table 1. Mass-based Stoichiometric yield for semi-volatile products from the oxidation of various VOC_i and C^* (in $\mu g/m^3$) of these products at T=290 K. $\alpha_{i,j,k}$ and $K_{i,j,k}$ values based on Griffin et al. (1999a, 1999b) and Kroll et al. (2006).

VOC_i	O_3+OH oxidation (OX_1)				NO_3 oxidation (OX_2)	
	Product type 1 (SV-SOG)		Product type 2 (MV-SOG)		Product type 3 (MV-SOG)	
	$\alpha_{i,1,1}$	$C_{i,1,1}$*	$\alpha_{i,1,2}$	$C_{i,1,2}$*	$\alpha_{i,2,3}$	$C_{i,2,3}$*
$i=1$	0.067	0.45	0.354	35.05	1	6.00
$i=2$	0.239	1.64				
$i=3$	0.069	0.64				
$i=4$	0.067	0.37				
$i=5$	1	1.99				
$i=6$	0.029	0.31				



Extended 2-product SOA formation model



$$\frac{C_{SOA_m}}{C_{SOG_m}} = K_{p,m} M_{absorb} = \frac{M_{absorb}}{C_m^*}$$

$$dC_{\text{MV-SOG}}/dt = P_{\text{VOC}} - K_{\text{ag}}[\text{OH}]\,\xi_{\text{MV->SV}}\,C_{\text{MV-SOG}} - L_{\text{par}}$$

$$dC_{\text{SV-SOG}}/dt = P_{\text{VOC}} + K_{\text{ag}}[\text{OH}]\,\xi_{\text{MV->SV}}\,C_{\text{MV-SOG}} - K_{\text{ag}}[\text{OH}]\,\xi_{\text{SV-SOG}}\,C_{\text{SV-SOG}} - L_{\text{par}}$$

$$dC_{\text{LV-SOG}}/dt = K_{\text{ag}}[\text{OH}]\,\xi_{\text{SV->LV}}\,C_{\text{SV-SOG}} - L_{\text{cond}}$$

Extended 2-product SOA formation model

SO_2

OH

NH_3

HNO_3

VOC_i

OH, O_3

OH, O_3, NO_3

Aging

Aging

LV-SOG
(C*=~0.01-1 ppt)

SV-SOG
(C*=~1-10^3 ppt)

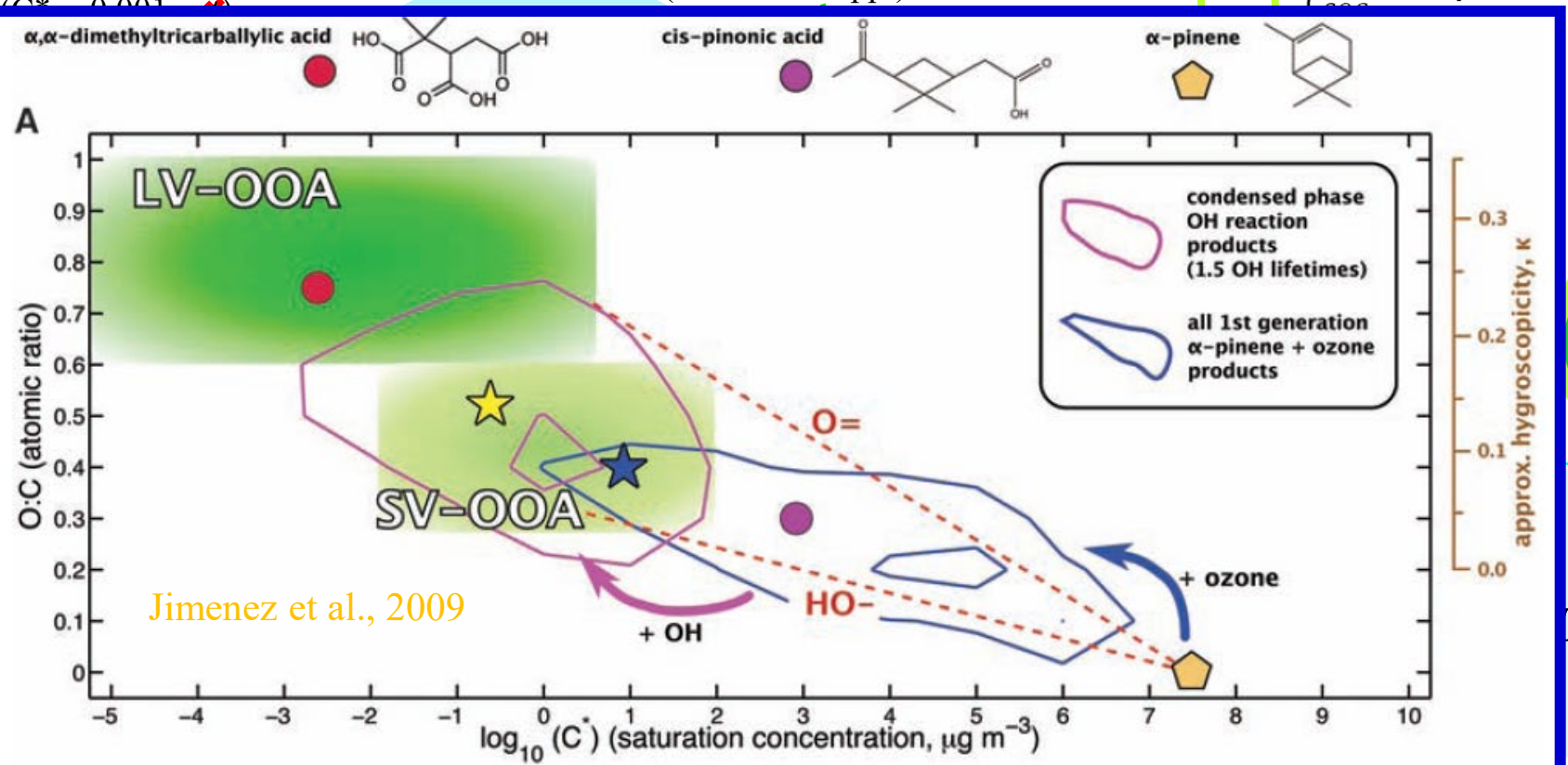
MV-SOG
(C*=~10^2 -10^5 ppt)

$$\frac{C_{SOA_m}}{C_{aer}} = K_{p,m} M_{absorb} = \frac{M_{absorb}}{C_m^*}$$

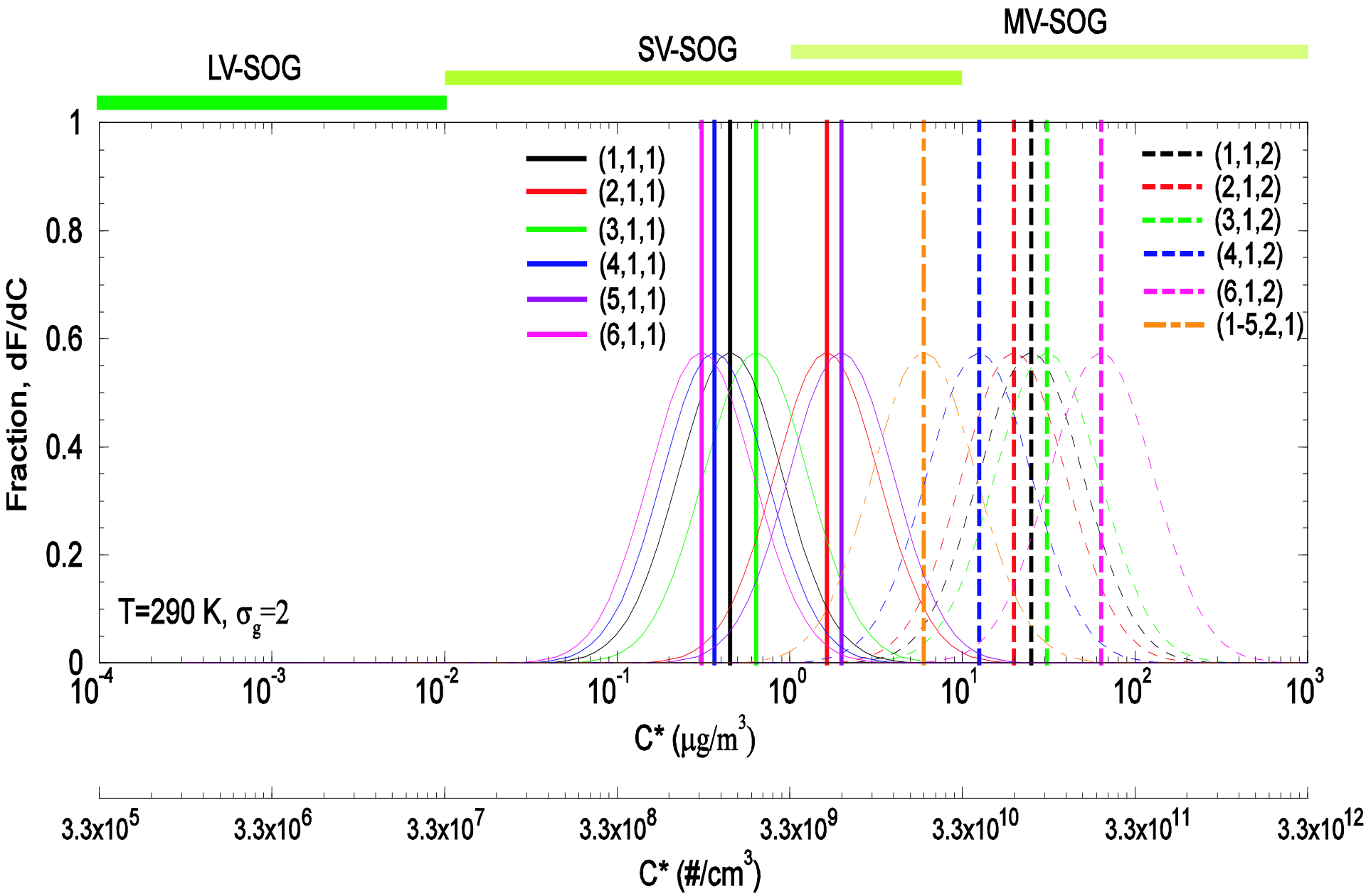
α,α-dimethyltricarballylic acid

cis-pinonic acid

α-pinene



$_{par}$


LV-SOG
SV-SOG
MV-SOG
(1,1,1)
(2,1,1)
(3,1,1)
(4,1,1)
(5,1,1)
(6,1,1)
(1,1,2)
(2,1,2)
(3,1,2)
(4,1,2)
(6,1,2)
(1-5,2,1)
T=290 K, σg=2
Fraction, dF/dC
C* (μg/m3)
C* (#/cm3)
3.3x10^5
3.3x10^6
3.3x10^7
3.3x10^8
3.3x10^9
3.3x10^10
3.3x10^11
3.3x10^12