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Organic Aerosol-an introduction

Mattias Hallquist
Department of Chemistry, Atmospheric Science

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Organic aerosol
Summer school 2008

- Topics of invited lectures
  - **Laboratory and theoretical framework**
    - Partitioning theory and smog chamber experiments Neil Donahue
    - SOA from biogenic precursors-Mattias Hallquist
  - **Field and aerosol measurements**
    - Off-line Chemical Analysis of Aerosols-Marianne Glasius
    - On-Line Measurements of Aerosols-Pete DeCarlo
    - Aerosol Field Measurements-Andre Prevot
  - **Atmospheric modelling**
    - Modelling of organic aerosols-David Simpson

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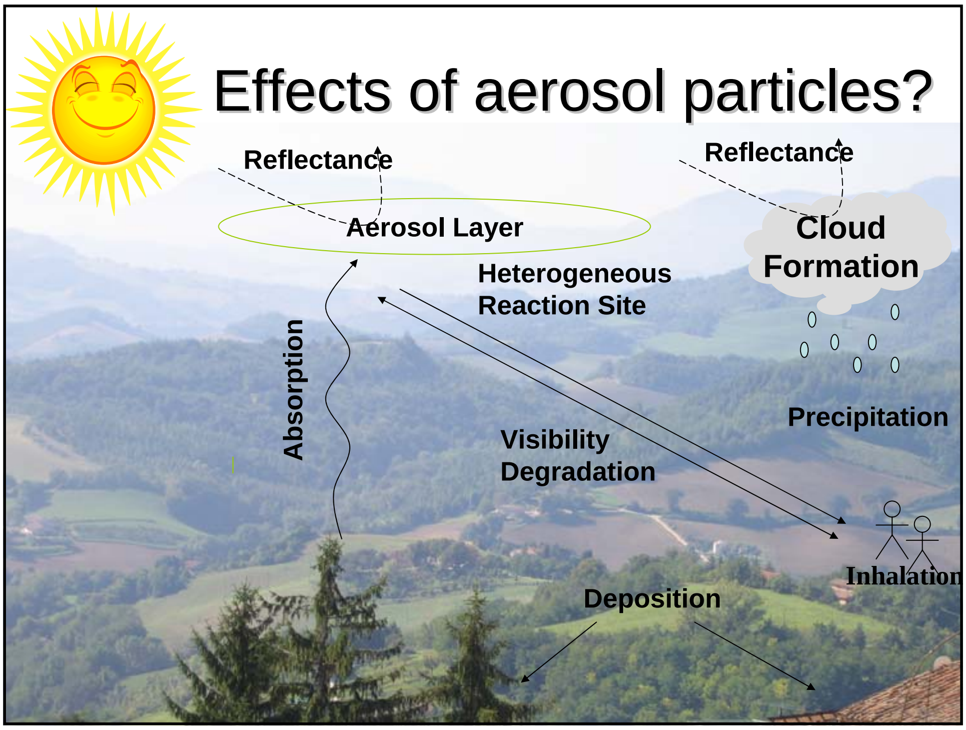
Outline

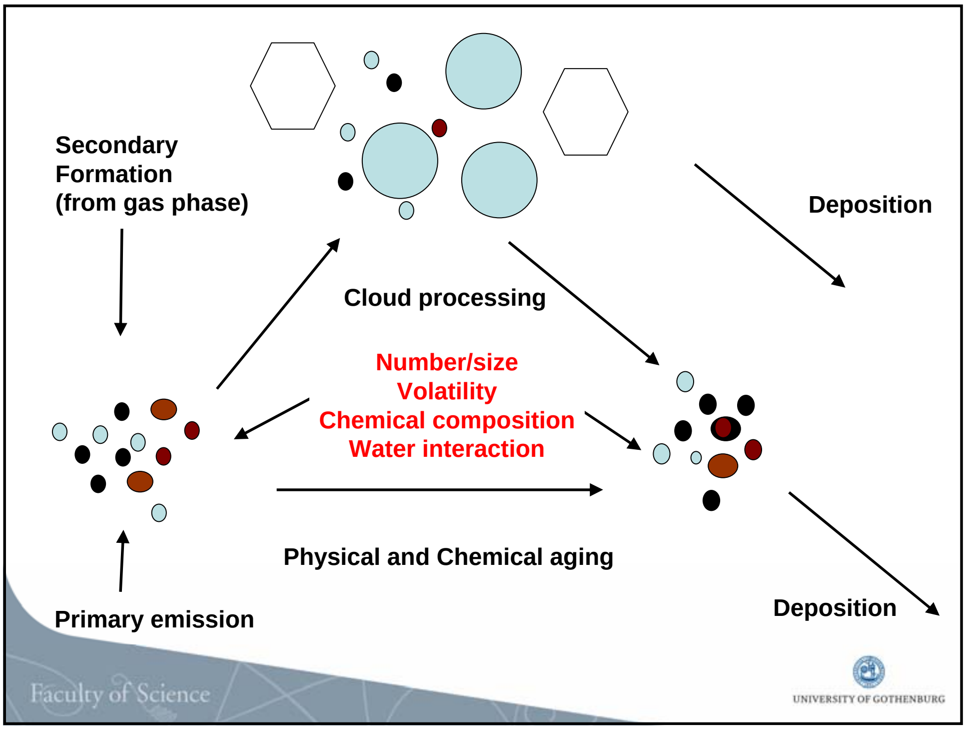
Motivation and background
- General processes and effects of aerosol
  - Health
  - Climate

Organic aerosol
- Classification
  - Definitions/ classifications
  - OC/EC
  - Anthropogenic vs natural
  - Examples classification-speciation
- Organic aerosol fraction
  - Sources
  - Contribution in atmospheric aerosol
  - Size dependence
- POA (Direct emissions)
- SOA (Secondary formation)

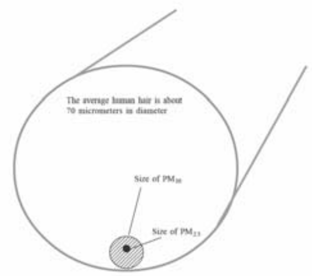
Selected issues

Effects of aerosol particles?





Health



Small but dangerous

Recent research indicates that fine particles ($PM_{2.5}$) in the air in the year 2000 caused an average shortening of statistical life expectancy of more than eight months in the EU, equivalent to 3.6 million life years lost annually. This means that these particles have the most serious effects on people's health of all air pollutants.

Source: The Swedish NGO Secretariat on Acid Rain , April 2006

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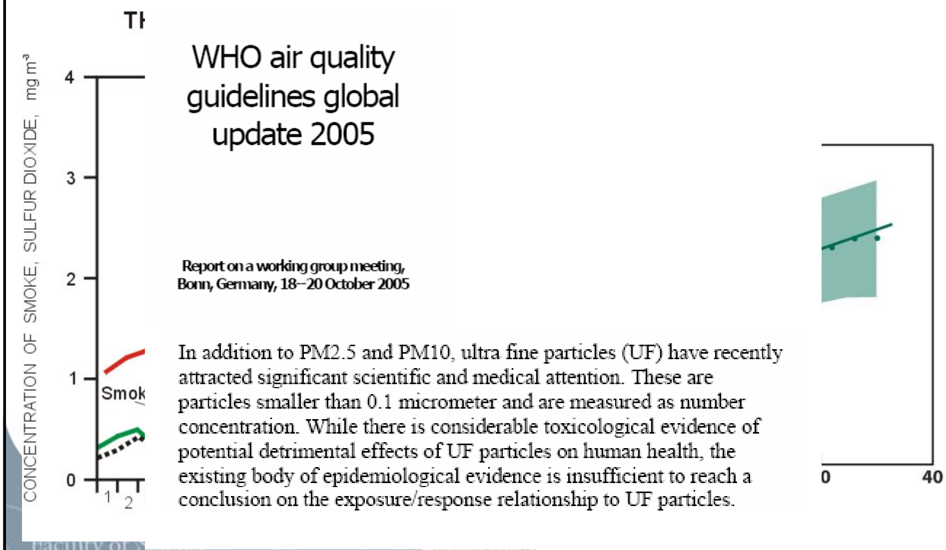
Health



WHO air quality guidelines global update 2005

Report on a working group meeting, Bonn, Germany, 18–20 October 2005

In addition to PM2.5 and PM10, ultra fine particles (UF) have recently attracted significant scientific and medical attention. These are particles smaller than 0.1 micrometer and are measured as number concentration. While there is considerable toxicological evidence of potential detrimental effects of UF particles on human health, the existing body of epidemiological evidence is insufficient to reach a conclusion on the exposure/response relationship to UF particles.

Source: http://www.ems.psu.edu/

Health

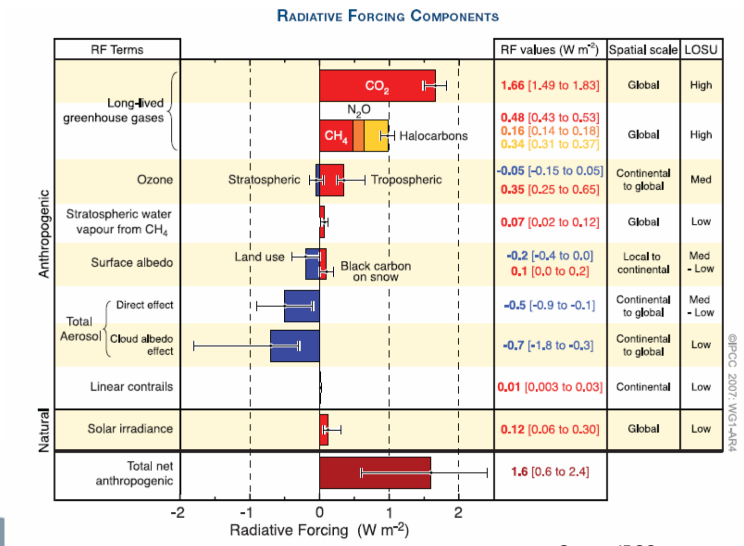
Table 1. Estimated health damage due to $PM_{2.5}$ in the EU 2000 and through implementation of current legislation (CLE) 2020. Source: EC 2005c.

Health effect	Units (1000s)	2000	2020 CLE
Mortality - long-term exposure	Life years lost	3,619	2,467
Mortality - long-term exposure	Premature deaths	348	272
Infant mortality	Cases	0.68	0.35
Chronic bronchitis	Cases	164	128
Respiratory hospital admissions	Cases	62	42
Cardiac hospital admissions	Cases	38	26
Restricted activity	Days	347,700	222,000
Respiratory medication use, children	Days	4,200	2,000
Respiratory medication use, adults	Days	27,700	20,900
Lower respiratory symptoms (LRS), children	Days	192,800	88,900
LRS, adults with chronic disease	Days	285,300	207,600

-Are organic particles different in a health perspective?

Source: The Swedish NGO Secretariat on Acid Rain , April 2006

Climate



Source: IPCC

Climate

Directs Effects - aerosol scatter or absorb radiation

Indirect Effects - aerosols modify clouds to increase albedo or cloud lifetimes

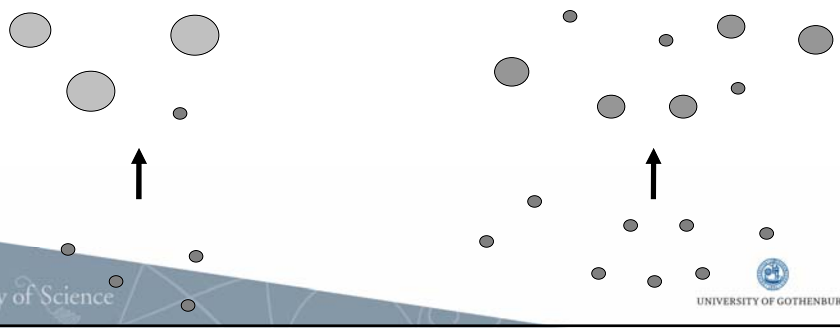
Simplified example

Clean Case: ←

fewer but larger droplets

→ Polluted Case:

more but smaller droplets



Climate

How do organic compounds effect properties of an aerosol?

Examples
- Nucleation-size distribution changes
- Surface tension
- Solubility
- Kinetics (aging and water uptake)
  - Light absorption/scattering

Organic aerosols
- definitions and classifications

o Common abbreviations
- o TC Total Carbon
- o EC Elemental carbon (sometimes=soot sometimes=BC, black carbon)
- o OC Organic Carbon
- o OM Organic matter (sometimes OC*1.4?)
- o WSOC Water soluble organic carbon
- o POA Primary organic aerosol
- o SOA Secondary organic aerosol
- o HOA Hydrocarbonlike organic aerosol (connected to AMS measurements)
- o OOA Oxidised organic aerosol (connected to AMS measurements)
- o Antrophogenic vs Biogenic?

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OC/EC classification

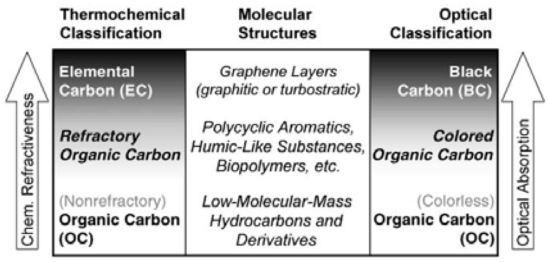

Figure 5. Optical and thermochemical classification and molecular structures of black carbon (BC), elemental carbon (EC), and organic carbon (OC = TC − BC or TC − EC).[57] Depending on the method of analysis, different amounts of carbon from refractory and colored organic compounds are included in OC and BC or EC.

Source: Pöschl 2005

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OC/EC classification

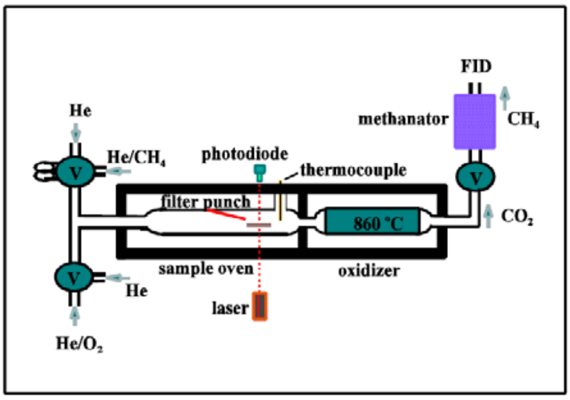

Figure 1. Schematic of Thermal-Optical Instrument (V=valve)

ELEMENTAL CARBON (DIESEL PARTICULATE): METHOD 5040, - Page 9 of 9

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OC/EC classification

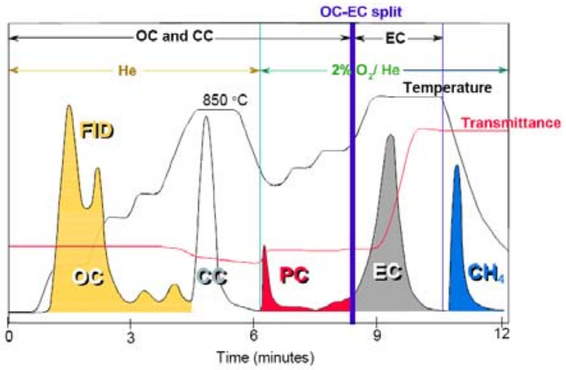


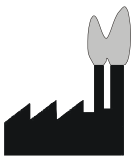
Figure 2. Thermogram for filter sample containing organic carbon (OC), carbonate (CC), and elemental carbon (EC). PC is pyrolytically generated carbon or 'char.' Final peak is methane calibration peak. Carbon sources: pulverized beet pulp, rock dust (carbonate), and diesel particulate.

NIOSH Manual of Analytical Methods (NMAM), Fourth Edition

Biogenic-anthropogenic?

Anthropogenic emissions

^{14}C extinct



Biogenic emissions

^{14}C contemporary

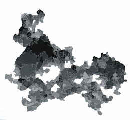
Flux $F_a = dm_a/dt$

$f_C = 0$ (!)

Flux $F_b = dm_b/dt$

$f_C = 1$ (!)

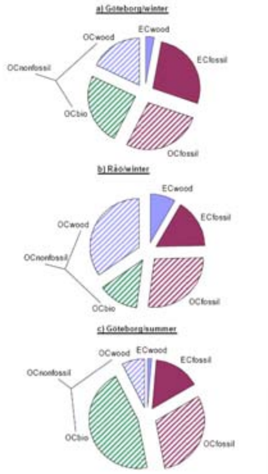
Carbonaceous aerosol particles

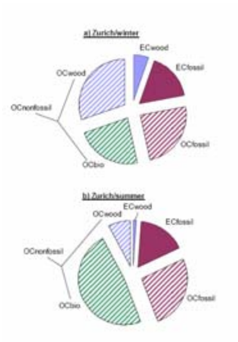


$$f_C = \frac{F_b}{F_a + F_b}$$

Szidat et al., Atmos. Environ., 2004a

Organic aerosol classification
-Examples from Gothenburg and Zurich





Source: Szidat et al.

Organic aerosol classification
-Examples Urban, Rural and Alpine air masses

Table 1: Characteristic aerosol data for urban, rural, and high alpine air in central Europe.[a]

	Urban (Munich)	Rural (Hohenpeissenberg)	Alpine (Zugspitze)
PM2.5 [$\mu g m^{-3}$]	20 ± 10	10 ± 5	4 ± 2
TC in PM2.5 [%]	40 ± 20	30 ± 10	20 ± 10
EC in TC [%]	50 ± 20	30 ± 10	30 ± 10
OC in TC [%]	40 ± 20	70 ± 10	70 ± 10
WSOC in TC [%]	20 ± 10	40 ± 20	60 ± 20
MWSOC in WSOC [%]	30 ± 10	50 ± 20	40 ± 20

[a] Rounded arithmetic mean values ± standard deviation determined from about 30 filter samples collected at each location during 2001–2003.

Source: Pöschl 2005

Organic aerosol speciation
-Identified compounds are many but with little mass

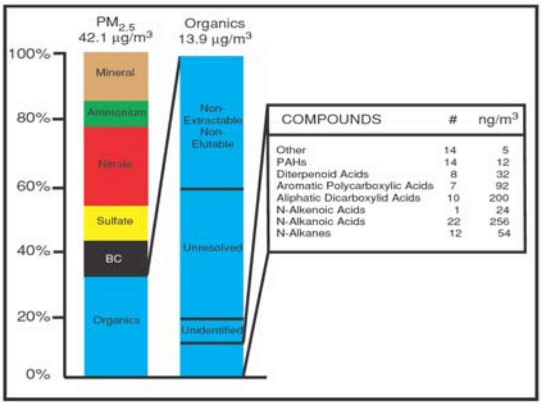


Figure 3.10. Speciation results for organic aerosol in Southern California (Rogge et al., 1993). Even if a hundred or so individual organic compounds are identified and quantified, they represent only 15 percent or so of the total organic mass.

Source: 2003 NARSTO Assessment

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Organic Aerosol Sources
-Global Estimates

Table 3. Estimated Source Budget of Organic Matter (OM) in the Global Atmosphere and the U.S. Contribution[a]

		U.S. Contribution	
Description	Global Source, Tg a^{-1}	%	Tg a^{-1}
	Primary Sources		
Open biomass burning[b]	**40** (21–91)[c,d]	3.4[c]	**1.3** (0.7–3.1)
Biofuel use	**10.4** (5.0–21)[c,d]	4.3[c]	**0.4** (0.2–0.9)
Fossil fuel use	**3.8** (1.9–11)[c,d]	10.4[c]	**0.4** (0.2–1.2)
	Secondary Formation		
Isoprene	**6.2** (2–6.2)[e,f]	4.8[g]	**0.3** (0.1–0.3)
Terpenes	**10.2** (10.2–19.1)[e,h]	6.3[g]	**0.6** (0.6–1.2)
Other biogenic VOCs	**15** (5–25)[h]	5.0[g]	**0.8** (0.3–1.3)
Urban VOCs	**8.0** (4.0–12)	25.9[i]	**2.1** (1.0–3.1)
Total	**94** (49–185)		**6.0** (4.7–17)

[a]Best estimates are bold; uncertainty ranges in parentheses.
[b]Includes savanna and forest fires, and agricultural burning.
[c]*Bond et al.* [2004].
[d]*Henze and Seinfeld* [2006].
[e]*Henze and Seinfeld* [2006].
[f]*Claeys et al.* [2004].
[g]*Guenther et al.* [1995].
[h]*Kanakidou et al.* [2005].
[i]EDGAR 3.2 [*Olivier et al.*, 2005].

Source: De Gouw et al., 2008

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Organic Aerosol Sources
-Example on local estimates

9364 M.K. Shrivastava et al. / Atmospheric Environment 41 (2007) 9353–9369

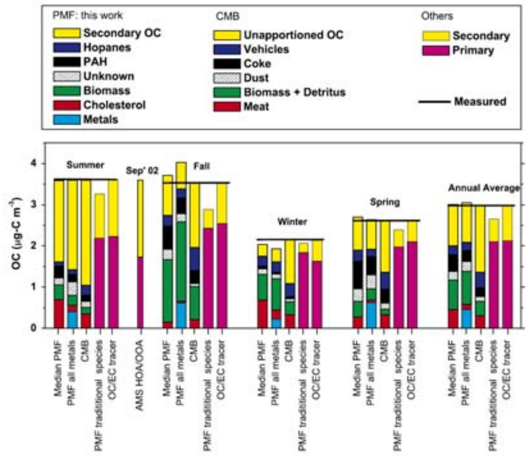
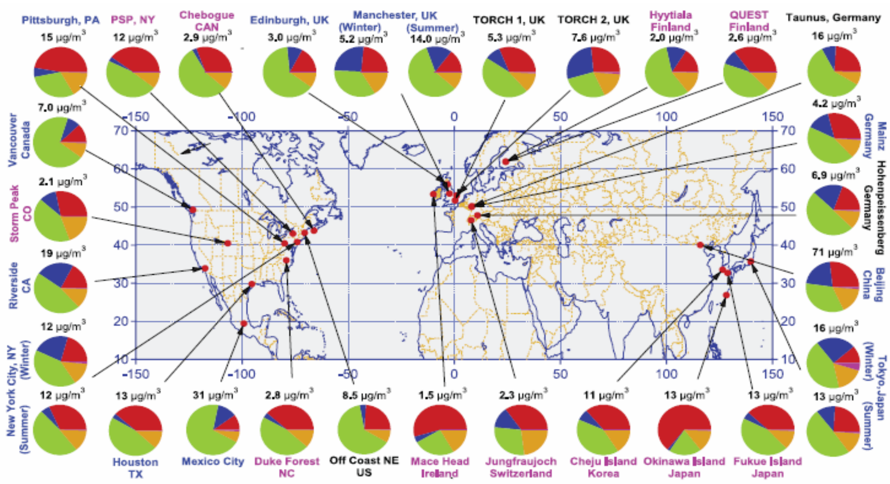


Fig. 5. Comparison of OC apportioned by the median PMF solution, the PMF solution with additional metals, and the best-estimate CMB solution of Subramanian et al. (2007). Also shown are primary–secondary splits estimated from PMF analysis of traditional species (Pekney et al., 2006), the EC-tracer method (Polidori et al., 2006), and factor analysis of AMS data (Zhang et al., 2005). "Biomass" for our PMF analysis represents sum of OC contributions from hardwood and open burn/primary biogenic factors. The data corresponding to this figure are listed in Table S-3 in the online supporting information.

Organic aerosol contribution



Source: Zhang et al., 2007

Organic aerosol contribution
-Examples Coarse, Fine and Ultrafine in Los Angeles

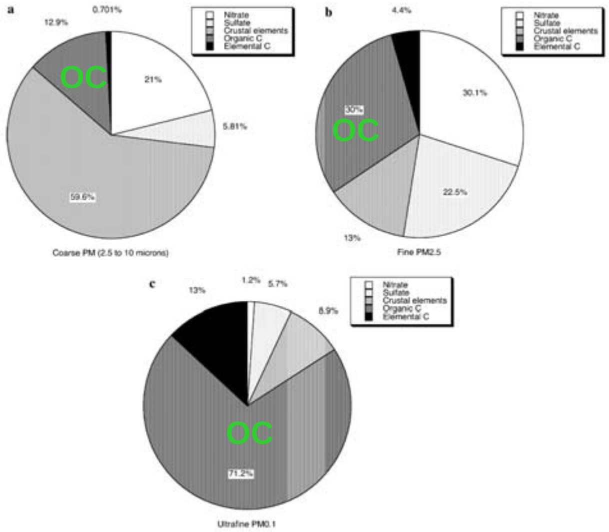


Fig. 1. Average composition of ambient aerosol particles in different size ranges during 2002–2003 at the USC EPA "Supersite" in Los Angeles. Carbon becomes increasingly important as the particle size reduces. Adapted from Report EPA-452/R-05-005 [90] based on data of Sardar et al. [22].

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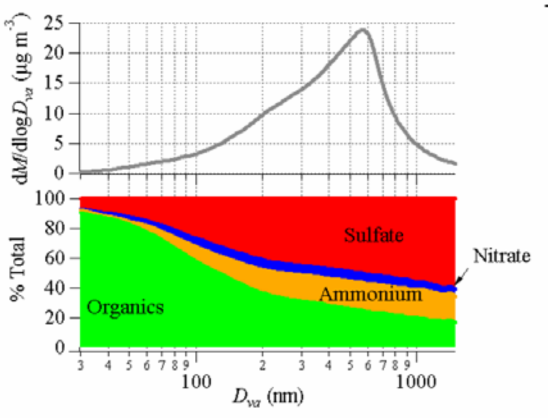
Organic aerosol contribution
-size distribution of non refractory material



Size dependent composition of ambient aerosols

Source: Zhang et al., 2005

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Size and processes

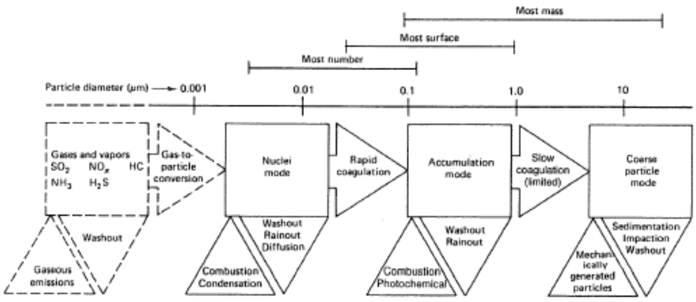

FIGURE 14.3 Schematic representation of the urban aerosol and the processes that modify it.

Source: Heinz and Finlaysson-Pitts

Size distributions

- o Particle size influences e.g.
  - o Particle toxicity (deposition efficiency, dose, surface area)
  - o Light scattering (0.1-1 μm most efficient for scattering solar radiation)
  - o Cloud nuclei activation (large enough to activate)
  - o Surface reactions
  - o Particle life time (c.f. diffusion and settling), transport time

Aerosol general

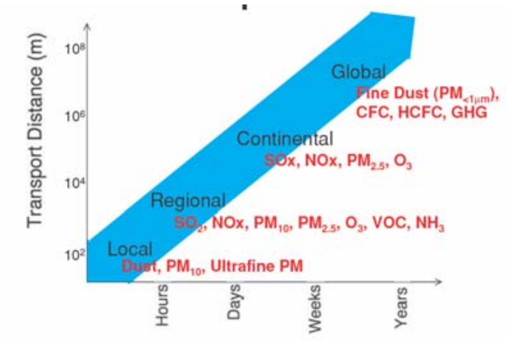

Figure 1.3. Illustrative transport scales for PM and other atmospheric pollutants.

Source: 2003 NARSTO Assessment

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Size distributions

- o Particle size influences e.g.
  - o Particle toxicity (deposition efficiency, dose, surface area)
  - o Light scattering (0.1-1 mm most efficient for scattering solar radiation)
  - o Cloud nuclei activation (large enough to activate)
  - o Surface reactions
  - o Particle life time (c.f. diffusion and settling), transport time
- o Number vs mass
  - o Primary emission distribution?
  - o Secondary
    - o nucleation
    - o condensation
    - o gas-to-particle partitioning

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POA emissions

- Fine particles: combustion related (biomass, biofuel and fossil fuel)
- OC/EC crucial in emission inventories
- Volatile vs non volatile
- For coarse particles: debris, pollen, fungi etc

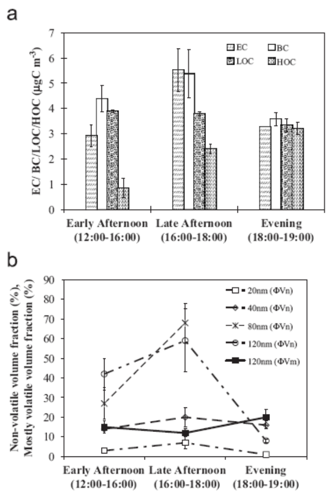
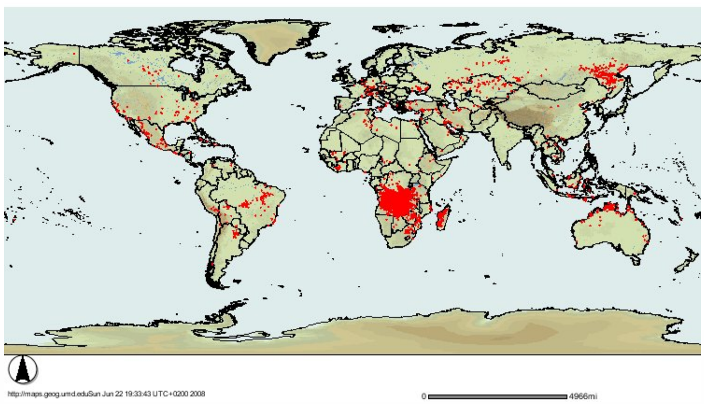


Fig. 7. (a) Concentration of elemental carbon, black carbon and organic carbon species, and (b) particle volatility ratios at site A, distinguished for different hours during the campaign.

Source: Biswas 2007

POA emissions

- Biomass burning:



SOA formation

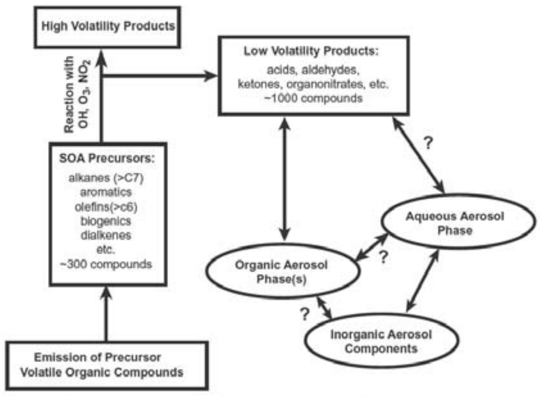
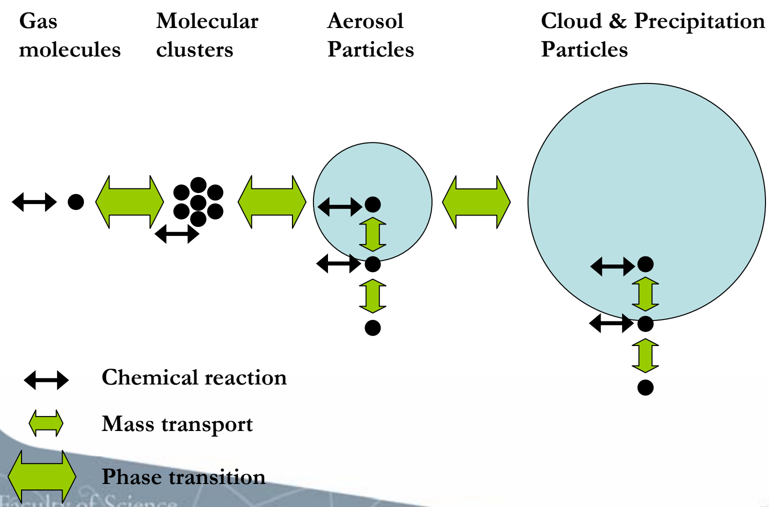


Figure 3.9. Schematic of the formation of secondary organic aerosol in the atmosphere.

Source: 2003 NARSTO Assessment

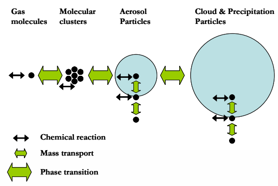
SOA formation

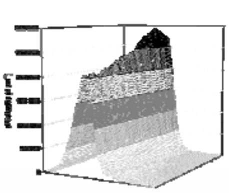


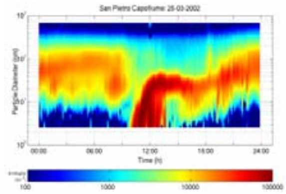
SOA formation

Primary Gas-Phase Organics → Oxidation OH, O_3, NO_3 → First-Generation Products → Oxidation OH, O_3, NO_3 → Second-Generation Products → Oxidation OH, O_3, NO_3

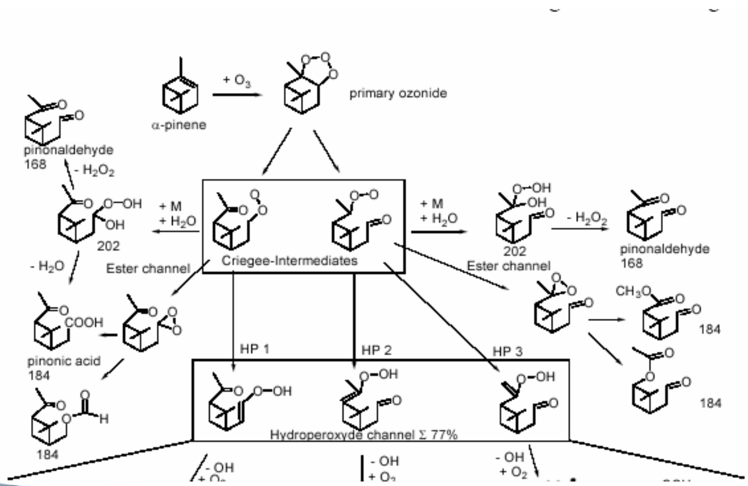
Partitioning, condensation or nucleation?







SOA formation



Ref: from Fuentes et al, 2000

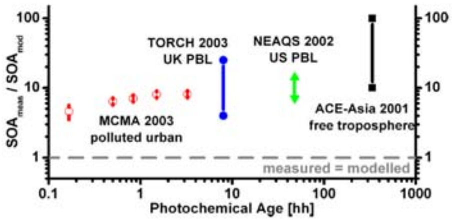
SOA in the Atmosphere

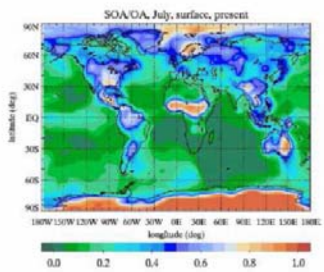
Models generally underestimates SOA formation (Volkamer et al. 2006→)

Global formation, uncertain but estimated to 12-72 Tg/year (Kanakidou et al 2005)

Estimates! Based on rather chemically simplified models, e.g. mostly α-pinene degradation

However , it is clear that SOA can dominate the OC fraction and that biogenic precursor gives significant input





Organic aerosol-hot issues..?

***Nature* 1960 & 2006,** Field observations of SOA

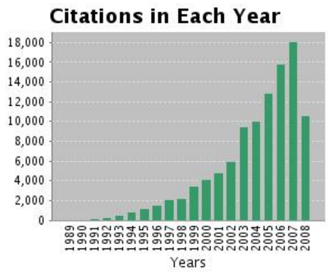
***Science* 2004** Can small molecules produce significant mass of SOA? (Isoprene)

***Science* 2002, 2004** Condensed phase processes, Polymerisation? Change in properties and yields.

***Science* 2004, 2003; *Nature* 2002** Importance of SOA for nucleation and growth? Compounds? Mechanisms?

Science 2006, Cloud-Nucleating Ability?

Science 2007 Definition of SOA/POA?



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