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ccem.ch Competence Center Energy and Mobility

NEADS
Next Generation Exhaust Aftertreatment for Diesel Propulsion Systems

LABOR FÜR ATMOSPHÄREN-CHEMIE

Primary and secondary organic aerosols from a diesel car during smog chamber experiments

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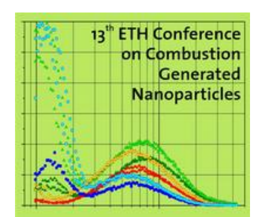


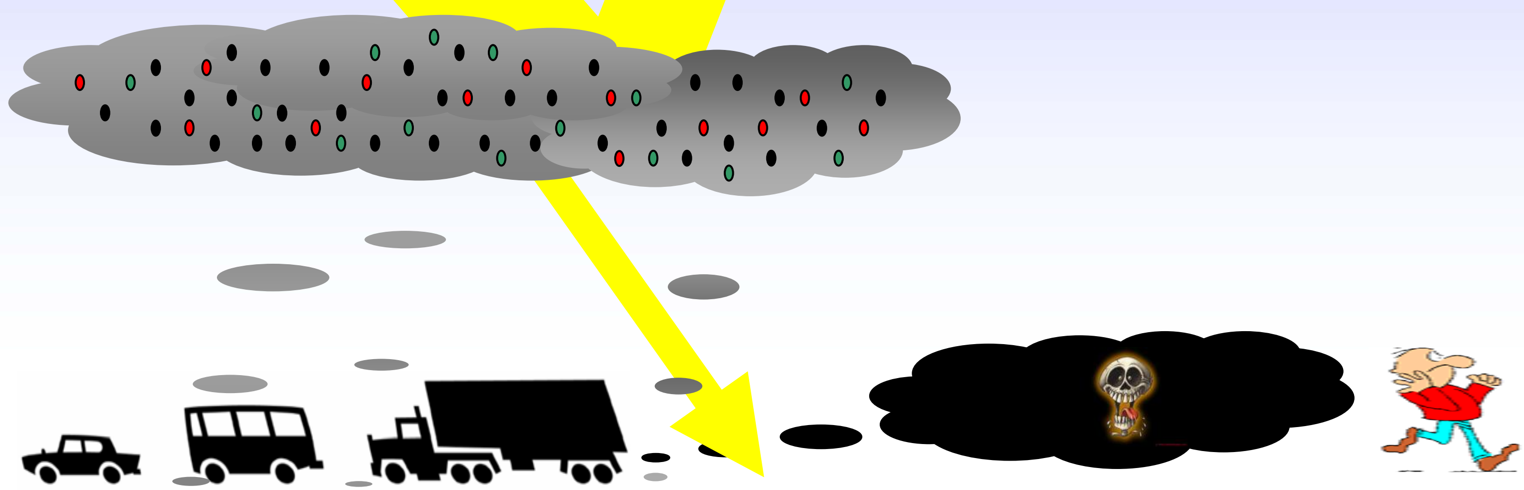
13TH ETH Conference, 22-24 June 2009

Why are we interested in aerosol particles ?

Direct radiative forcing
Scattering and absorption of solar and infrared radiation
Indirect radiative forcing
Alteration of the formation and precipitation efficiency of liquid water, ice and mixed-phase clouds

Health effect
Respiratory and carcinogenic effects

Importance of aerosol size (d < 1µm) and composition (PAHs associated to particles)



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Diesel passenger cars

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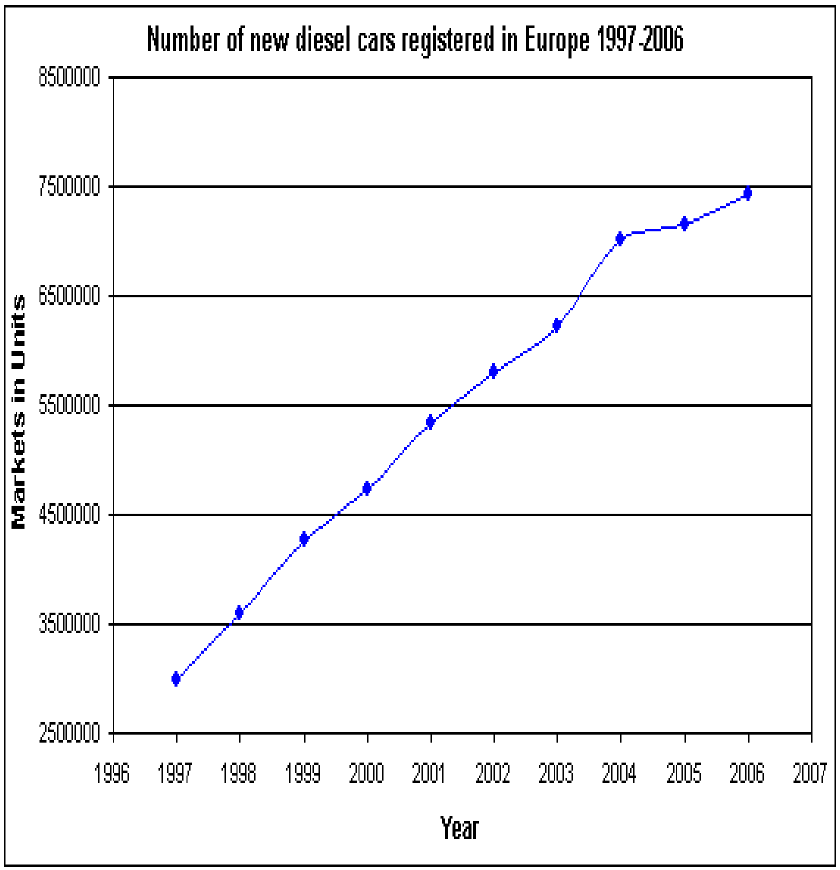
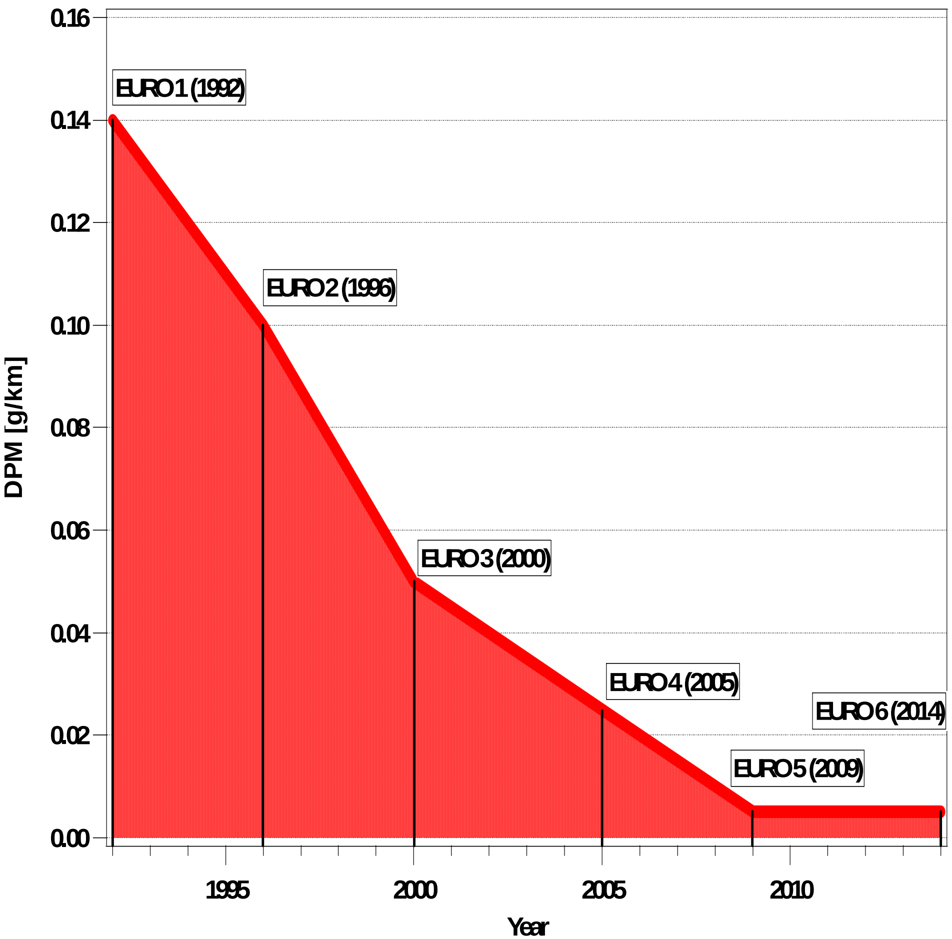
Number of new diesel passenger cars in Europe



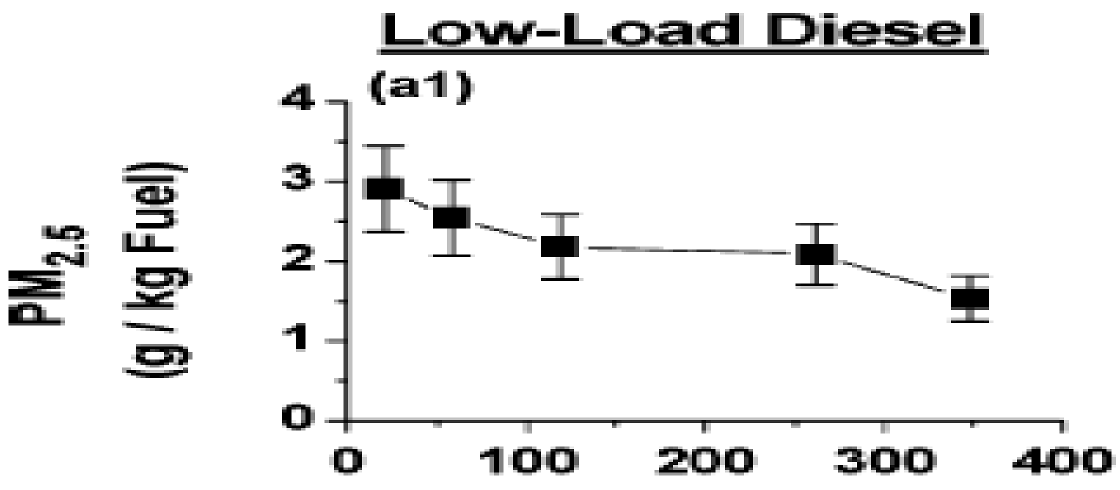
EU Emission Standards for Diesel Particulate Matter



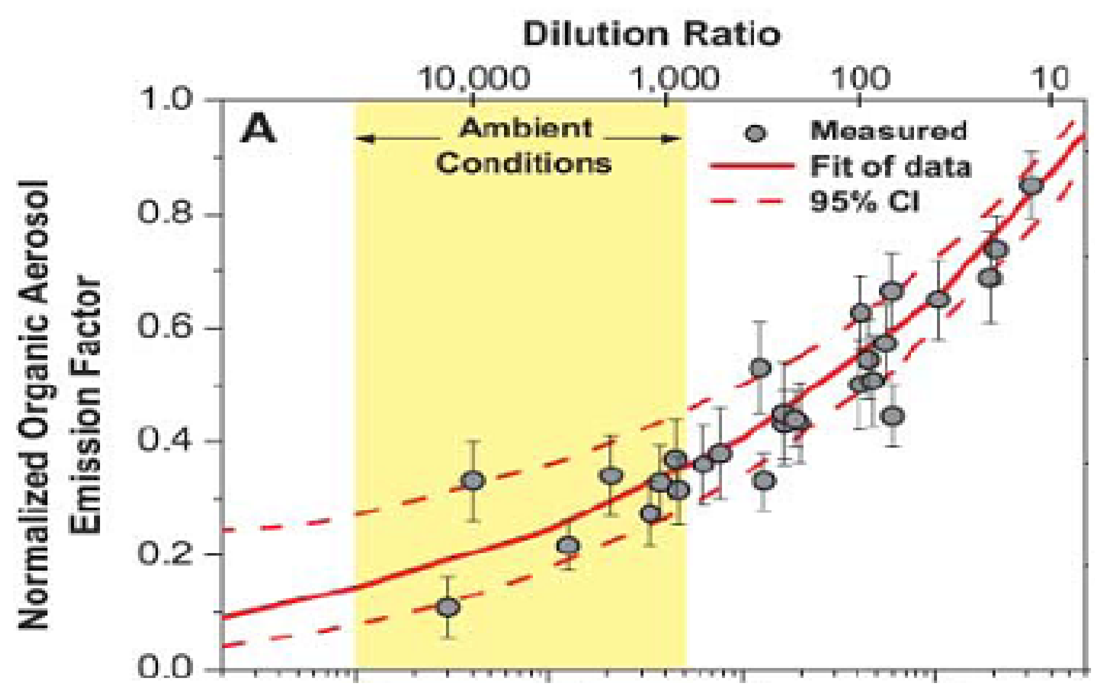
(ACEA, 2008; EPA, 2002; Automotive Industry Data Newsletter)

Dilution effect on PM mass

Fine particulate mass with initial OM/BC=2 can decrease by 50% when dilution ratio is increased from 20:1 to 350:1

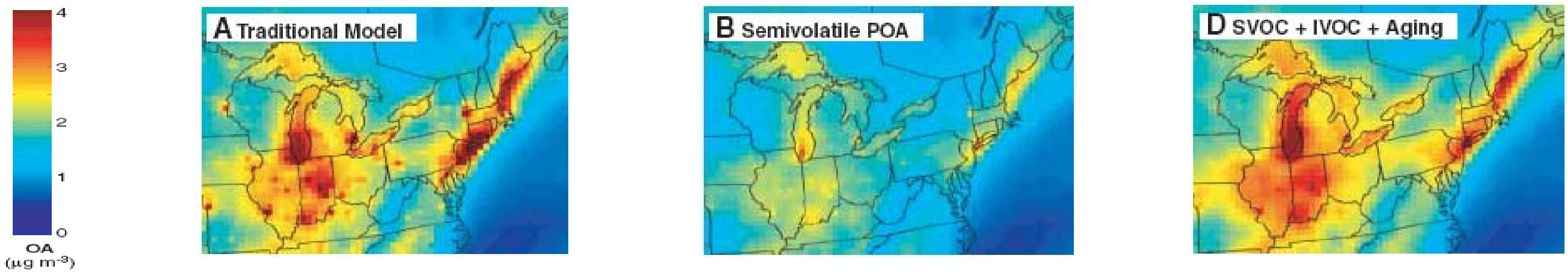


Primary Organic Aerosols (POA) contains Semi-Volatile Organic Compounds (SVOCs) that partially evaporate.



(Robinson et al., Science 2007; Lipsky and Robinson, ES&T 2006)

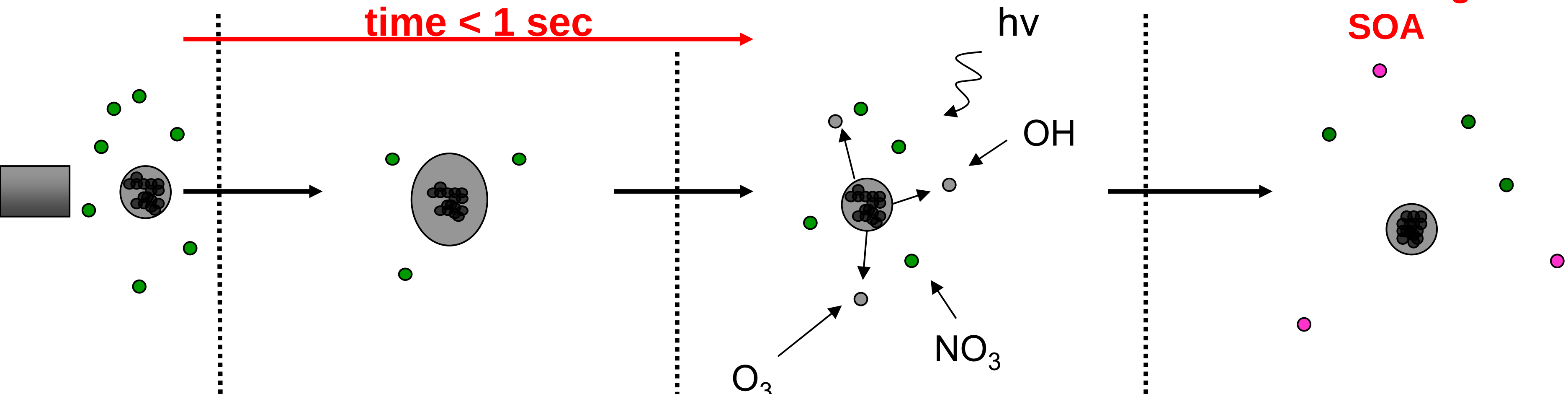
Primary and Secondary organic aerosols



POA constituents as non volatile
OA mainly present in urban areas
POA main constituent of OA

POA constituents as volatile
Decrease of OA

Photochemical aging of SVOCs
Considerable amount of Urban and Regional SOA



High temperature

Ambient temperature
Low dilution ratio (10-100)

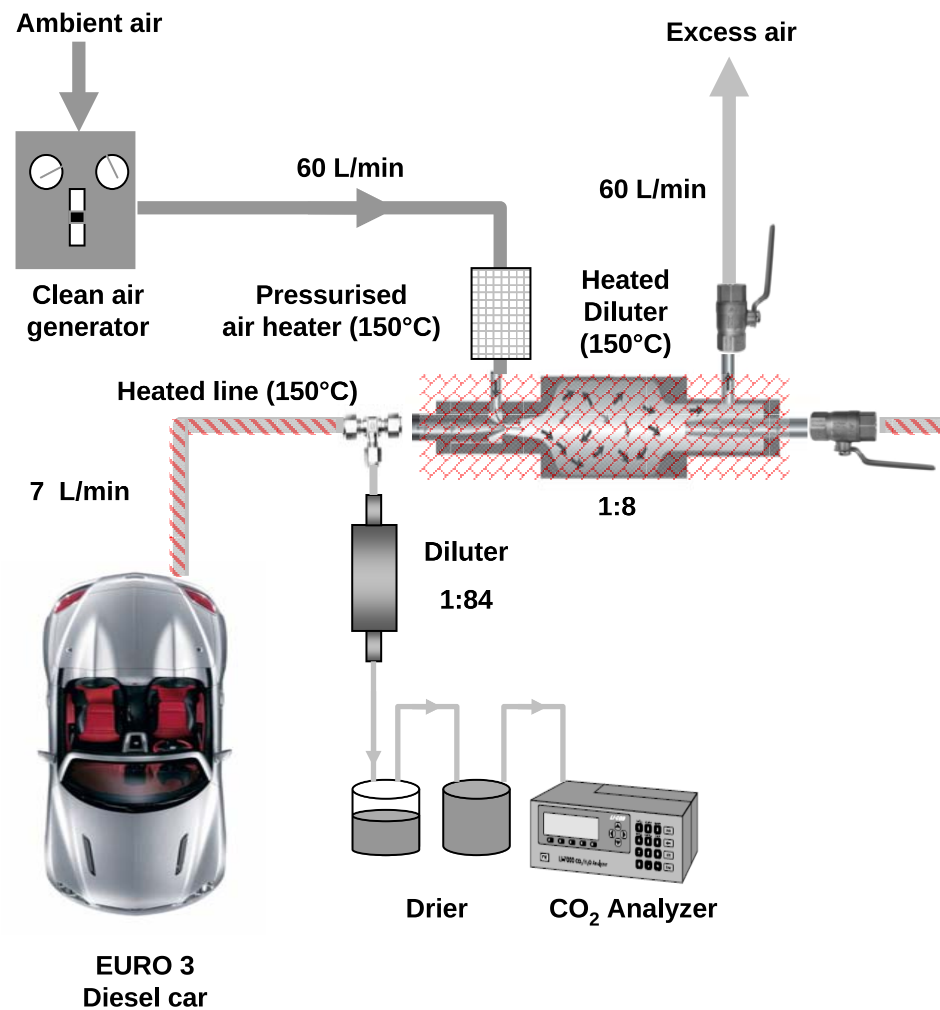
Ambient temperature
High dilution ratio (1000-10000)

Primary Organic Aerosols

Secondary Organic Aerosols

(Robinson et al., Science 2007)

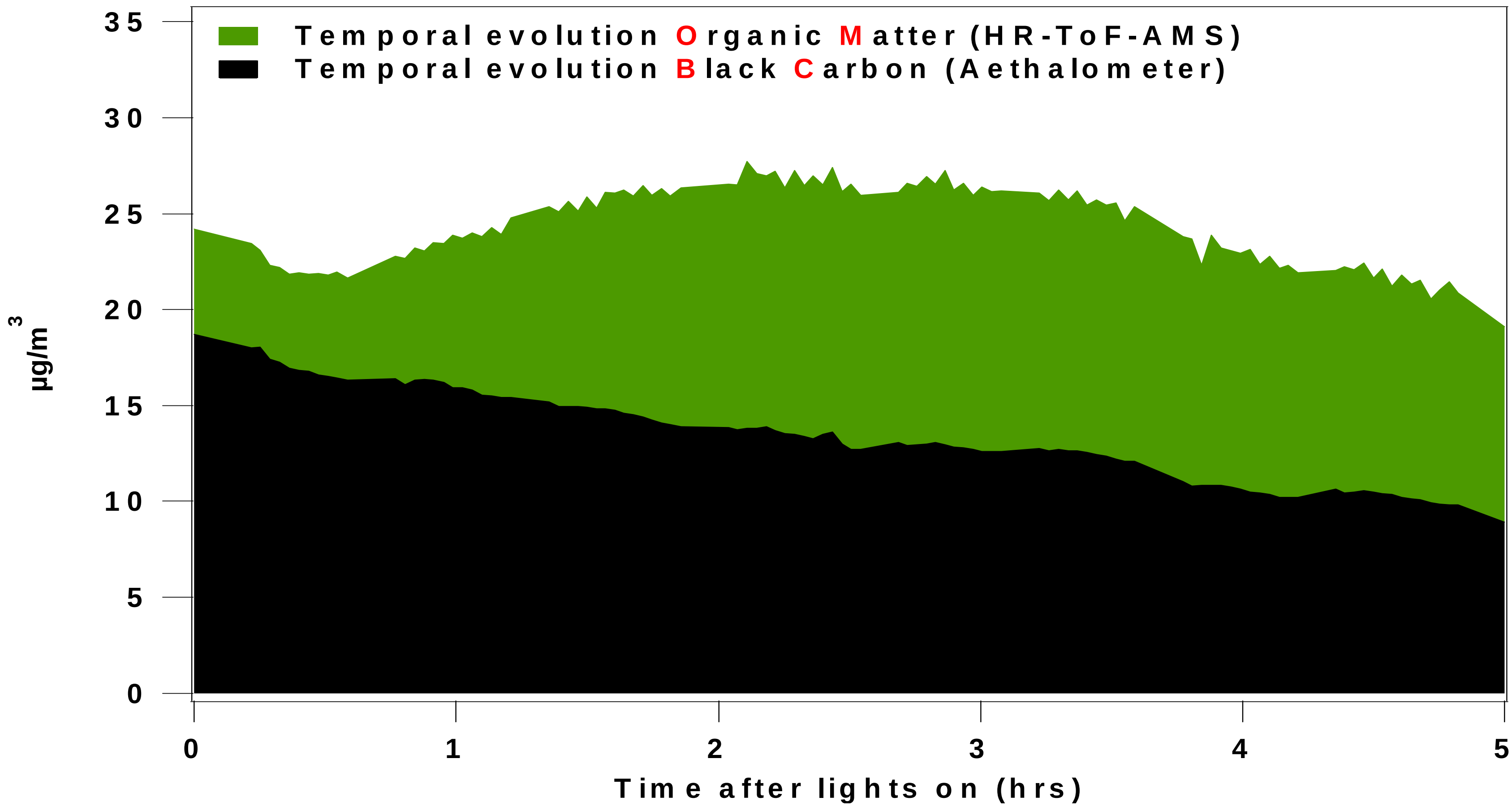
Set up for smog chamber experiments



Dilution factors: 300-1200

Idle – 60 km/h

HR-ToF-AMS and Aethalometer



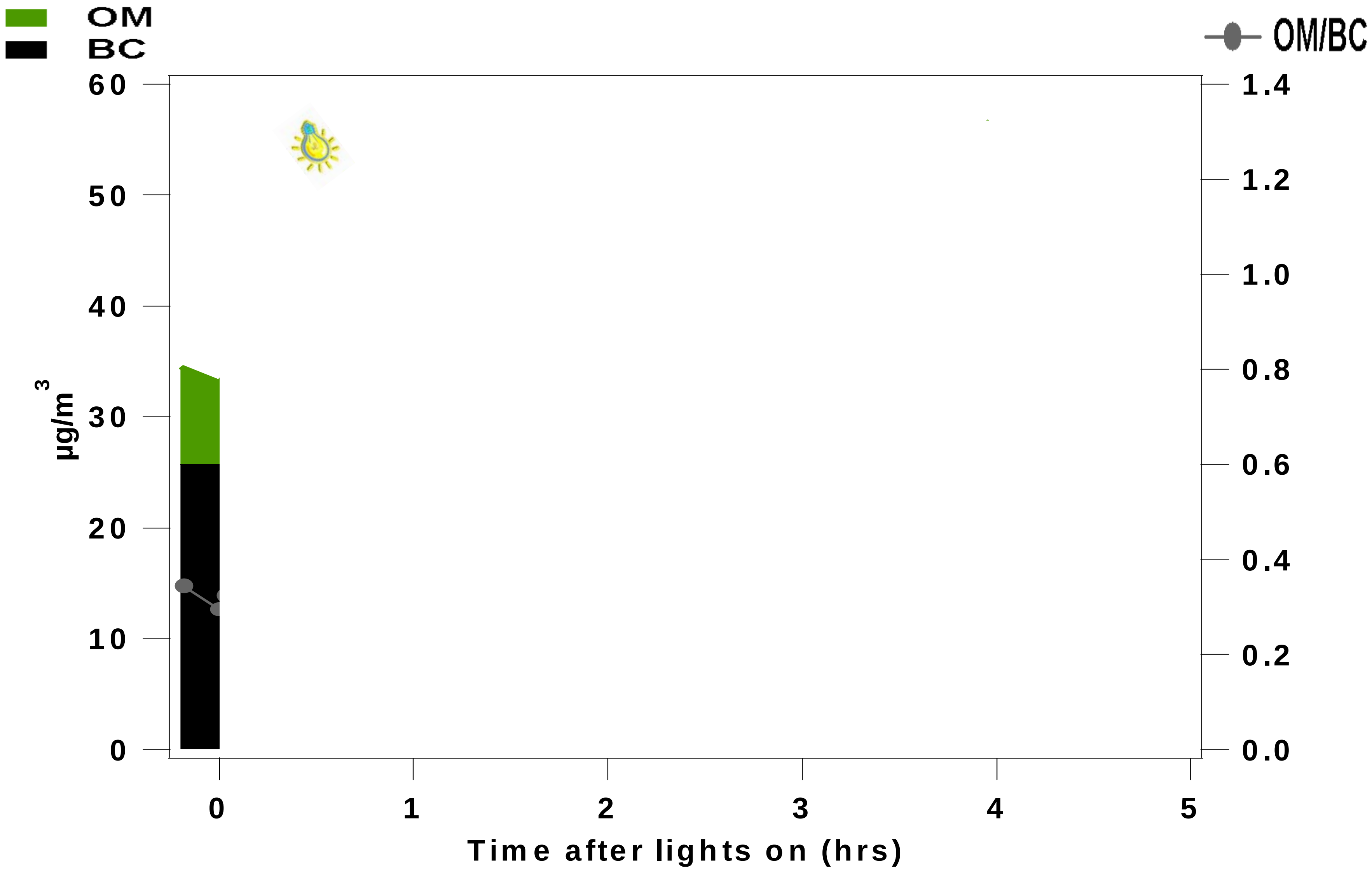
Aerosols are internally mixed

BC can be used as tracer for chamber wall loss

$$\text{Estimated OM}(t) = \text{Measured OM}(t) \times \left[\text{BC}(t_0)/\text{BC}(t) \right]$$

(De Carlo et al., Anal. Chem. 2006; Weingartner et al., Aerosol Sci. 2003)

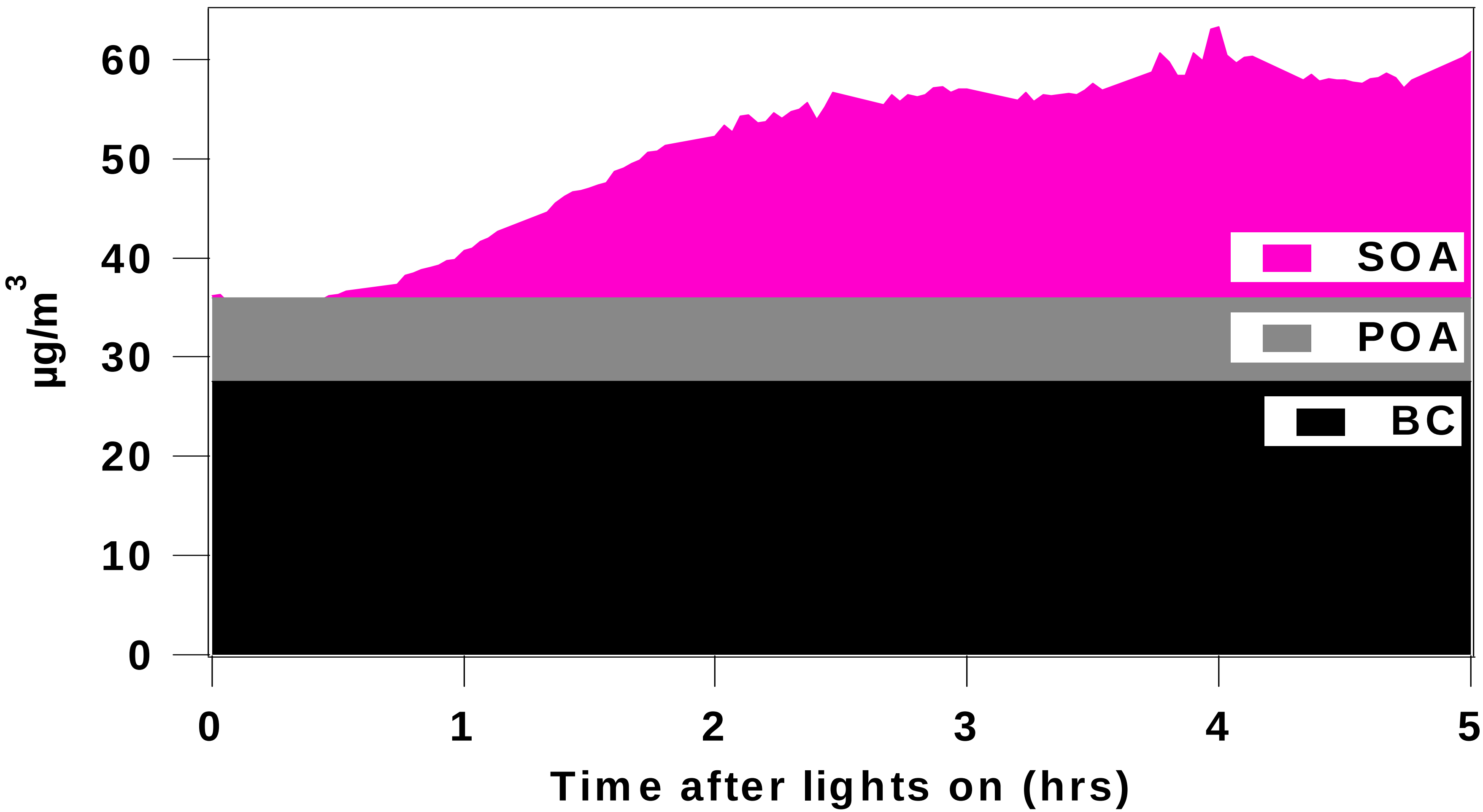
Characteristic aging experiment of diesel exhaust



Primary aerosols consist mainly of BC with a low fraction of Organic Matter (OM)
Photo-oxidation of gaseous organics produces SOA

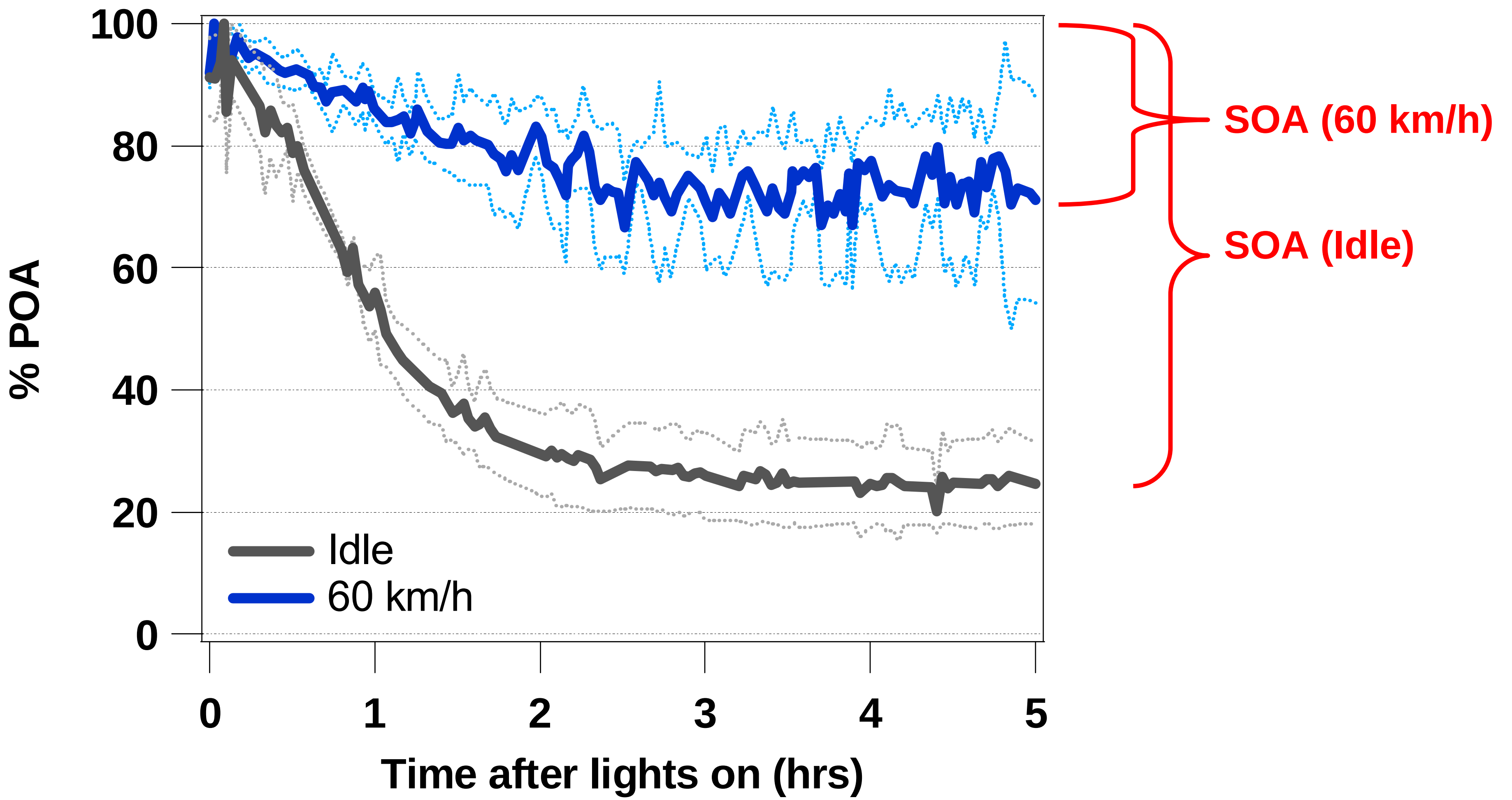
Primary and Secondary organic aerosols

Starting POA concentration assumed constant



SOA contribution to total organic mass

$$\%POA(t) = \left[POA(t_0)/OM(t)\right] \times 100$$



After 5 hours of aging SOA is 30-80 % of the Total Organic Aerosols

Organic Aerosol Mass Spectra

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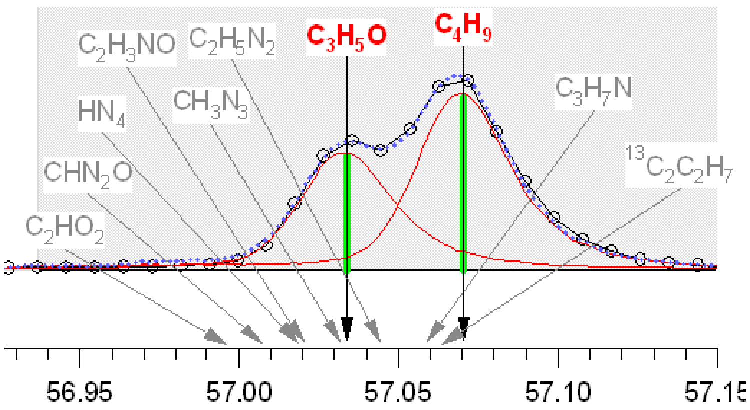


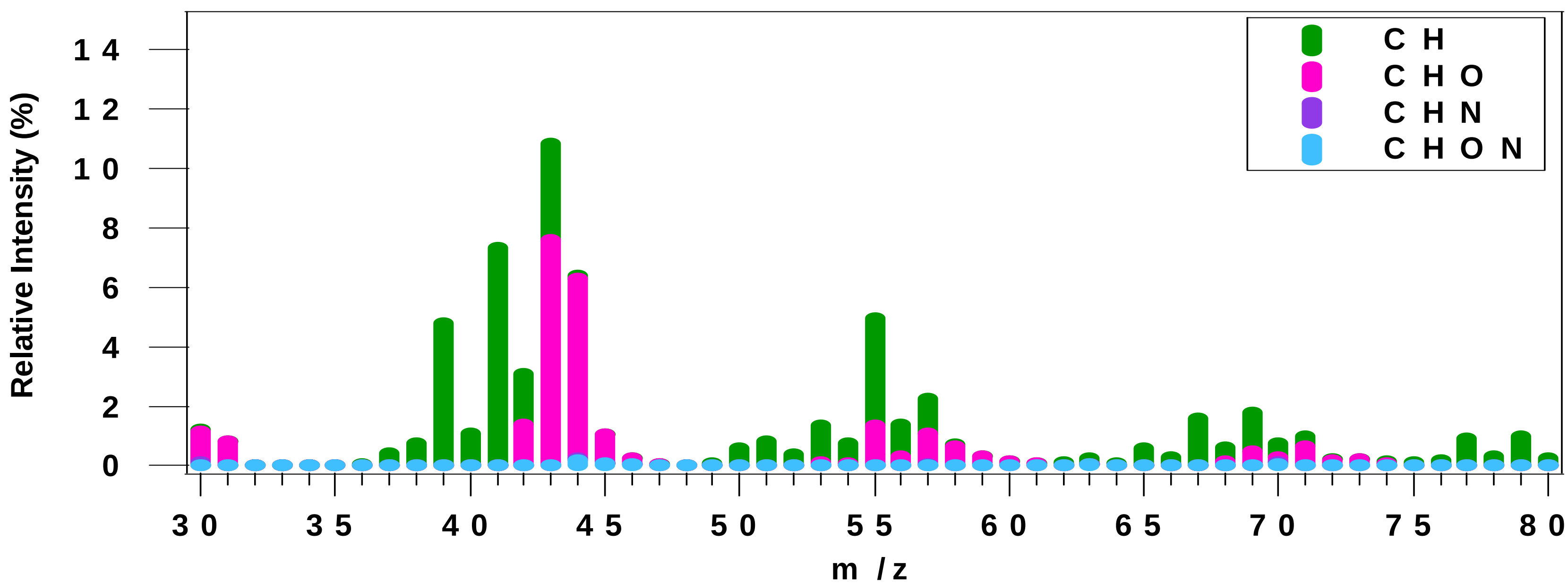
Average mass spectrum for an ensemble of submicron particles with a time resolution of few seconds

High resolving power (2000-5000)

Discrimination between ions with the same nominal mass

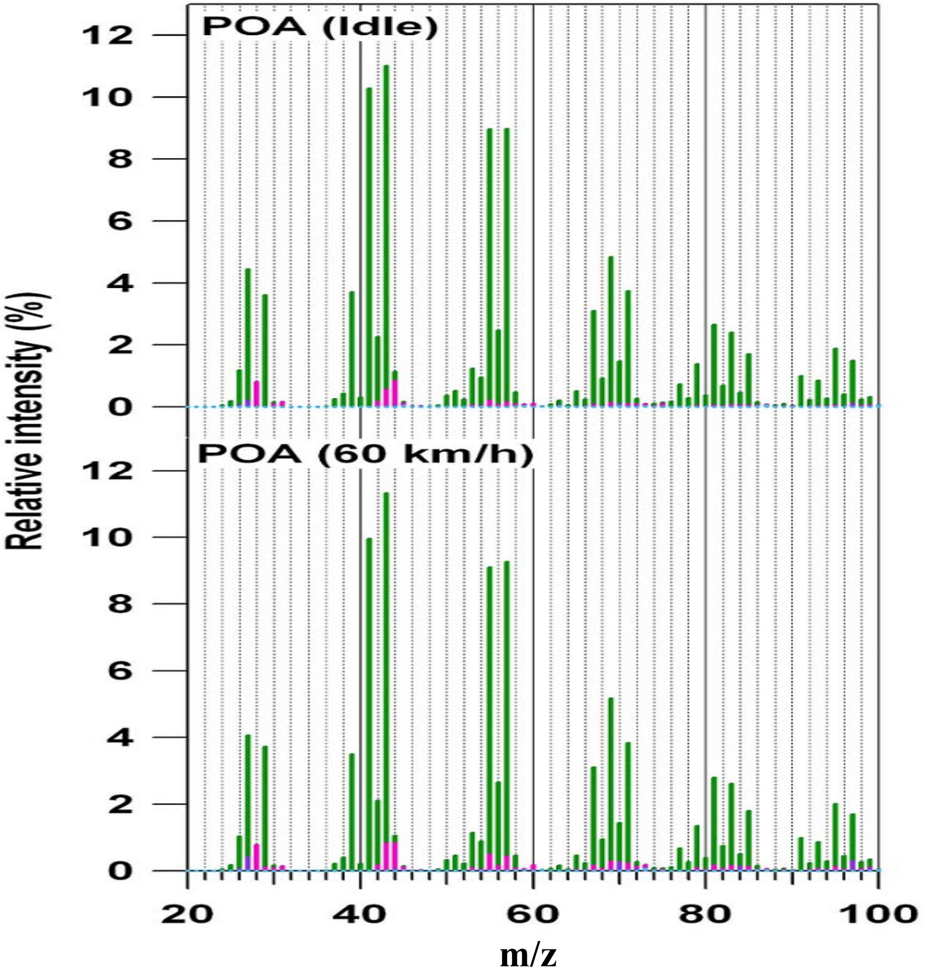
CH CHO CHN CHON

Ions grouped into 4 different organic classes depending on the atom combination



Organic Aerosol Mass Spectra from diesel exhaust

CH CHO CHN CHON

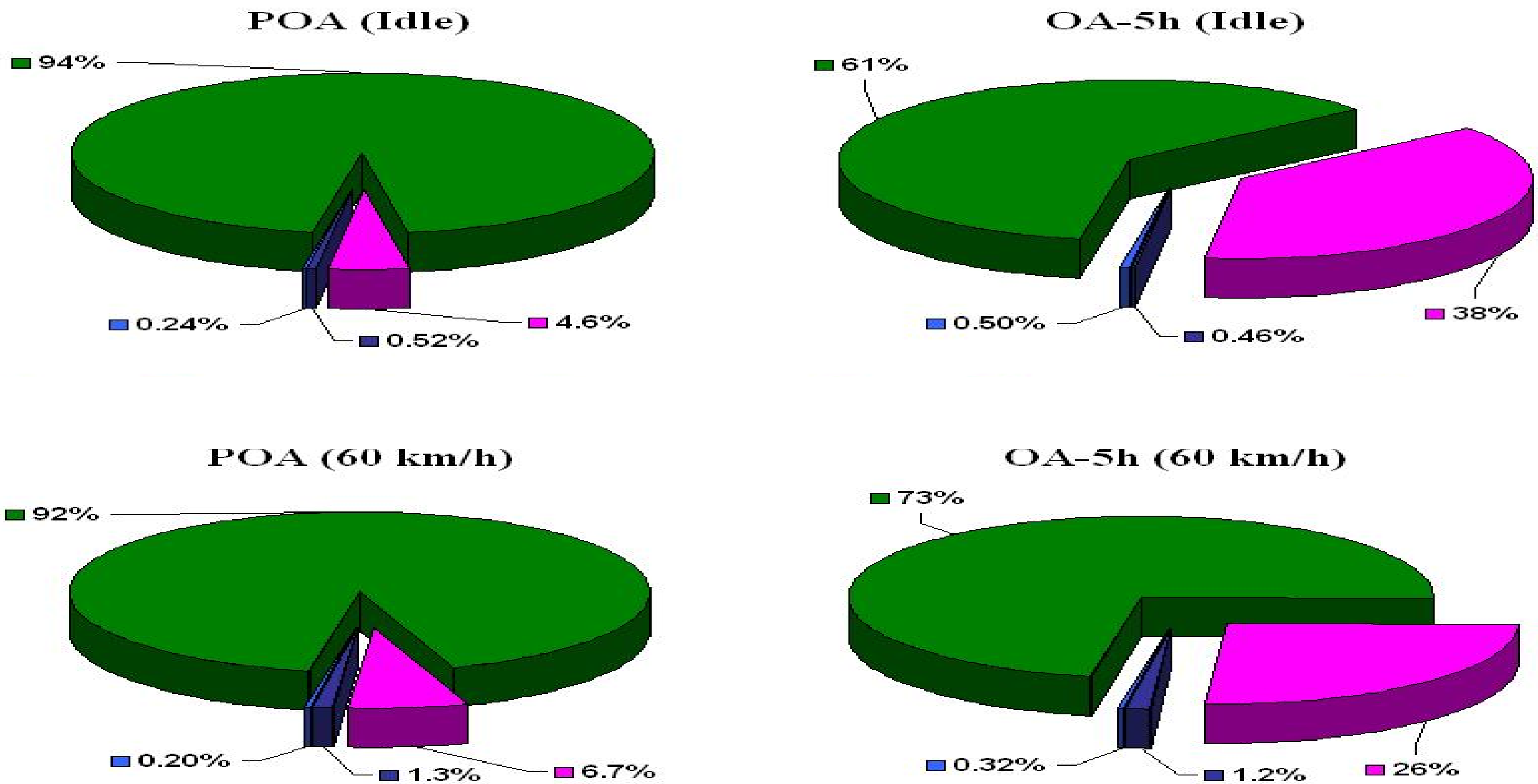


Hydrocarbon-like Organic Aerosols

(Fragmentation pattern similar to that one of long chain hydrocarbons)

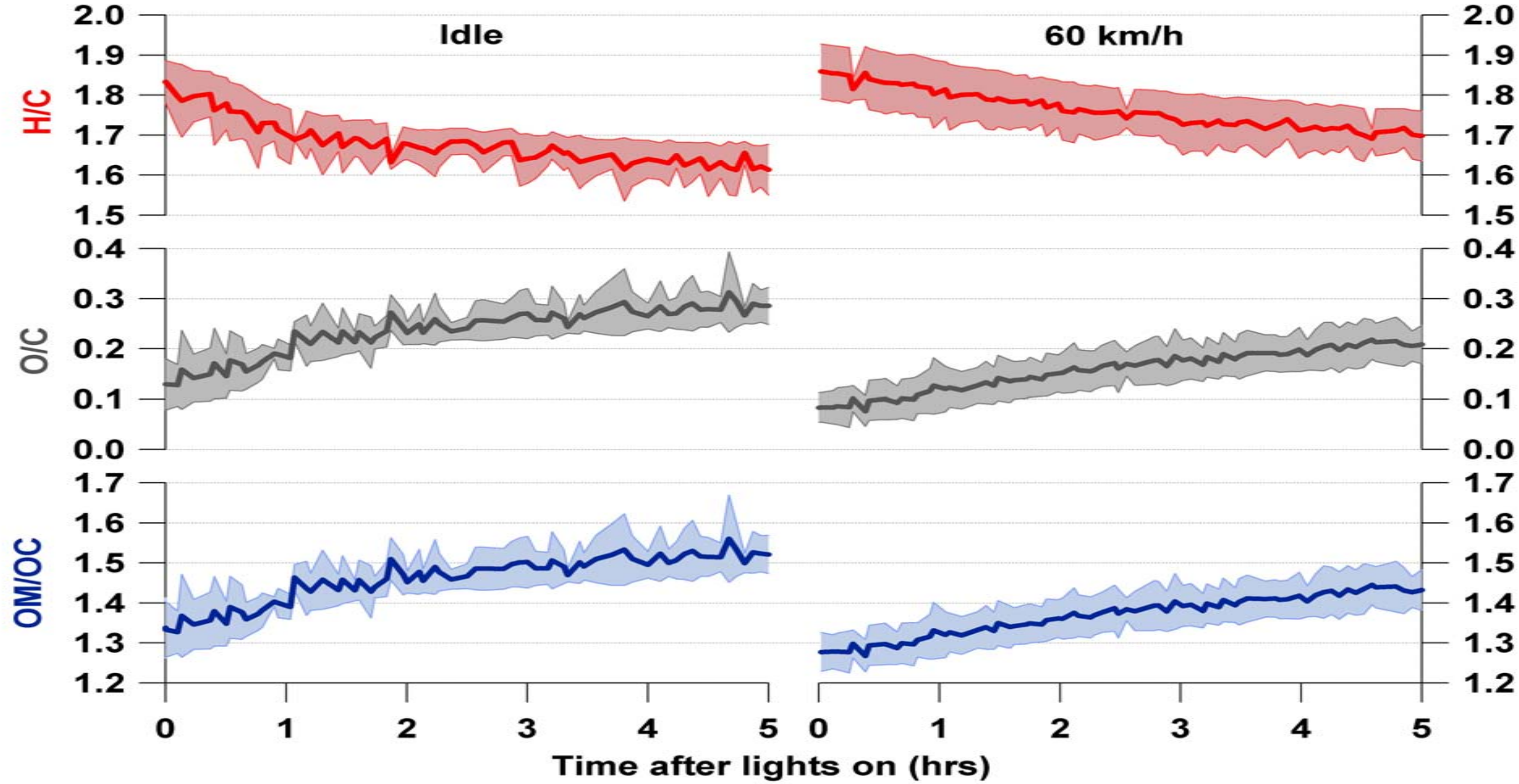
Organic Aerosol Mass Spectra from diesel exhaust

CH CHO CHN CHON



Higher contribution of the CHO family to the organic aerosols after 5 hours of aging

Atomic ratios and OM/BC ratios

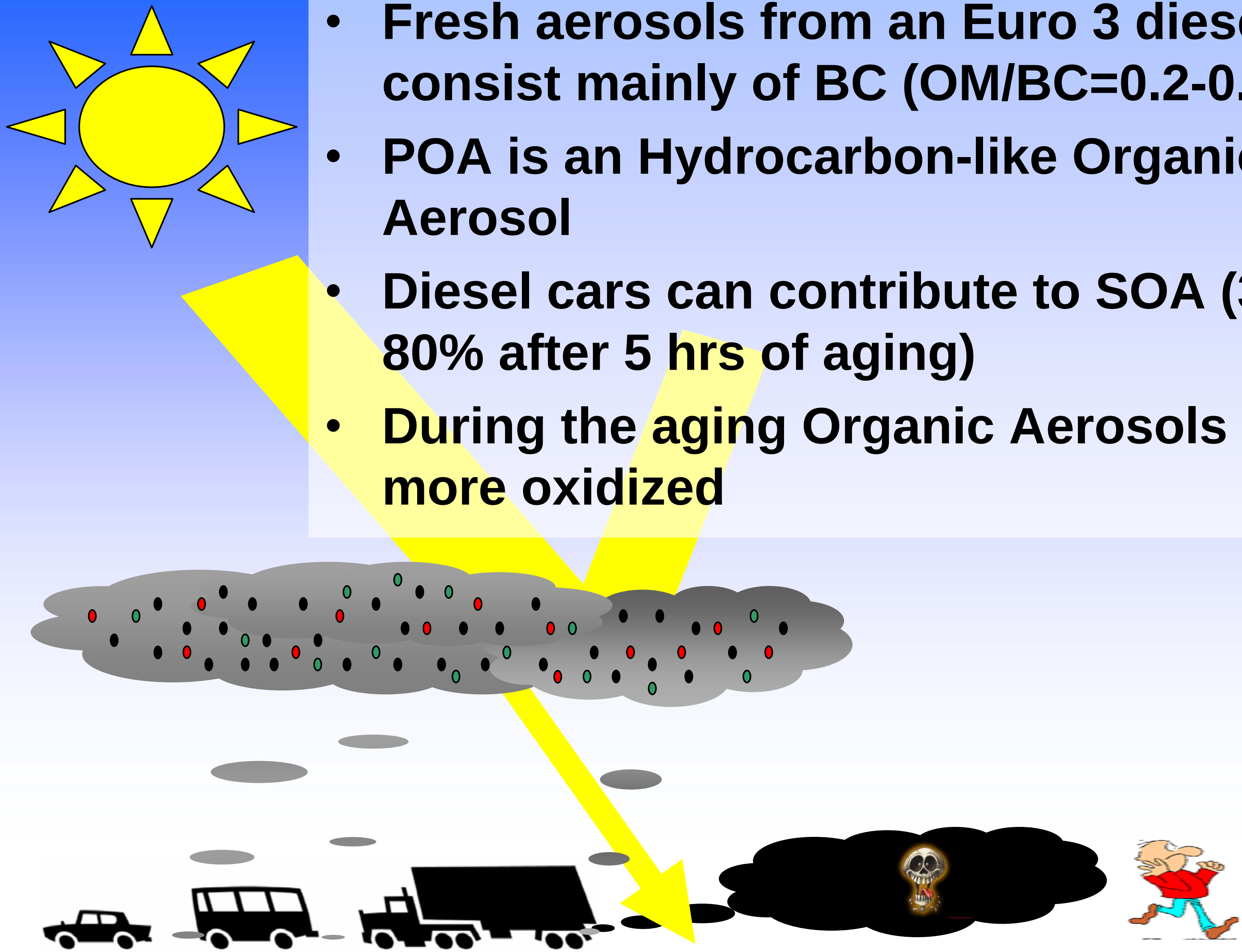


H/C ↓ O/C and OM/OC ↑

OM/OC (POA)= 1.28-1.33
(60 km/h) (idle)

Conclusions

- **Fresh aerosols from an Euro 3 diesel car consist mainly of BC (OM/BC=0.2-0.3)**
- **POA is an Hydrocarbon-like Organic Aerosol**
- **Diesel cars can contribute to SOA (30-80% after 5 hrs of aging)**
- **During the aging Organic Aerosols get more oxidized**



Thanks to…….

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Next Generation Exhaust Aftertreatment for Diesel Propulsion Systems

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Thank you for your attention

Vielen Dank für Ihre Aufmerksamkeit

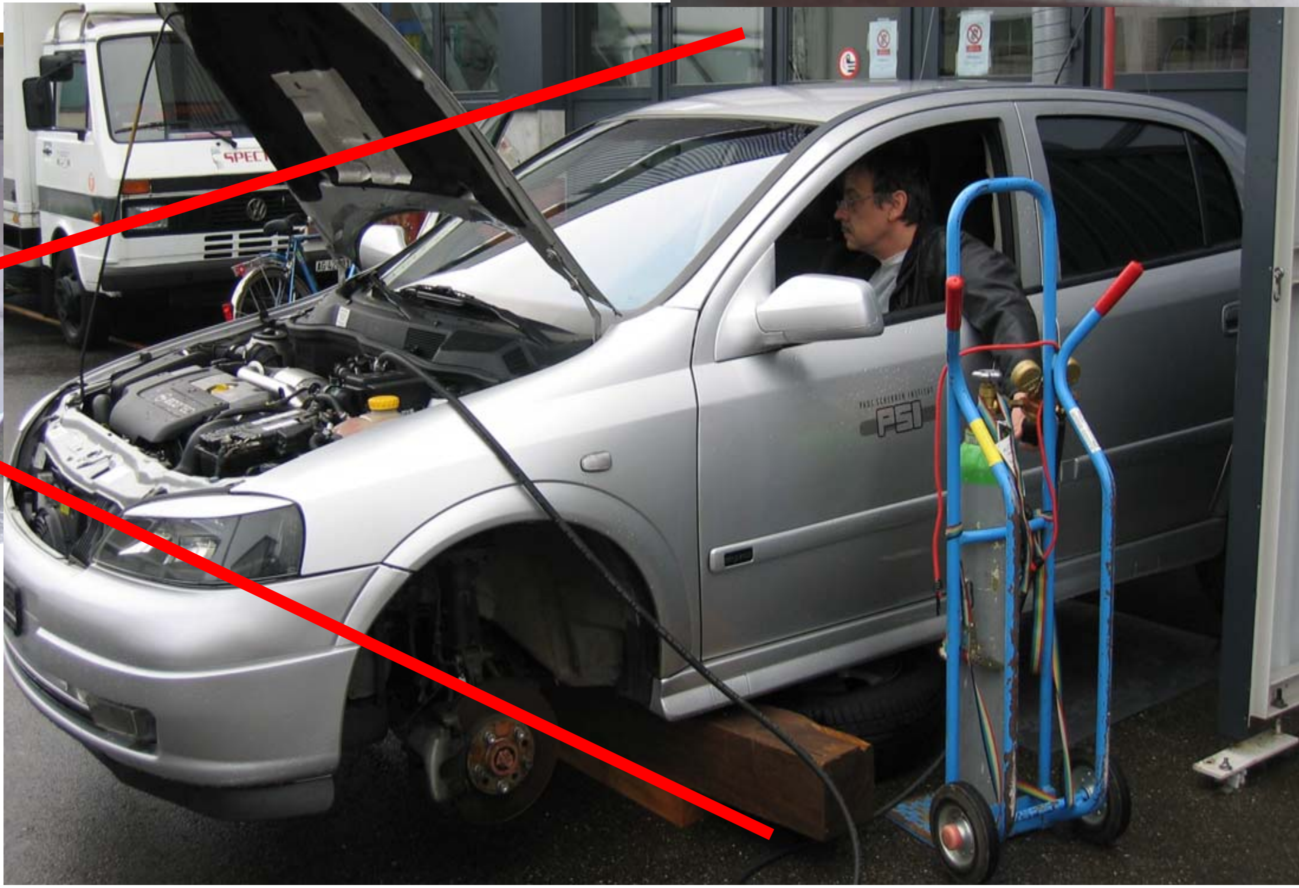
Merci pour votre attention

Grazie per la vostra attenzione

http://www.chrismadden.co.uk

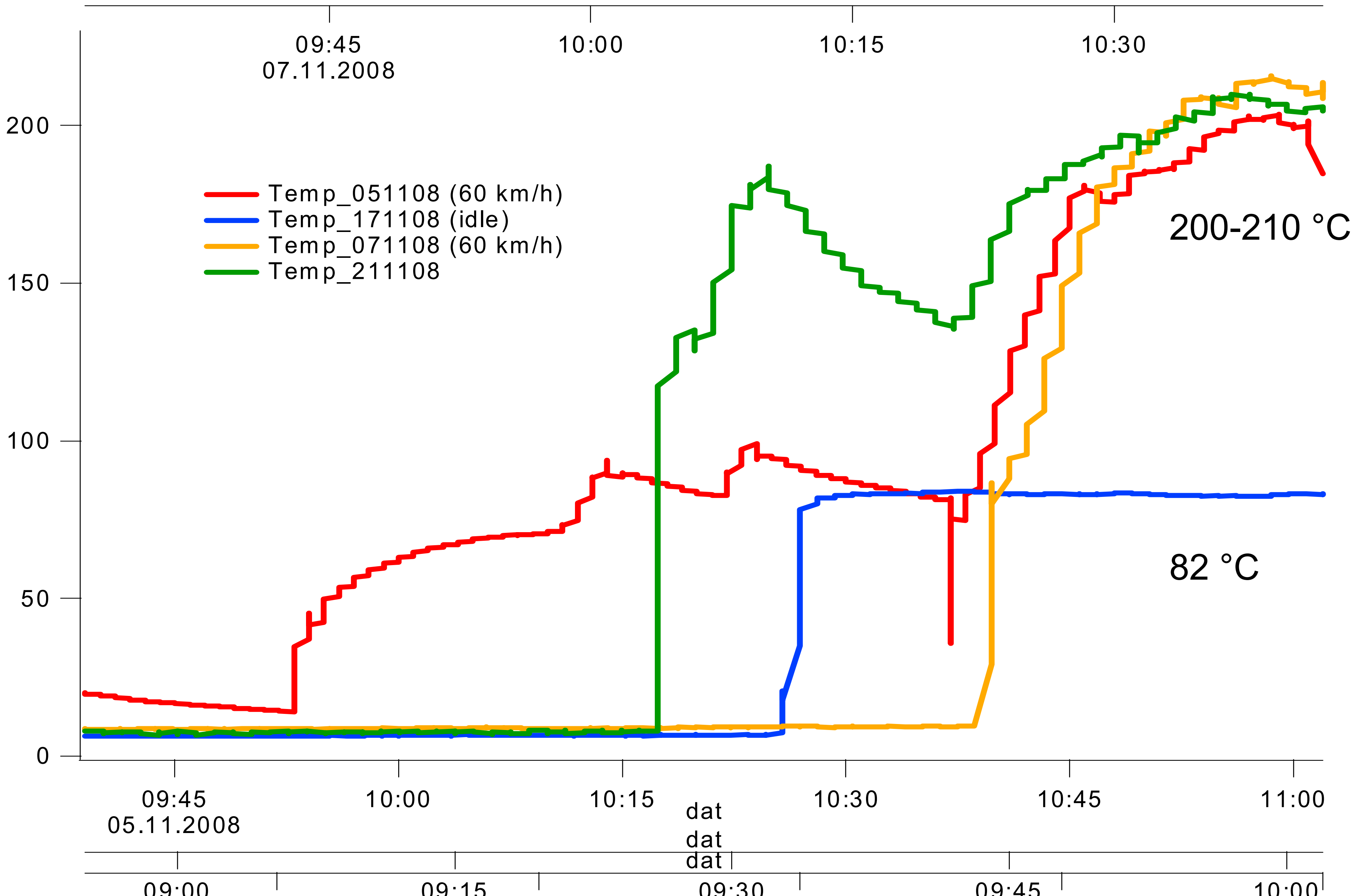
Aging of diesel exhaust in the PSI smog chamber

Euro 3 diesel car running at 60 km per hour



Filling the chamber in ~15 min

Exhaust temperature



Diesel Oxidation Catalyst

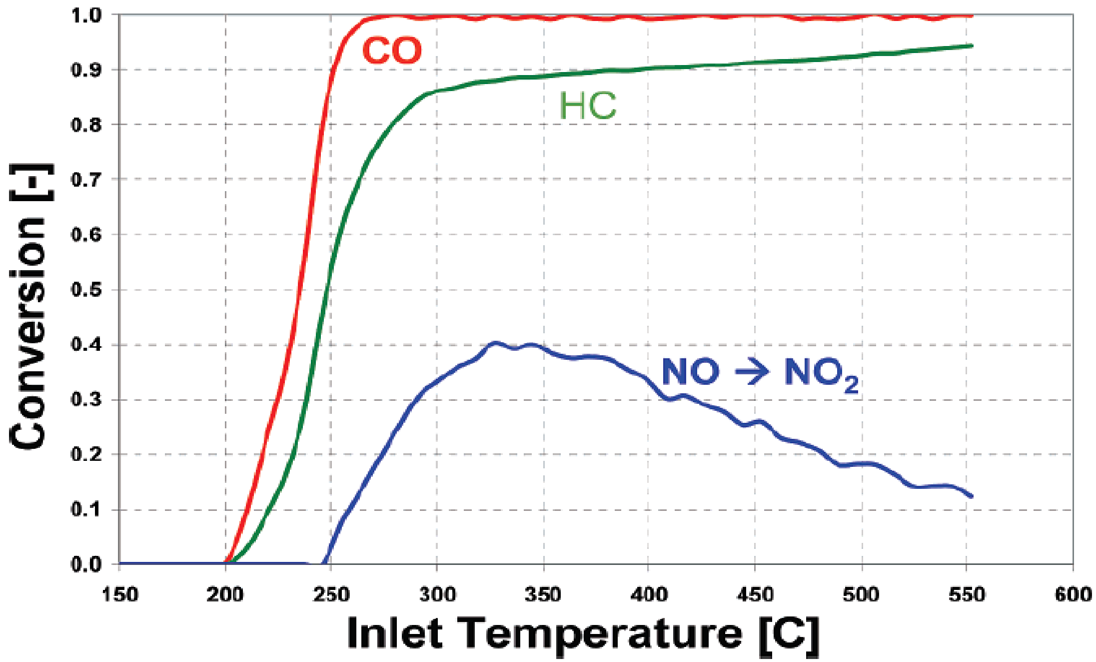
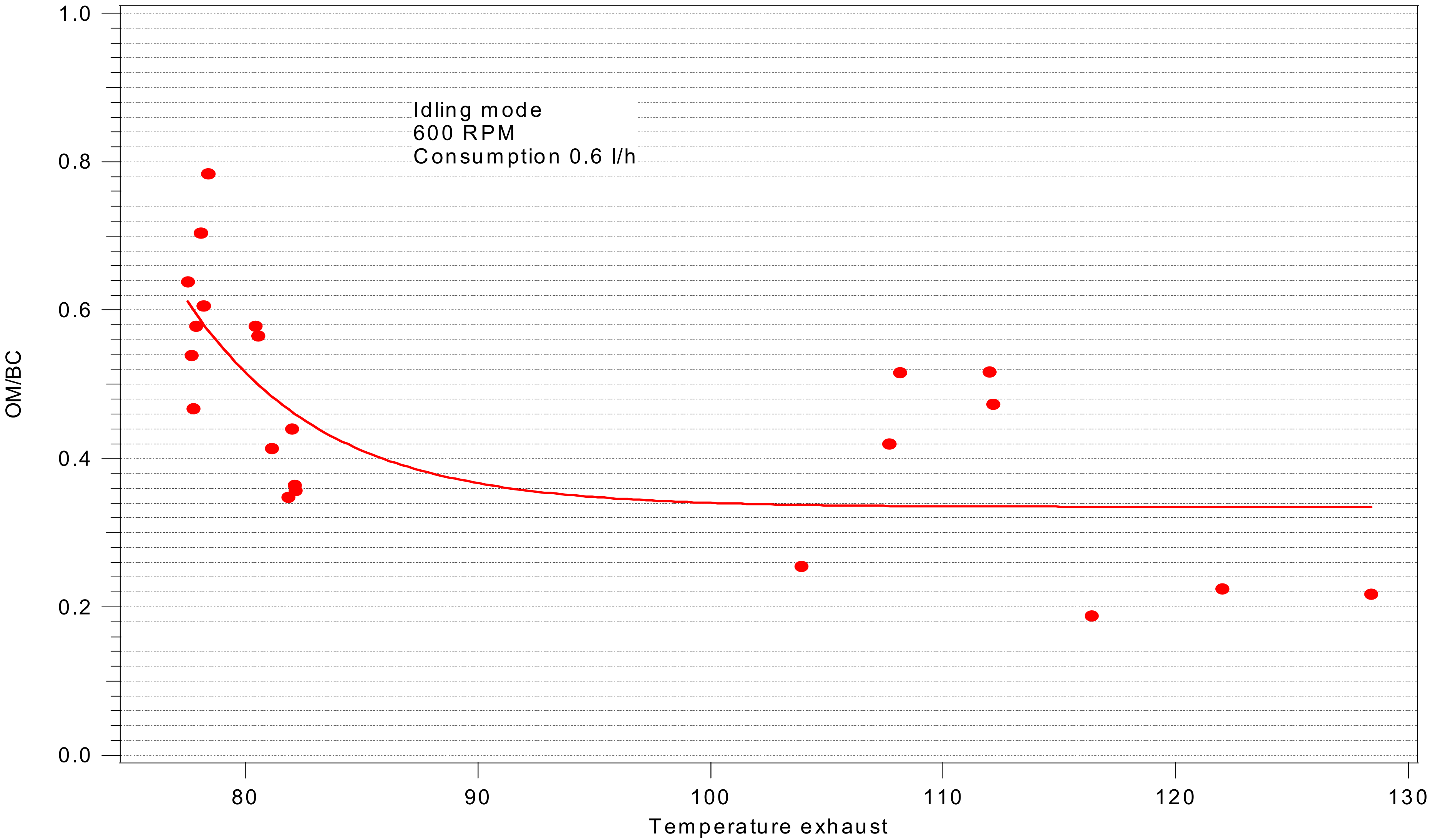


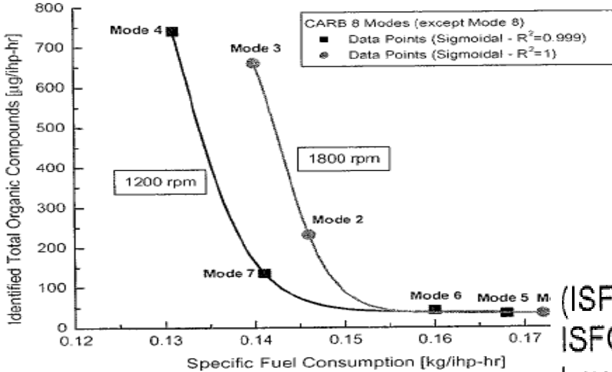
Figure 3. Typical pulsator map used to compute CO, HC, and NO oxidation reaction rates in the DOC model. Data correspond to a relatively fresh catalyst at a SV of 35000 h^{-1}.

the oxidation of NO to NO2 is constrained kinetically at low temperatures and thermodynamically at higher temperatures

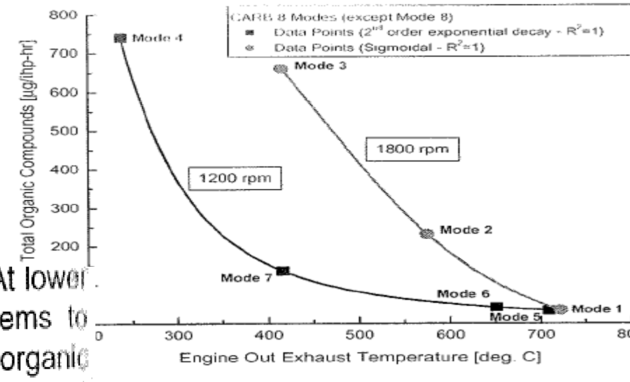
Direct measurement: Temperature effect



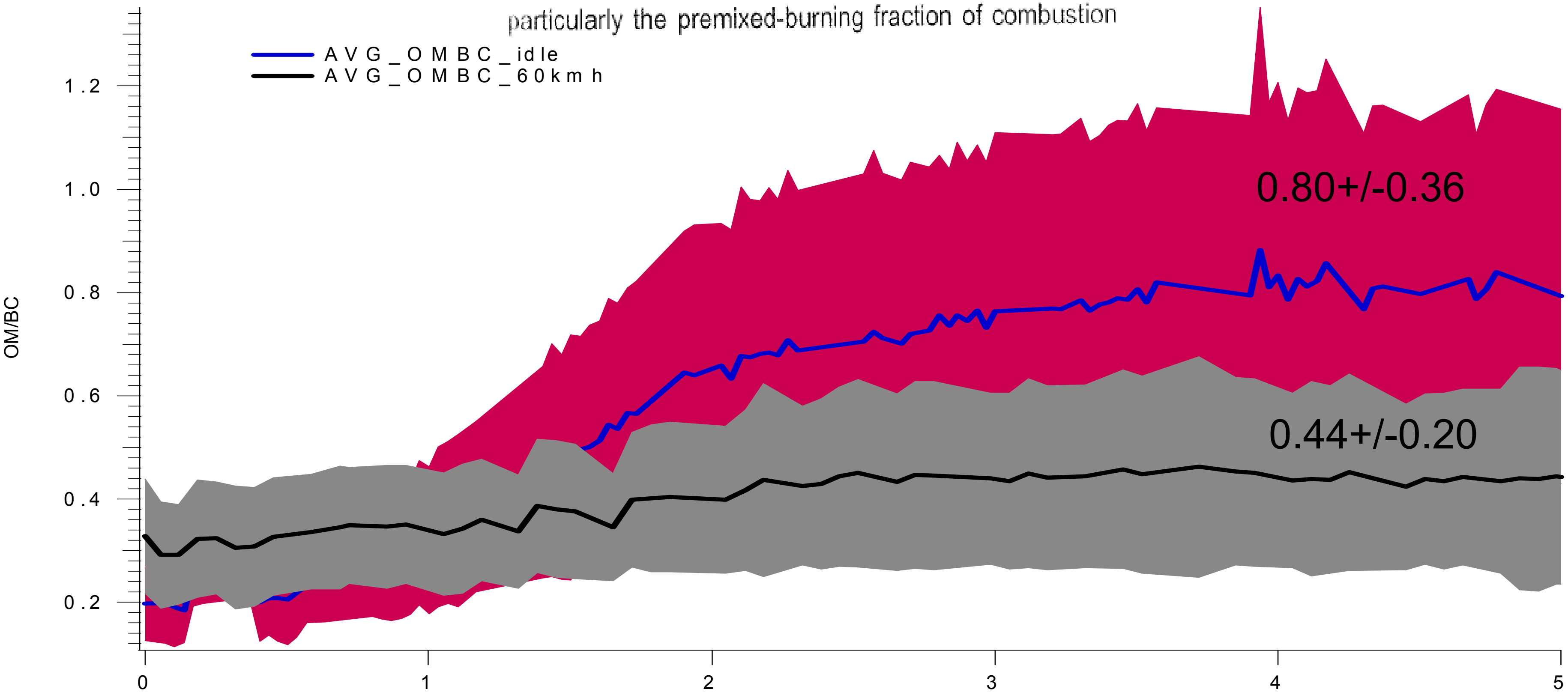
OM/BC



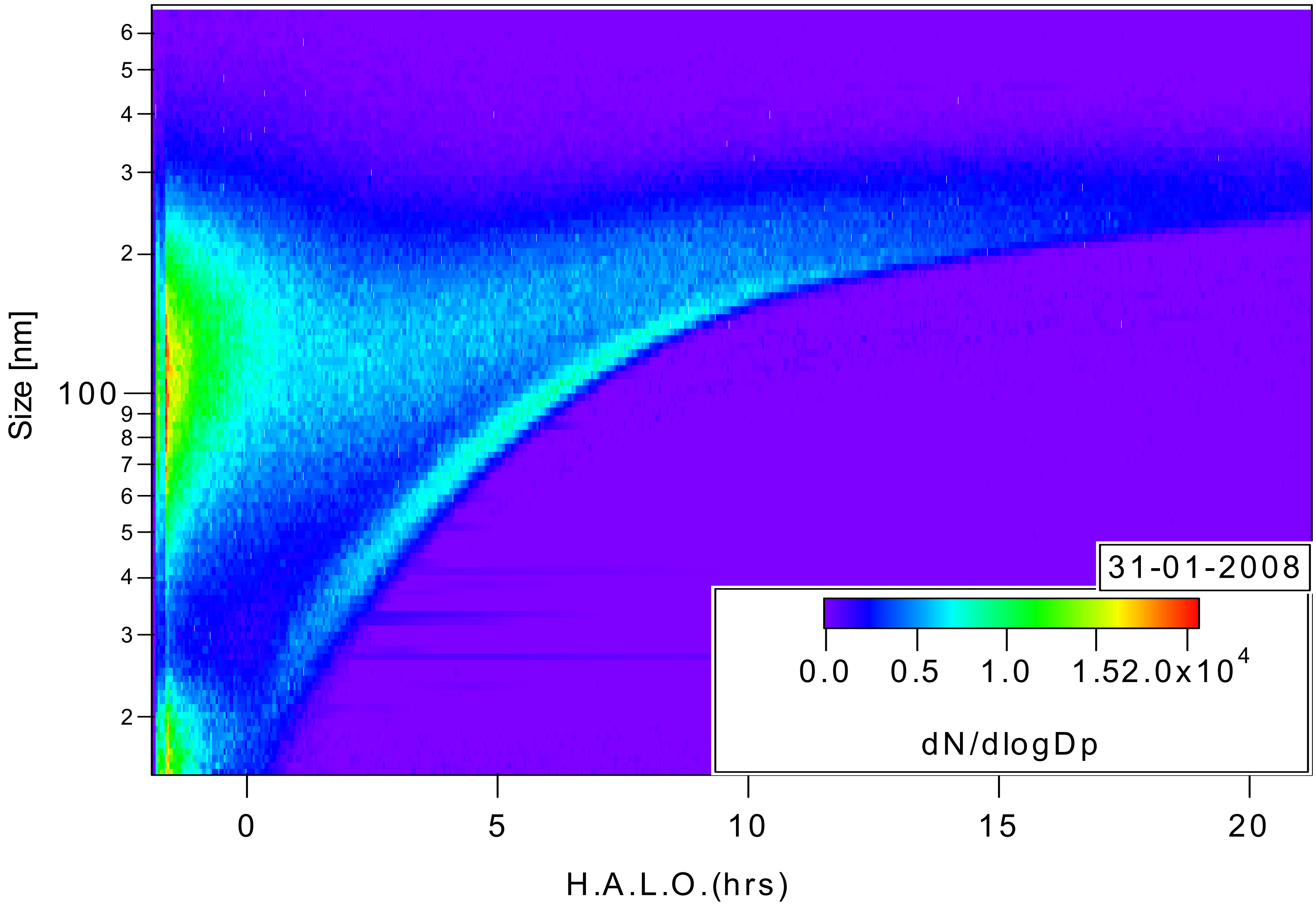
(ISFC) by using the Sigmoidal Fit in Figure 13. At lower ISFC (i.e. below 0.155), the engine speed seems to have significant impact on the particle-phase organic compounds. The higher engine speed (i.e. 1800 rpm) produced more particle-phase organic compounds than the lower engine speed (i.e. 1200 rpm) at the same



result in an increase in ignition delay, which influences particularly the premixed-burning fraction of combustion

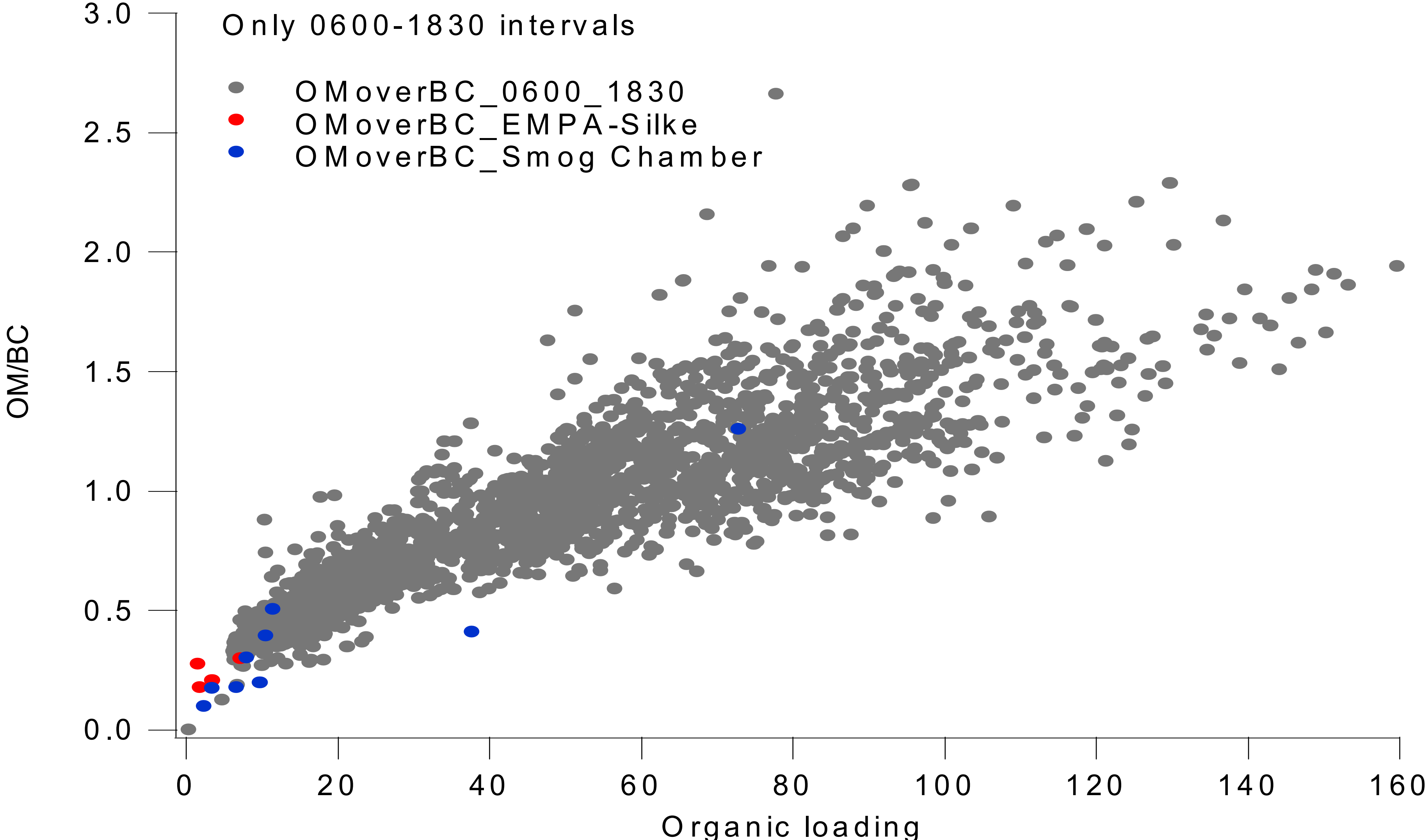


Size distribution



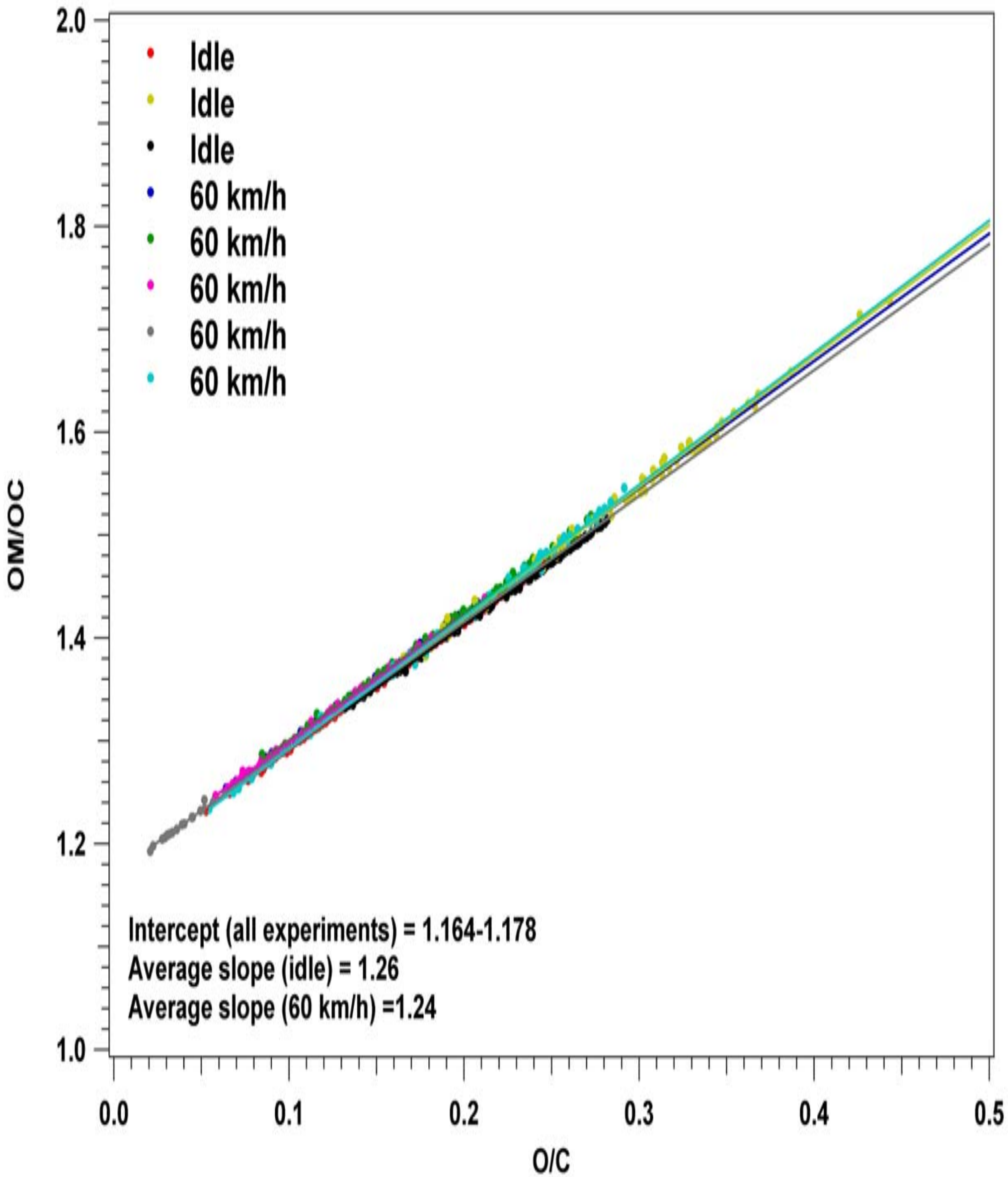
idle

OM/BC vs Org



Only 0600-1830 intervals
OMoverBC_0600_1830
OMoverBC_EMPA-Silke
OMoverBC_Smog Chamber
OM/BC
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
20
40
60
80
100
120
140
160
Organic loading

OM/OC vs O/C



<u>Diesel fuels</u>

C10-C25 hydrocarbon mixtures

<u>Lubricating oils</u>

C14-C45 hydrocarbon mixtures

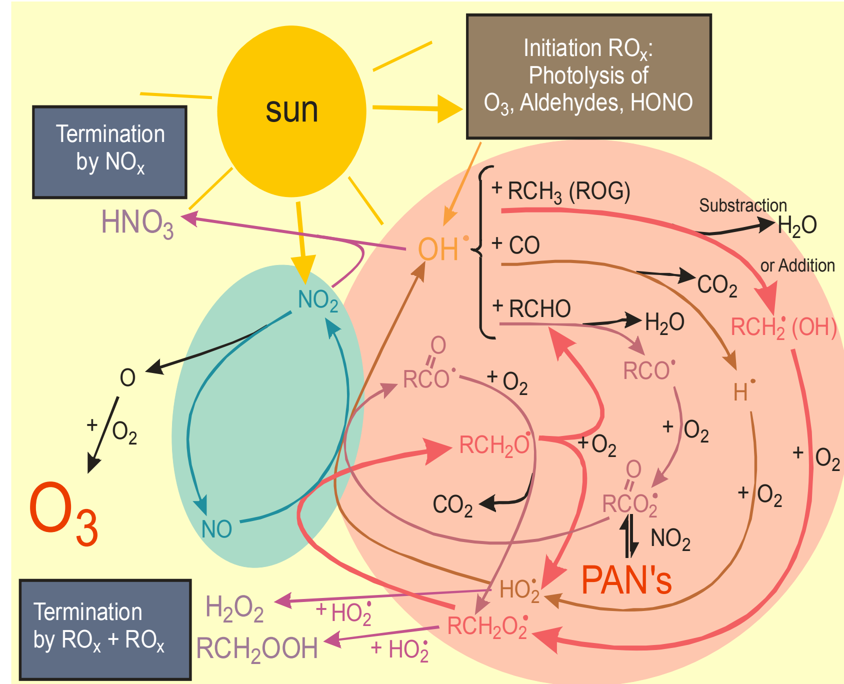
OM/OC (C10-C45 long chain alkanes) 1.17 -1.19

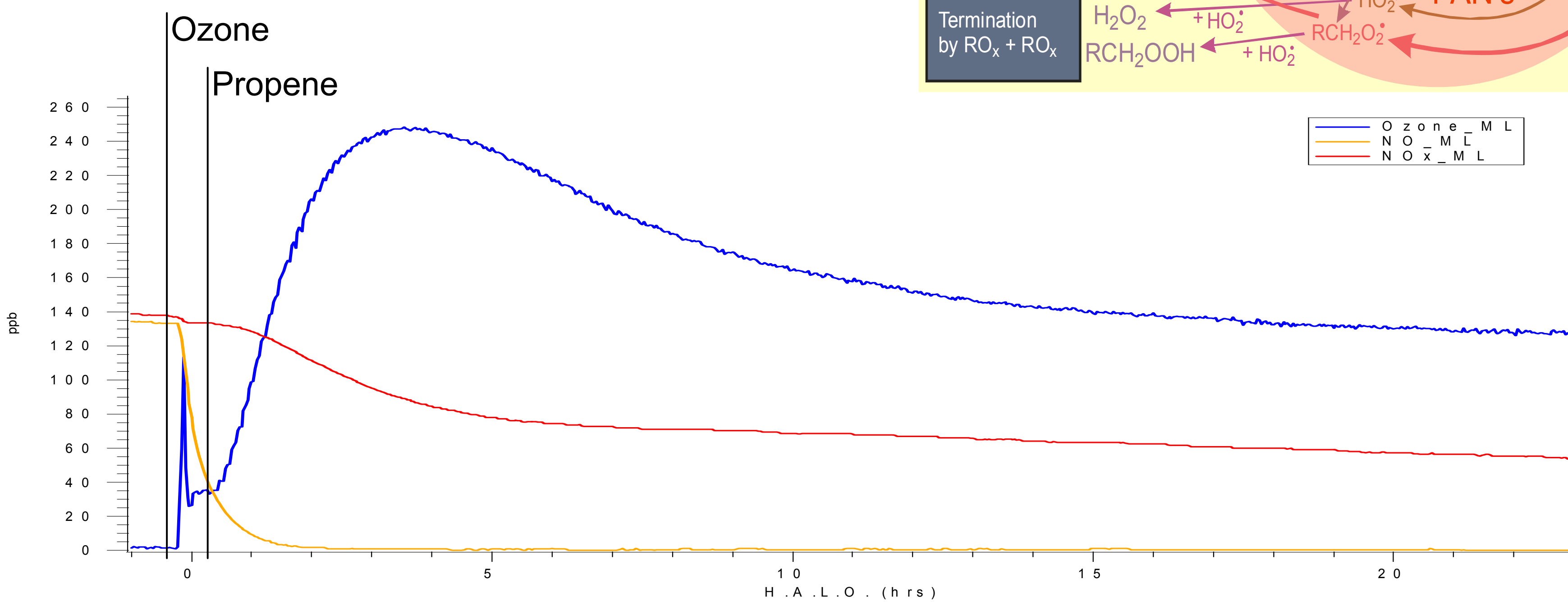
VOC/NO_X ratio

VOC/NO_X ratio needs to be increased

High NO_X (~NO) conc. from diesel exhaust

OH reacts about 5.5 times more rapidly with NO_2 than with an average urban VOC mix





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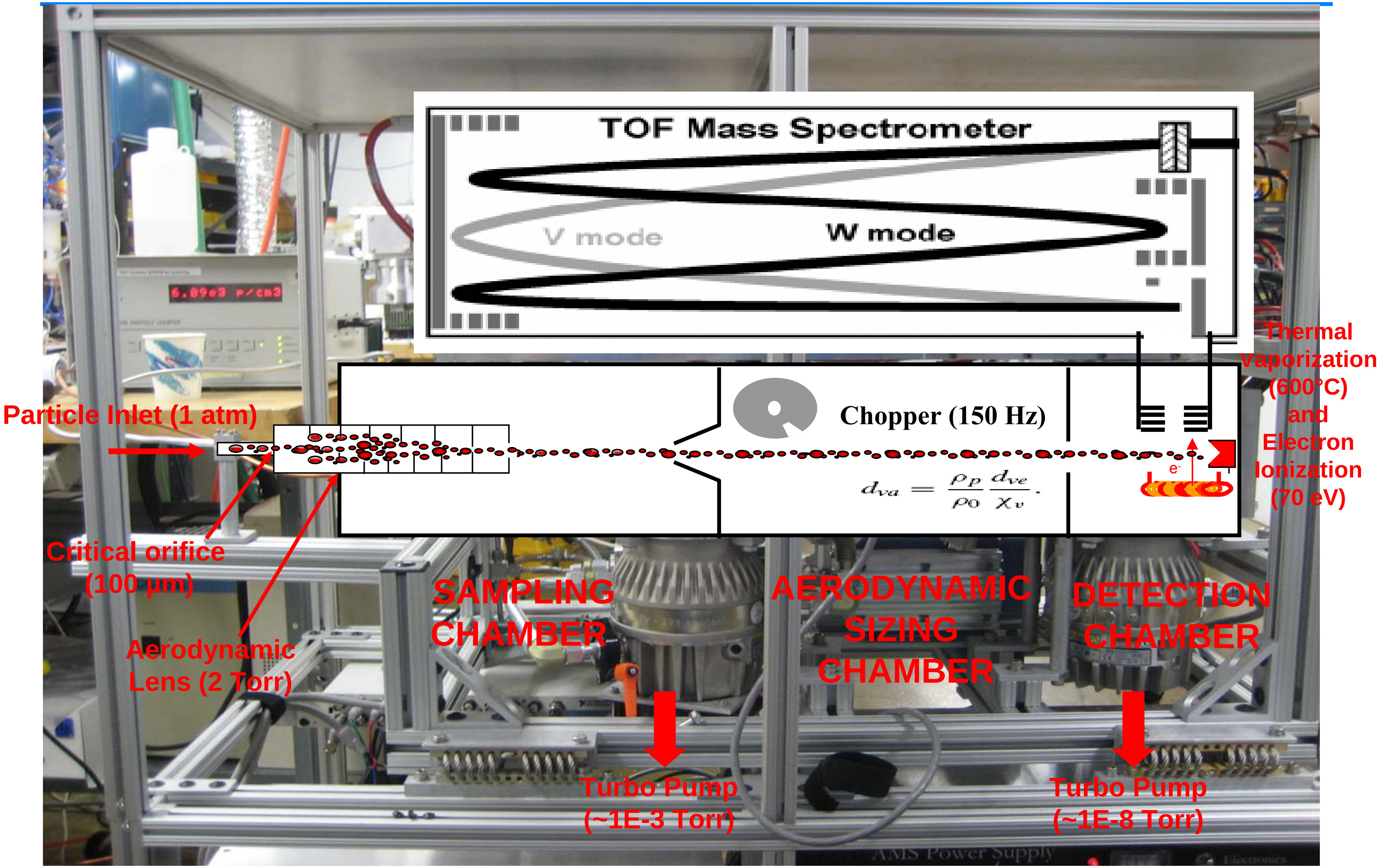
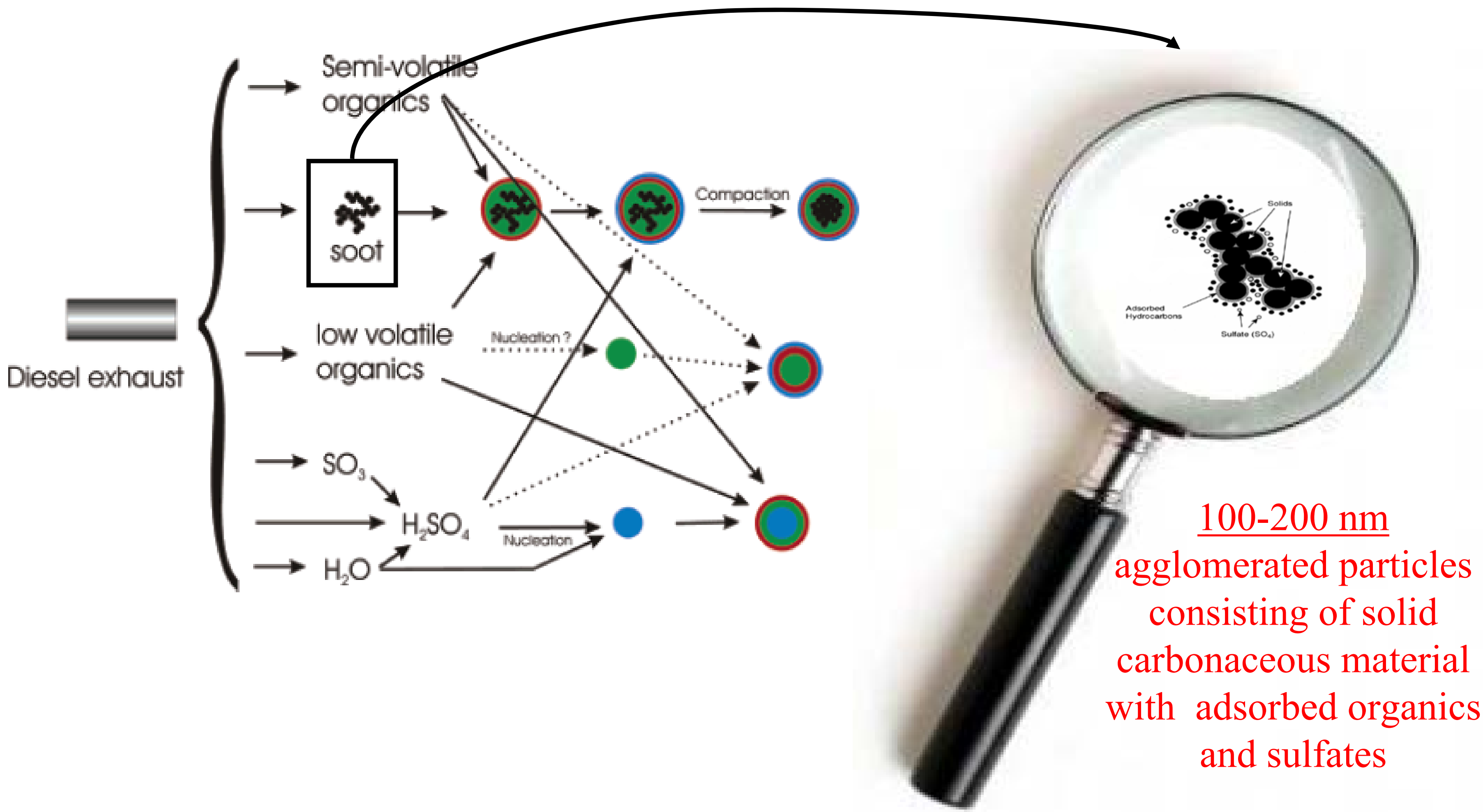
HR-ToF-AMS (MS mode)

Labor für Atmosphären-Chemie



(Jayne et al., 2000; De Carlo et al., 2006)

Composition of diesel emissions



100-200 nm agglomerated particles consisting of solid carbonaceous material with adsorbed organics and sulfates

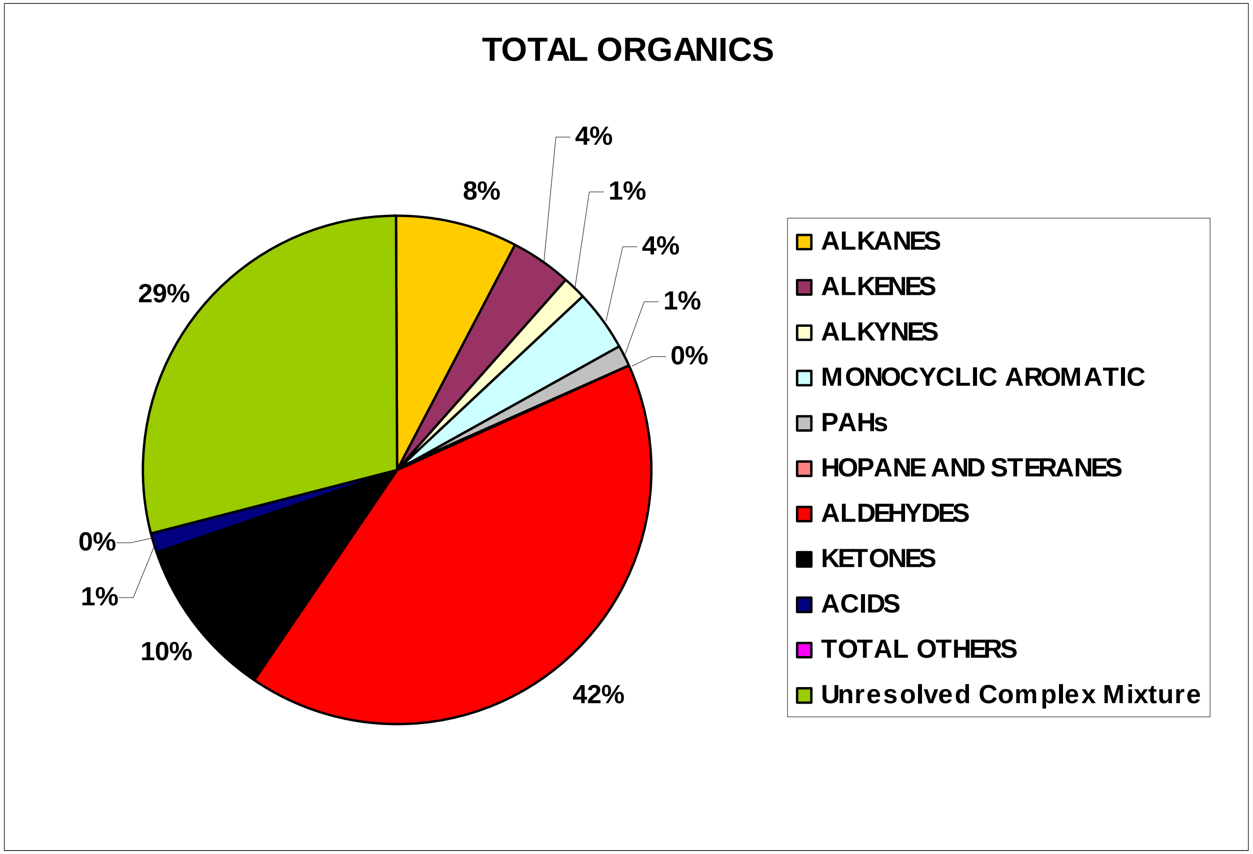
● **Primary Organic Aerosols (POA)**

(Schneider et al., ES&T 2005)

Composition of the organic fraction

Hundreds of different organic compounds

Aldehydes
Ketones
Alkanes
PAHs

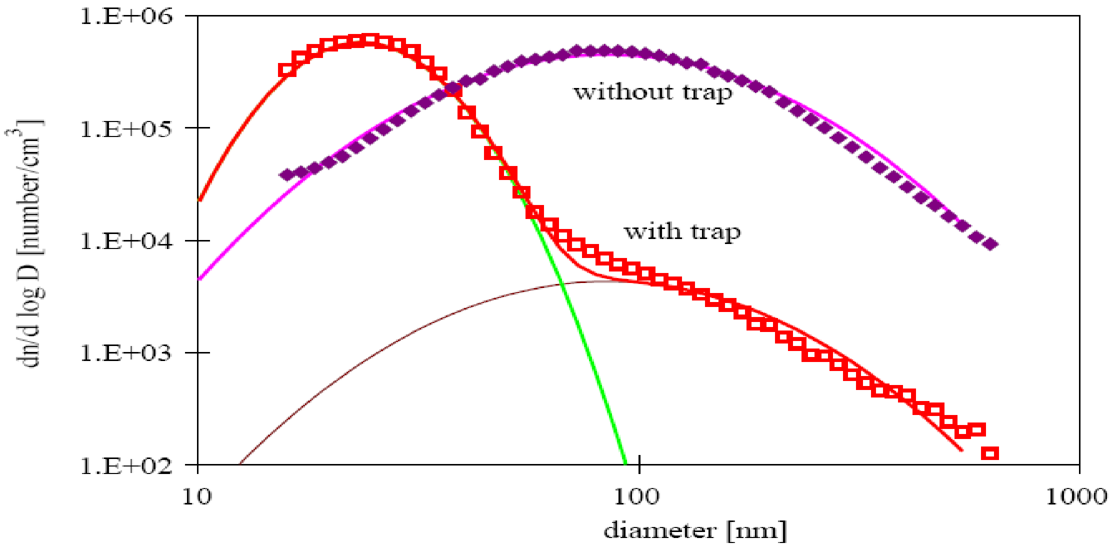


(Schauer et al., ES&T 1999)

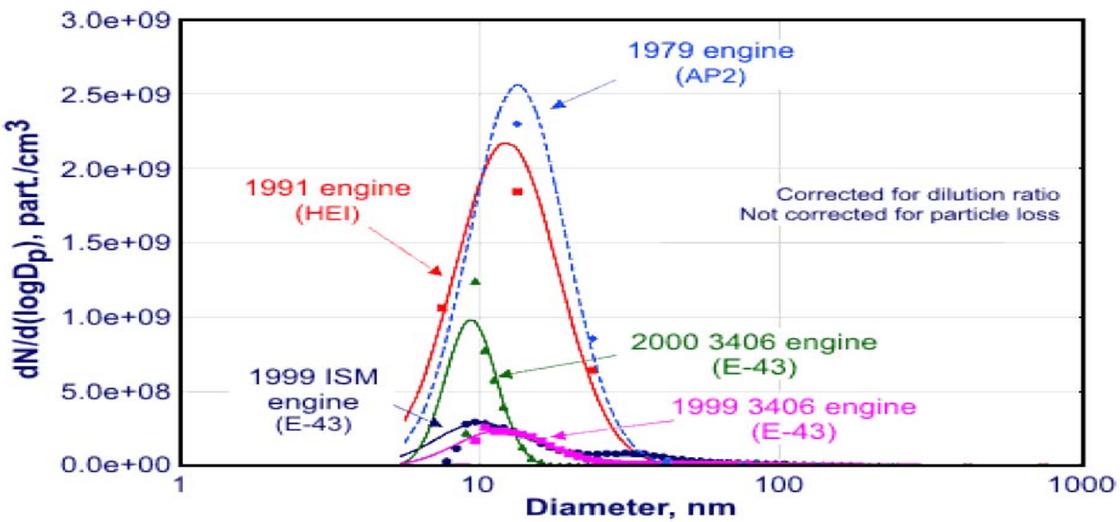
Diesel particle number concentration

Older diesel cars → high conc of soot particles→ large surface area

Newer diesel cars → low conc of soot particles → little surface area → nucleation more likely



PARTICLE NUMBER IN THE NUCLEI MODE HAS INCREASED WITH NEWER DIESEL CAR WITH PARTICLE TRAP



THE TOTAL PARTICLE NUMBER HAS DECREASED WITH NEWER DIESEL ENGINES

(Burtscher, 2005; Kittelson et al., 1998; www.dieselnet.com)

Kelvin effect

The saturation vapor pressure is defined as the equilibrium partial pressure for a plane (flat) liquid surface at a given temperature. If the liquid surface is sharply curved, such as the surface of a small droplet, the partial pressure required to maintain mass equilibrium is greater than that for a flat surface. The curvature of the surface modifies slightly the attractive forces between surface molecules, so that the smaller the droplet, the easier it is for molecules to leave the droplet surface. To prevent this evaporation-that is, to maintain mass equilibrium- the partial pressure of vapor surrounding the droplet must be greater than ps.

For pure liquids, the relationship between the saturation ratio required for equilibrium (no growth or evaporation), called the Kelvin ratio Kr, and the droplet size is given the Kelvin equation

$$Kr = pd/ps = \exp(4\gamma M/\rho RTd)$$

γ =surface tension

M=molecular weight

$$P/P_0 = \exp[2\gamma(\mathrm{MW})/r\rho RT].$$

P=density

of the droplet liquid

D=Kelvin diameter, the diameter of the droplet that will neither grow nor evaporate when the partial pressure of vapor at the droplet surface is pd

This equation defines a specific saturation ratio required to mantain mass equilibrium for a given particle size d

WdV forces = $1/R^6$

(Hinds, 1999)

Gas-particle partitioning

Gas-particle partitioning of organics

Absorption into the aerosol organic matter

$$K_P = \frac{F/TSP}{A}$$

F (ng/m³) is the particulate-associated concentration of org
TSP is the concentration of the total suspended particulate (µg/m³)
A (ng/m³) is the gas-phase concentration of org

Ideal conditions: fi=pi

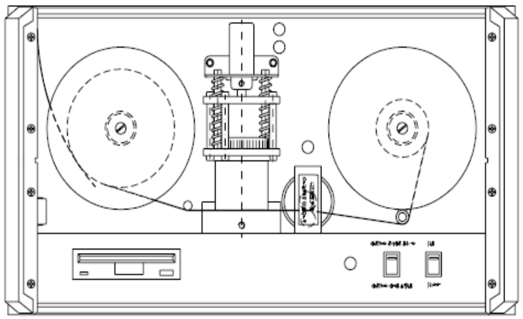
$$f_{i,g} = f_{i,om} \qquad f_{i,om} = \chi_{i,om}\gamma_{om}p^0_{L,i} \qquad \frac{n_{i,g}}{V}(mol\,i/m^3) = \frac{p_i}{760RT}$$

$$K_P = \frac{f_{om}\,760RT}{MW_{om}\,p^0_L\,\gamma_{om}\,10^6}$$

$$\propto \frac{\text{fraction of organic matter}}{MW_{\text{org phase}},\ \text{vapor pressure, activity}}$$

(Pankow, Atm Environ 1994)

Aethalometers measure the light attenuation through a quartz filter matrix where the fiber filter is assumed to act as a perfect diffuse scattering matrix in which the light-absorbing particles are embedded.



The absorption coeffcient (b_{abs}) is defined with Beer–Lambert's law

$$I = I_0\, e^{-b_{abs} \cdot x},$$

Absorption coefficient (m^{-1})

where I_0 is the intensity of the incoming light and I the remaining light intensity after passing through a medium with the thickness x. The attenuation (ATN) is typically given as percentage values and is defined by the relationship

$$\mathrm{ATN} \equiv \ln\left(\frac{I_0}{I}\right)$$

According to the Beer–Lambert's law, the aerosol absorption coefficient of the filtered aerosol particles bATN (or attenuation coefficient) is defined as

$$b_{\mathrm{ATN}} \equiv \frac{A}{Q}\frac{\Delta \mathrm{ATN}}{\Delta t},$$

Attenuation coefficient (m^{-1}) of the system composed by filter and particles is measured

where A is the filter spot area (m2), Q the volumetric flow rate (m3/s)and ΔATN is the change in attenuation during the time interval Δt.It is well known that b_{ATN} may differ significantly from the true aerosol absorption coeffcient b_{abs} of airborne particles. Therefore, the calibration factors C and R(ATN) are introduced, which can be used to convert aethalometer attenuation measurements to "real" absorption coefficients:

$$b_{\mathrm{abs}} = b_{\mathrm{ATN}} \frac{1}{C \cdot R(\mathrm{ATN})},$$

C and R describe the two effects which change the optical properties of filter embedded particles with respect to the properties of the same particles in the airborne state

C = is greater than unity and is caused by multiple scattering of the light beam at the filter fibers in the unloaded filter. This leads to an enhancement of the optical path and thus to enhanced light absorption of the deposited particles. C depends on the λ. It was experimentally determined during smog chamber studies a C = 2.14± 0.21

R(ATN) = varies with (a) the amount of aerosol particles embedded in the filter and (b) optical properties of the deposited particles. For unloaded filters R is set to unity, i.e. R(ATN = 0) = 1. With the gradual increase in attenuation due to the accumulating particles in the filter the absorbing particles in the filter absorb a higher fraction of the scattered light which leads to a reduction of the optical path in the filter (R¡1). As a consequence, generally lower attenuation coefficients are measured for higher filter loadings than for lightly loaded filters (Shadowing effect)

The aerosol black carbon mass concentration M_{BC} (gm^{-3}) is related to the absorption and attenuation coefficients by

$$M_{\mathrm{BC}} = \frac{b_{\mathrm{abs}}}{\sigma_{\mathrm{abs}}} = \frac{b_{\mathrm{ATN}}}{\sigma_{\mathrm{ATN}} \cdot R(\mathrm{ATN})},$$

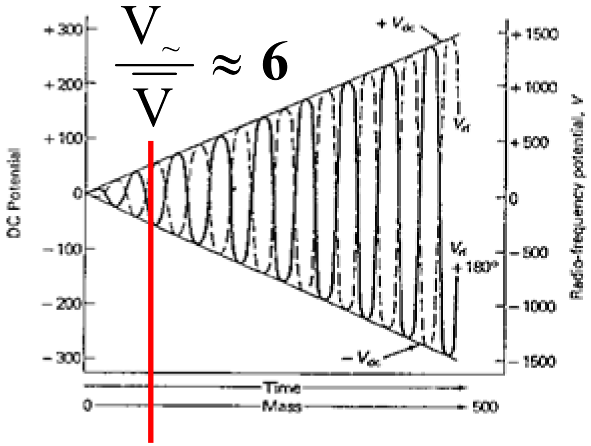
where σ_{abs} and $\sigma_{ATN} \equiv \sigma_{abs} \cdot C$ are the mass specific absorption and attenuation cross-sections (m2 g−1), respectively. σ_{ATN} strongly depends on the aerosol type and age. They depend on λ.

$\sigma_{ATN} \equiv \sigma_{abs} \cdot C$ *Mass specific attenuation cross-sections (m^2/g). σ_{ATN} (λ=880 nm)=16.6 m^2/g (this value is given by the manual)*

b_{ATN} and σ_{ATN} relate light attenuation to BC mass in the case of filter based measurement method while b_{abs} and σ_{abs} are used for suspended particle in the air

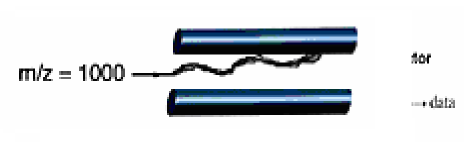
Q vs ToF Spectrometers – Time resolution

Q



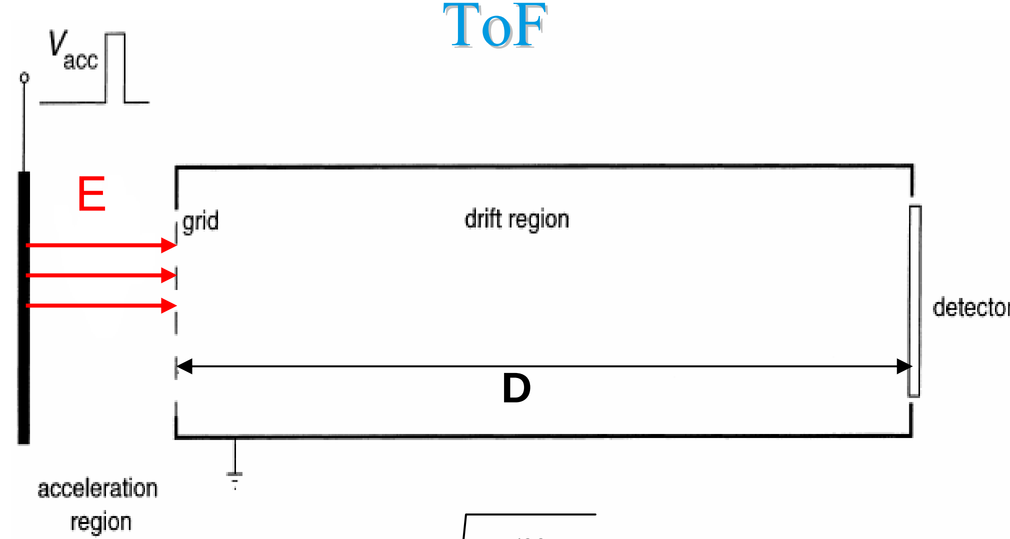
$$\frac{V_{\sim}}{\overline{V}} \approx 6$$

m/z=100

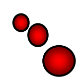


A MASS SPECTRUM IS SCANNED OVER A MASS RANGE OF m/z 1-300 WITHIN 300ms

ToF



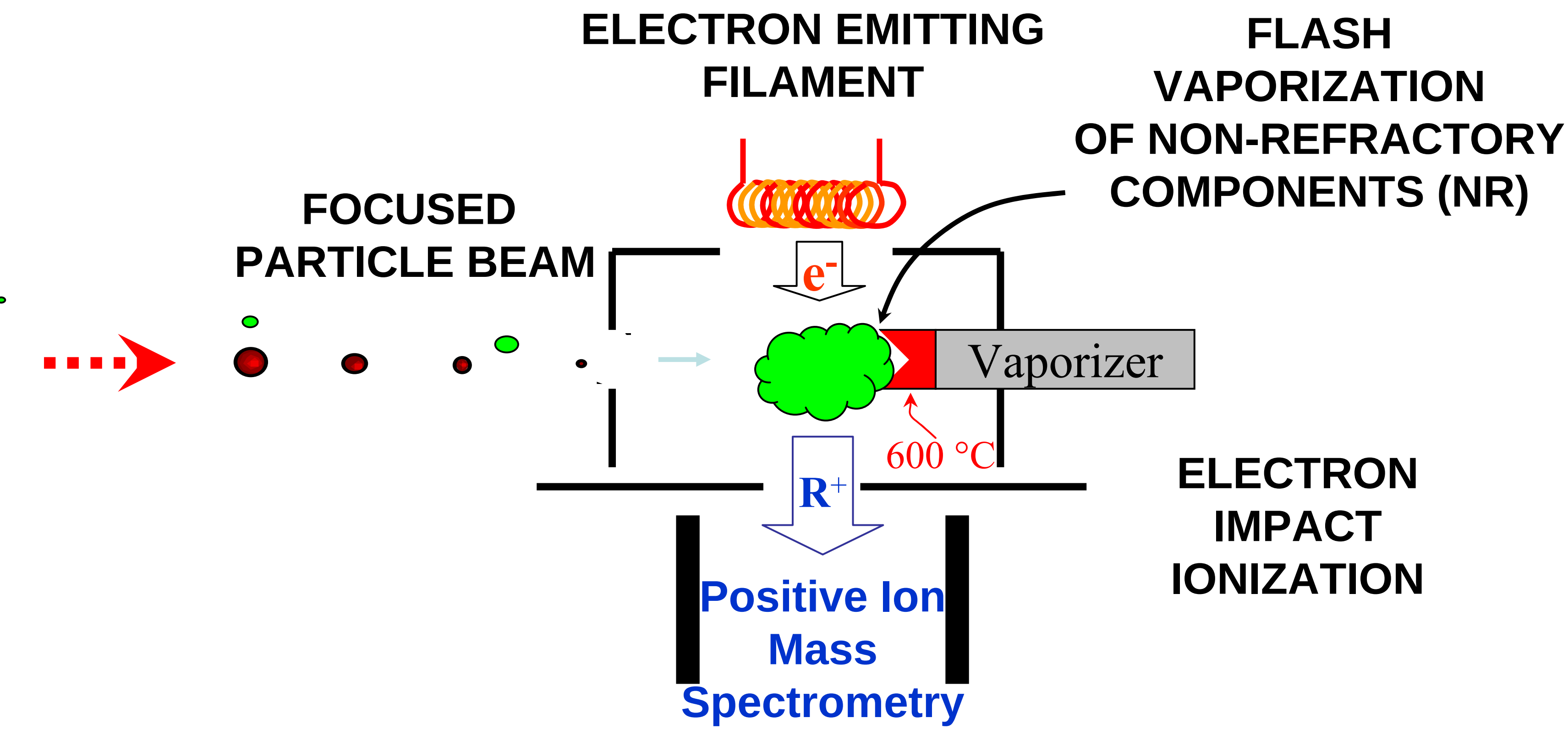
$$t = D\sqrt{\frac{m}{2zeEs}}$$



A COMPLETE MASS SPECTRUM IS ACQUIRED EVERY 12 µs

Shorter averaging time for representative particle counting statistics

Evaporation/ionization chamber



UNIVERSAL AND QUANTITATIVE CHEMICAL ANALYSIS

The term <u>'non-refractory'</u> (NR) is defined operationally as those species that evaporate rapidly (<5 s) at the AMS temperature and vacuum conditions. (Allan, 2004)

<u>'non-refractory'</u>=less than ~1 ms (when on time-of-flight mode) ;~1 s (when on mass spectrum mode) (Jimenez, 2003)

MS Signatures for Aerosol Species Identification

Group	Molecule/Species		Ion Fragments	Mass Fragments
Water	H_2O	$\xrightarrow{e^-}$	H_2O^+ , HO^+ , O^+	18, 17, 16
Ammonium	NH_3	$\xrightarrow{e^-}$	NH_3^+, NH_2^+, NH^+	17, 16, 15
Nitrate	HNO_3	$\xrightarrow{e^-}$	HNO_3^+, NO_2^+, NO^+	63, 46, 30
Sulfate	H_2SO_4	$\xrightarrow{e^-}$	$H_2SO_4^+$, HSO_3^+, SO_3+	98, 81, 80
			SO_2^+, SO^+	64, 48
Organic *(Oxygenated)*	$C_nH_mO_y$	$\xrightarrow{e^-}$	H_2O^+, CO^+, CO_2^+ $H_3C_2O^+$, HCO_2^+, $C_{n'}H_{m'}^+$	18, 28, 44 43, 45, ...
Organic *(hydrocarbon)*	C_nH_m	$\xrightarrow{e^-}$	$C_{n'}H_{m'}^+$	27,29,41,43,55,57,69,71...

Standard electron impact ionization @ 70 eV

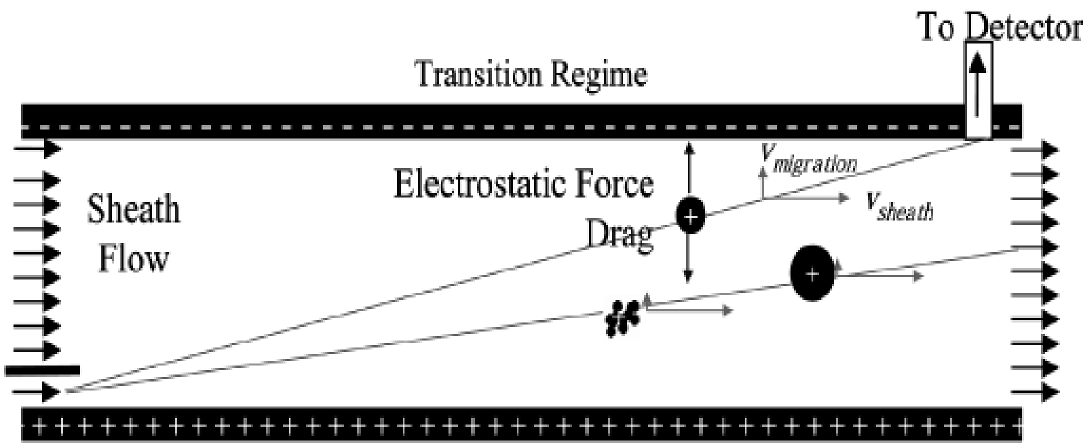
Easy to quantify

Comparable to the NIST MS library

Easy to separate inorganic and organic components

Speciation of organic composition is challenging

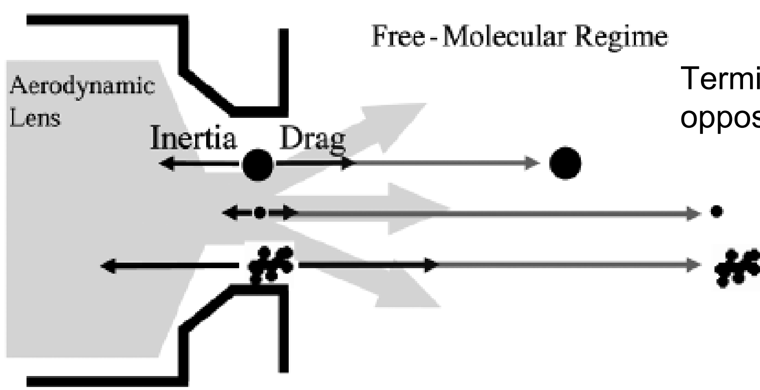
dm vs dva



(a)

$$Z_p = \frac{neC_c(d_{ve})}{3\pi\eta\chi_t d_{ve}} = \frac{neC_c(d_m)}{3\pi\eta d_m}. \qquad [24]$$

$$\frac{d_m}{C_c(d_m)} = \frac{d_{ve}\cdot\chi_t}{C_c(d_{ve})}. \qquad [25]$$



(b)

$$F_G = m_p g = \rho_p \frac{\pi}{6} d_{ve}^3 g = \frac{3\pi\eta v_{TS} d_{ve}\chi}{C_c(d_{ve})} = F_{drag}.$$

Terminal velocity is obtained when the gravitational force (*FG*) is equal and opposite to the drag force

$$d_{ca} = d_{ve}\sqrt{\frac{\rho_p}{\rho_0\chi_c}}.$$ *Continuum Regime Aerodynamic Diameter*

$$d_{va} = \frac{\rho_p}{\rho_0}\frac{d_{ve}}{\chi_v}.$$ *Vacuum Aerodynamic Diameter*

$$\frac{\frac{d_{va}\chi_v\chi_t\rho_0}{\rho_p}}{C_c\left(\frac{d_{va}\chi_v\rho_0}{\rho_p}\right)} = \frac{d_m}{C_c(d_m)}.$$

for irregular particles of
standard density, *dm > dve > da*

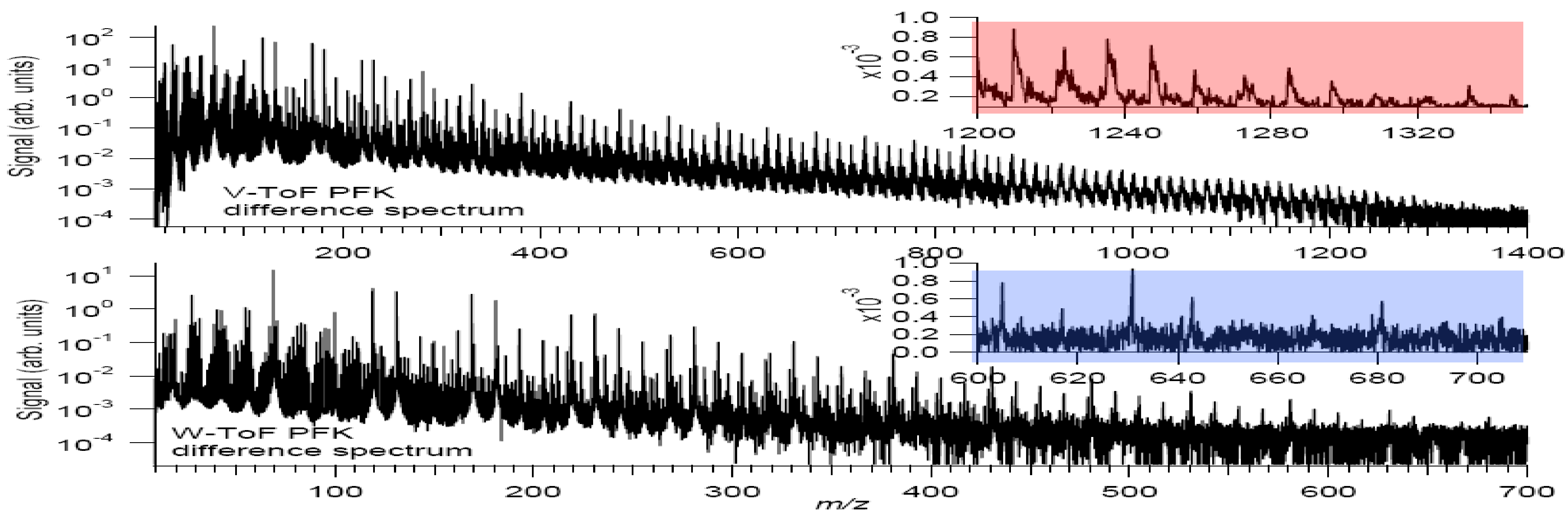
Sensitivity

The V-Mode data show detectable signal up to

m/z 1300

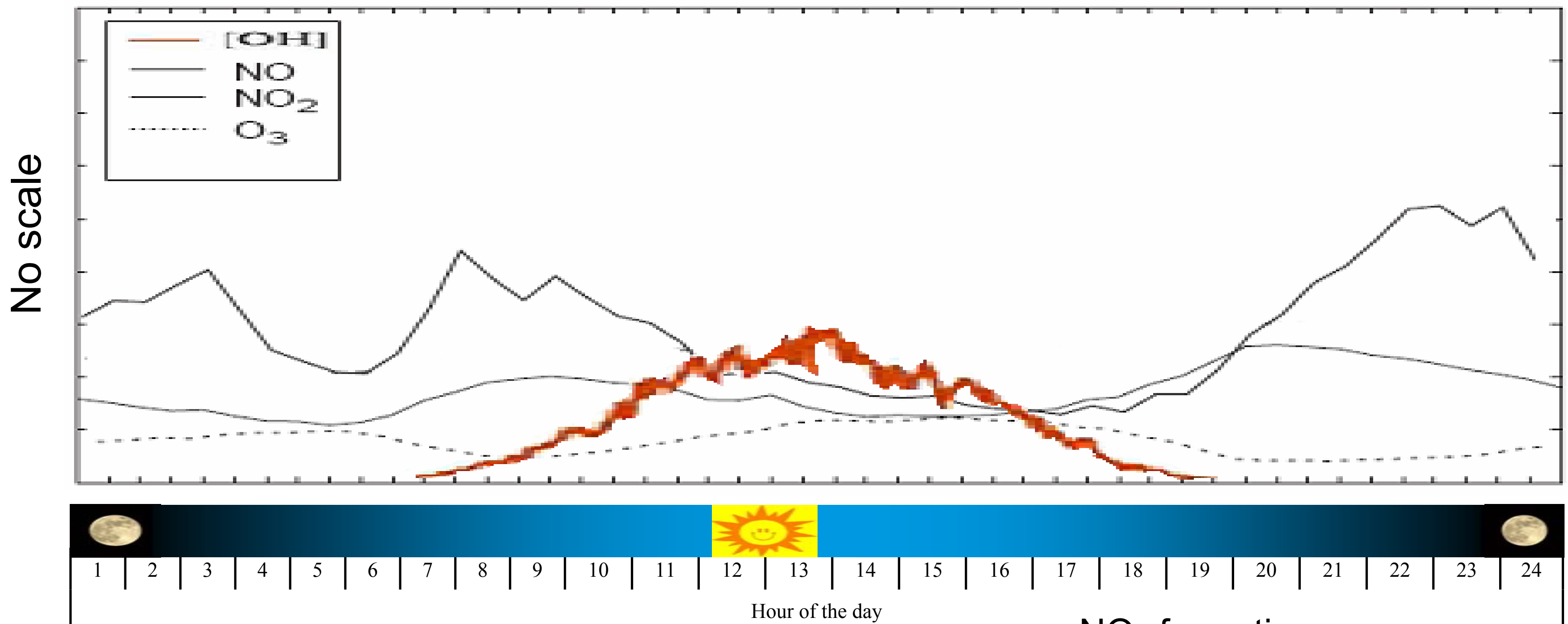
The lower sensitivity of W-mode results in detectable signal up to

m/z 700



(De Carlo et al., 2006)

Oxidant concentrations and diurnal variation



Oxidant concentrations in urban areas

O_3 conc = 80-150 ppb

NO_X conc = 30-80 µg/m^3

(Milano 150 µg/m^3)

NO_3 conc = 1×10^{10} molecules/cm^3 (nighttime)

OH conc =5-10$\times10^6$ molecules/cm^3

(summertime)

(Arey et al., 1989; Reisen and Arey, 2005; EEA, 2006)

NO_3 formation

$$\cdot NO2 + O3 \rightarrow \cdot NO3 + O2$$

Rate constant(298 K)=1.8*10-14 cm3/molecules sec

OH formation

$$O3 + h\nu\ (\lambda<320\ nm) \rightarrow O2\ (1\Delta g) + O\ (1D)$$

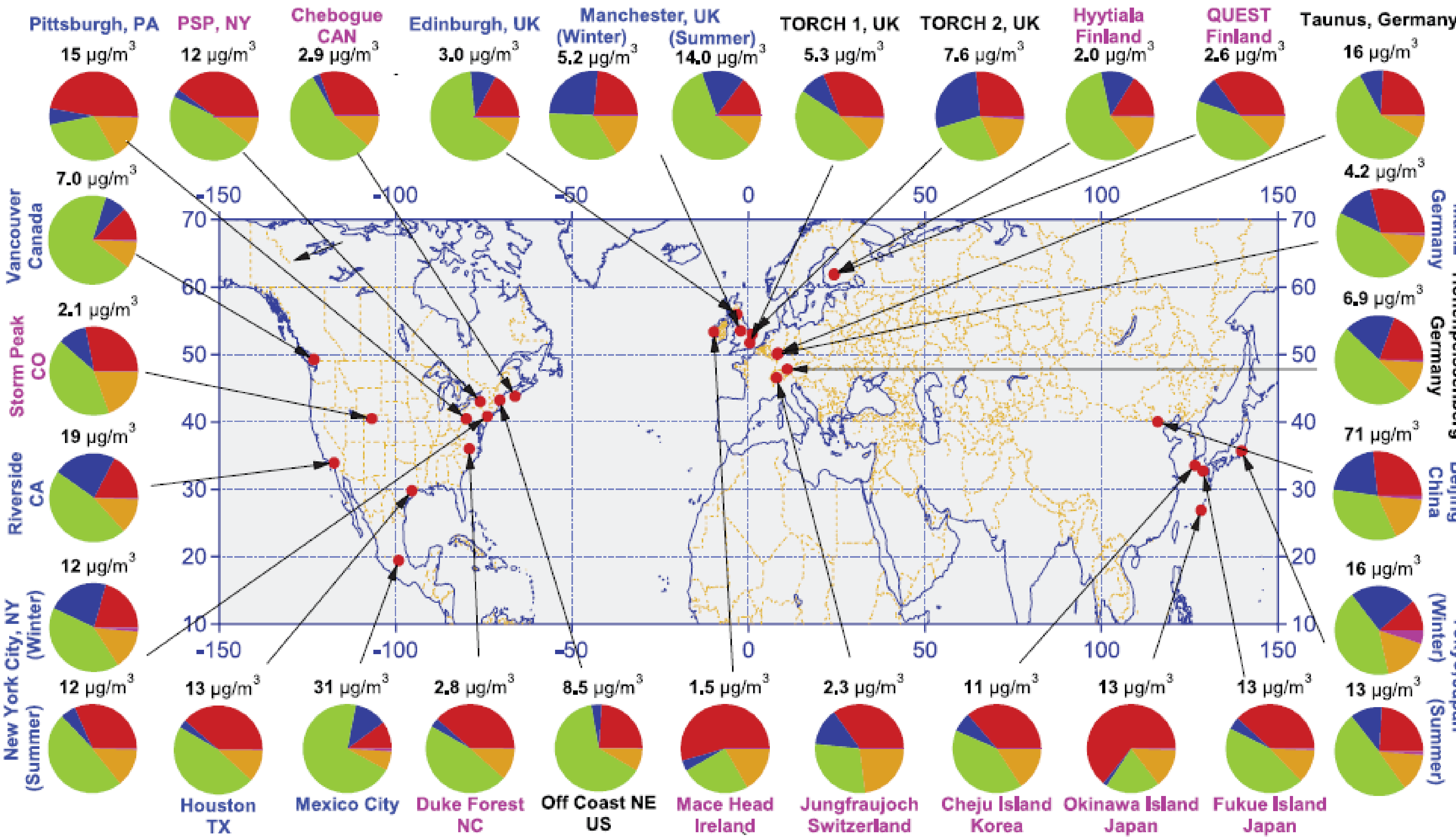
$$O\ (1D) + H2O \rightarrow 2\ \cdot OH$$

O_3 formation

$$\cdot NO_2 + h\nu\ (\lambda<420\ nm) \xrightarrow{J_1} \cdot NO + O\ (^3P)$$

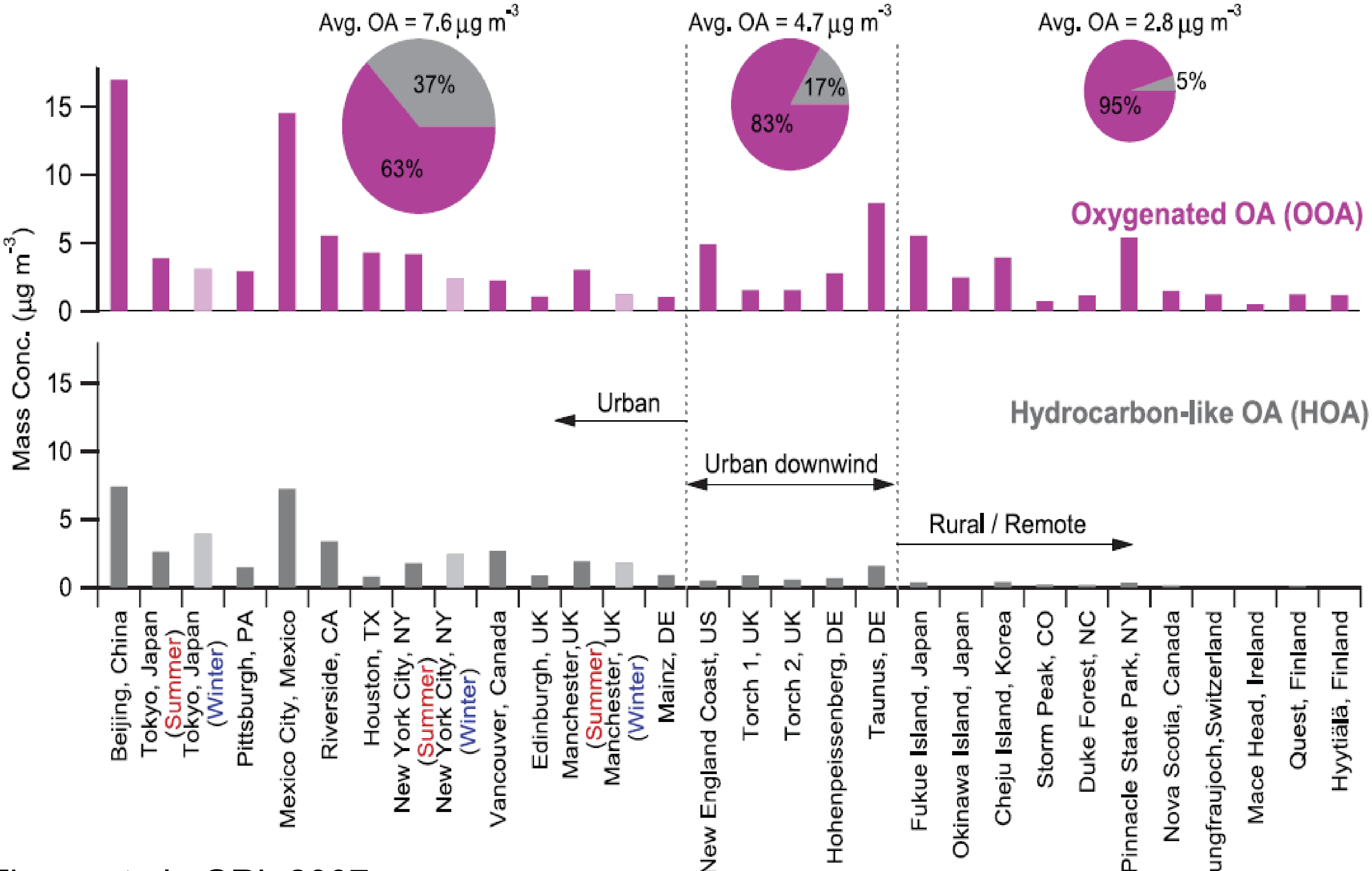
$$O_2 + O\ (^3P) + M \xrightarrow{K_2} O_3 + M\ \ (M = N_2, O_2).$$

Worldwide AMS measurements show the abundance of organics in the atmospheric aerosol



Zhang et al., GRL 2007

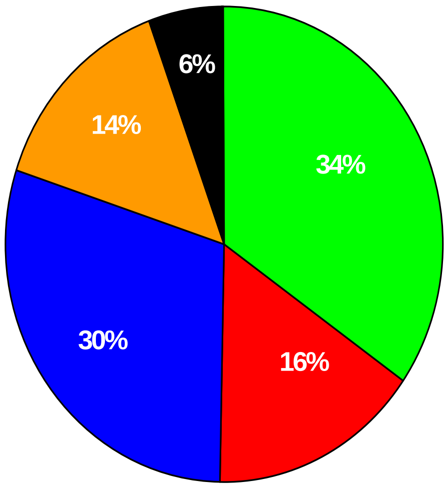
Worldwide AMS measurements show the abundance of organics in the atmospheric aerosol



Zhang et al., GRL 2007

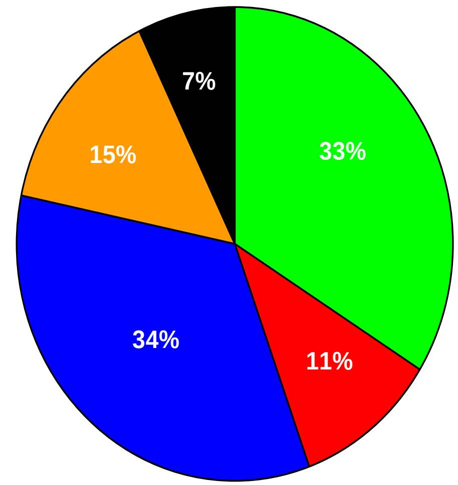
Fractions of BC, OM, NO3, SO4 and NH4 and fossil and non-fossil contribution to EC and OC

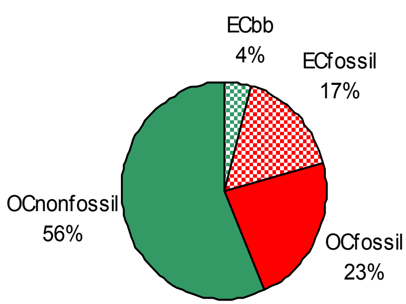
Zürich



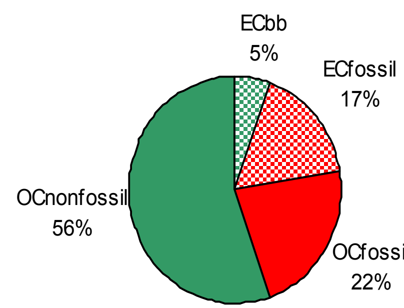
Black Carbon
Organic mass
Nitrate
Sulfate
Ammonium

Reiden





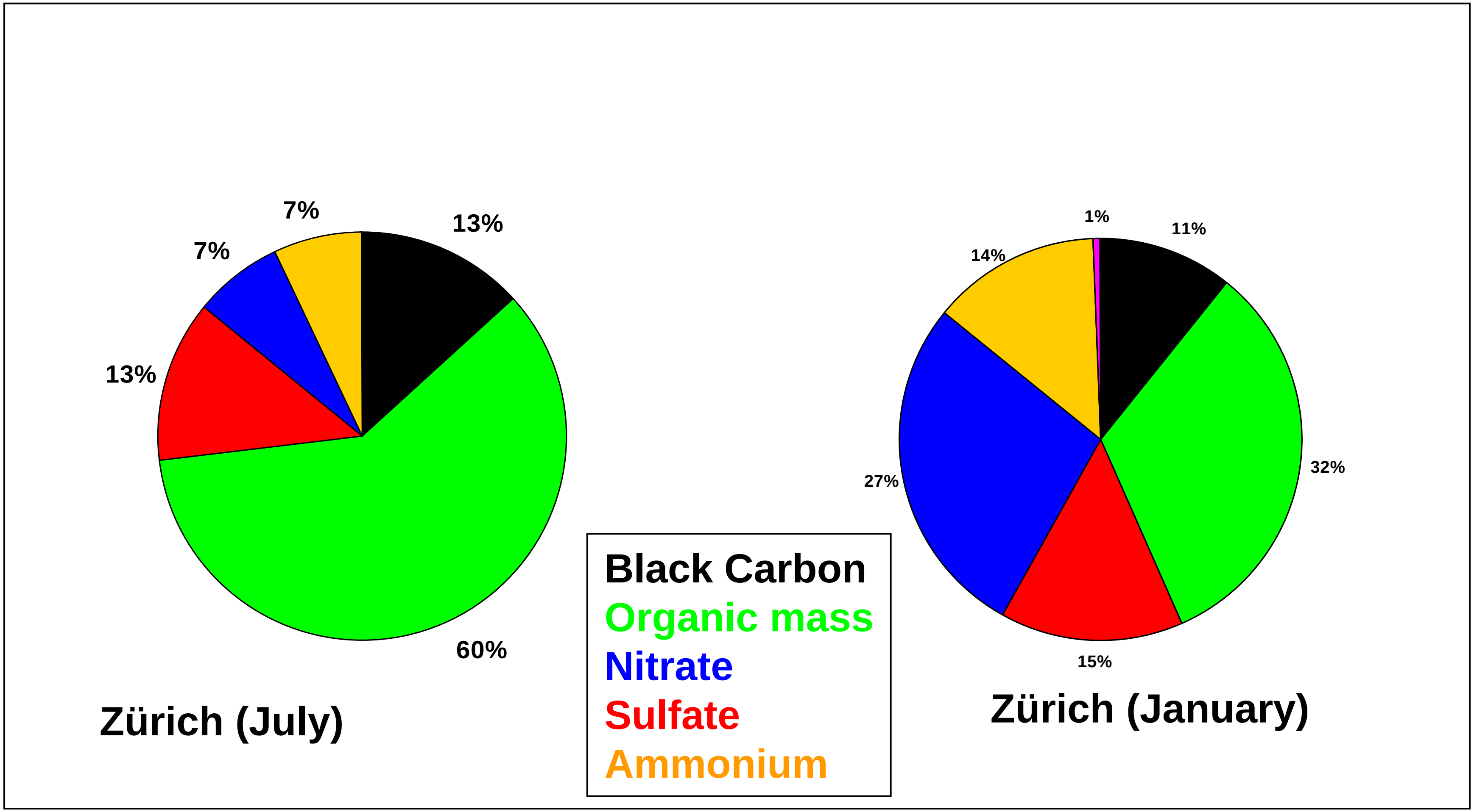
Urban background



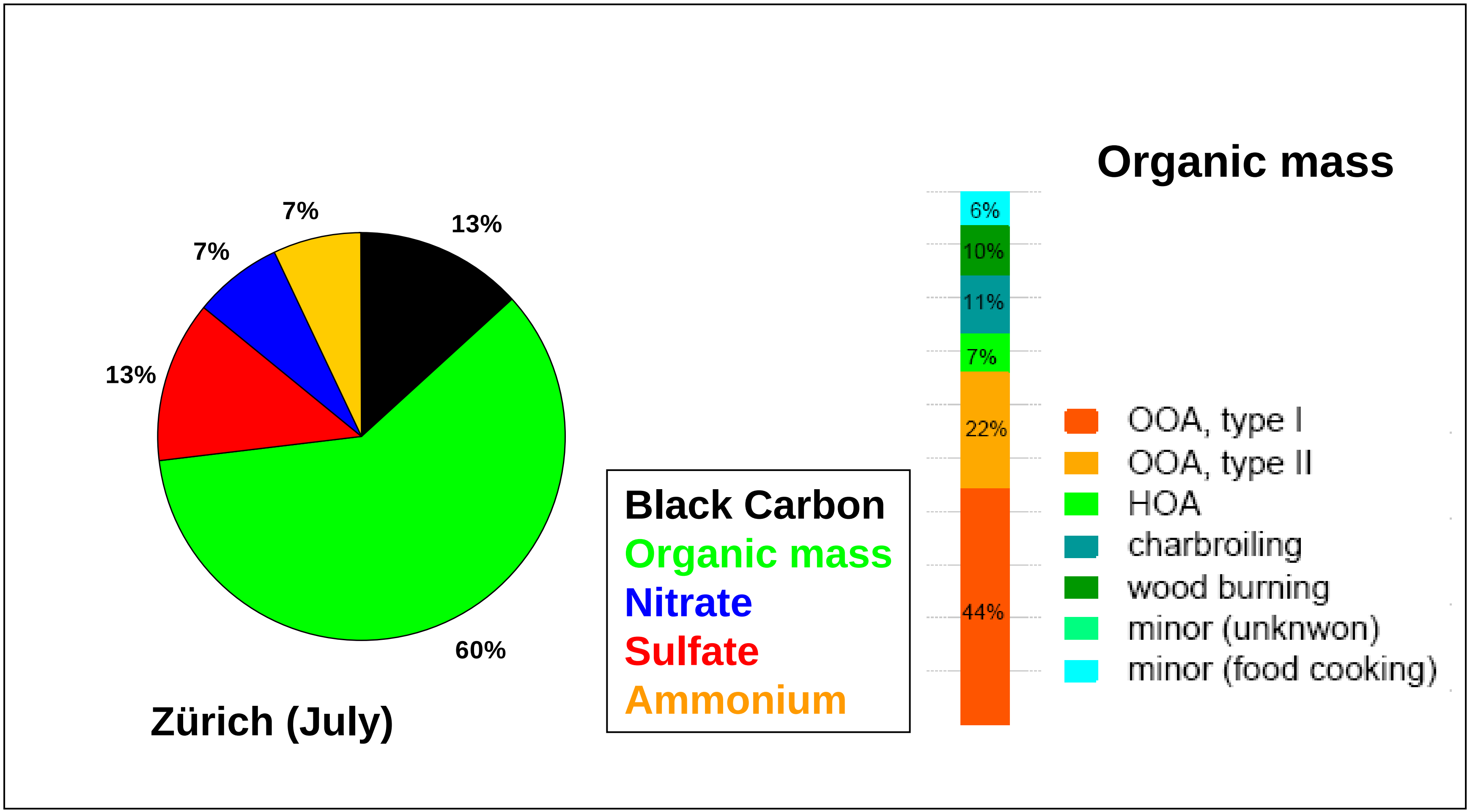
Highway/rural

Nearly identical composition

Average composition in Zürich in summer and winter



Chemical composition in Zürich summer and



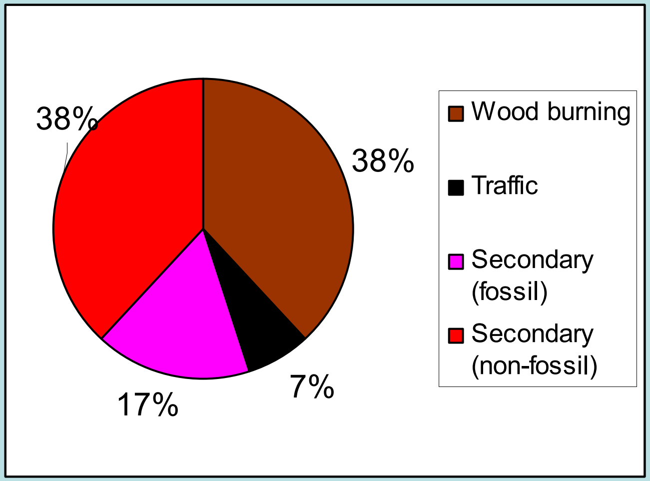
Lanz et al., ACP (2007)

OOA: Secondary organic aerosol

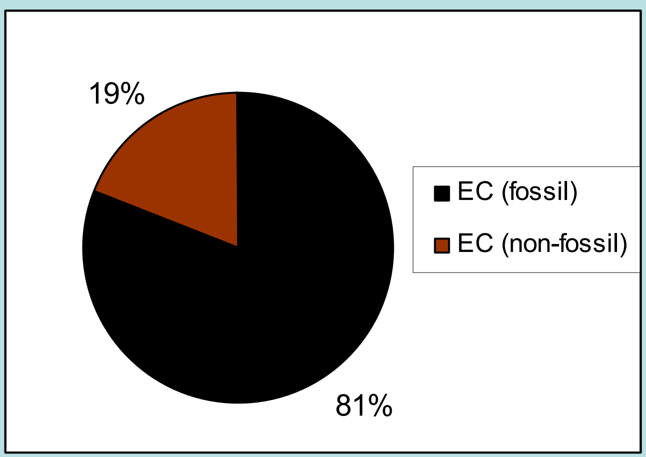
HOA: mostly traffic

Carbon apportionment using 14C analysis
Estimation of fossil and non-fossil SOA contribution

OM



EC



Use of AMS analysis :

- wood burning 38%

- HOA 7%

Assumptions :

- only SOA, HOA and wood burning present

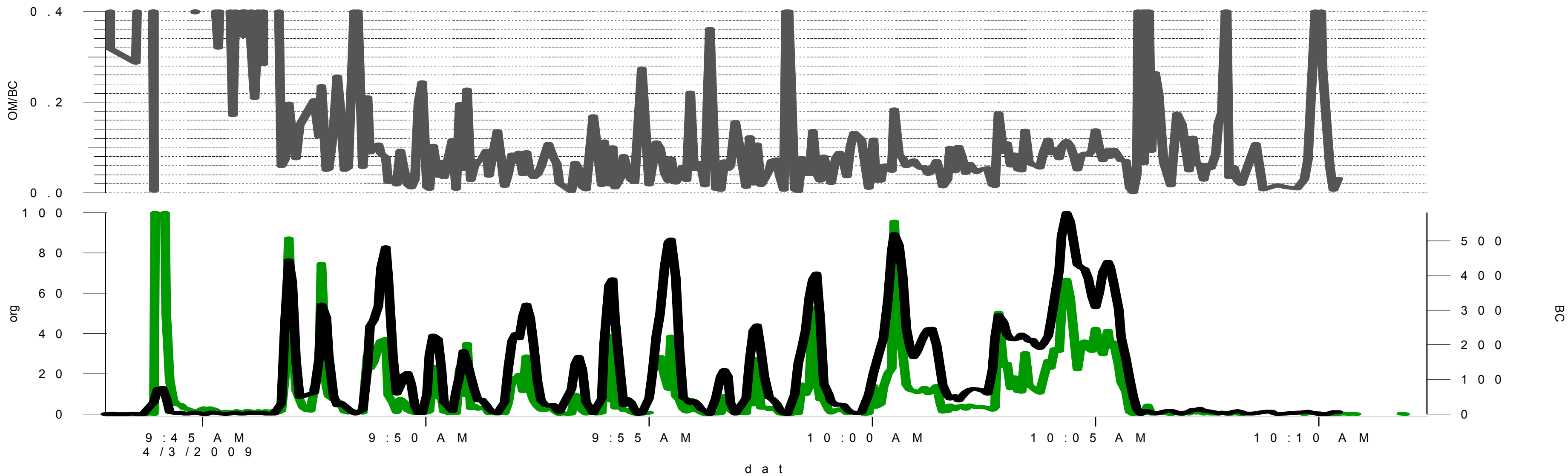
- OM/OC=2 for wood burning and SOA and OM/OC=1.2 for HOA

- RESULT : SOAnonfossil: 69% SOAfossil: 31%

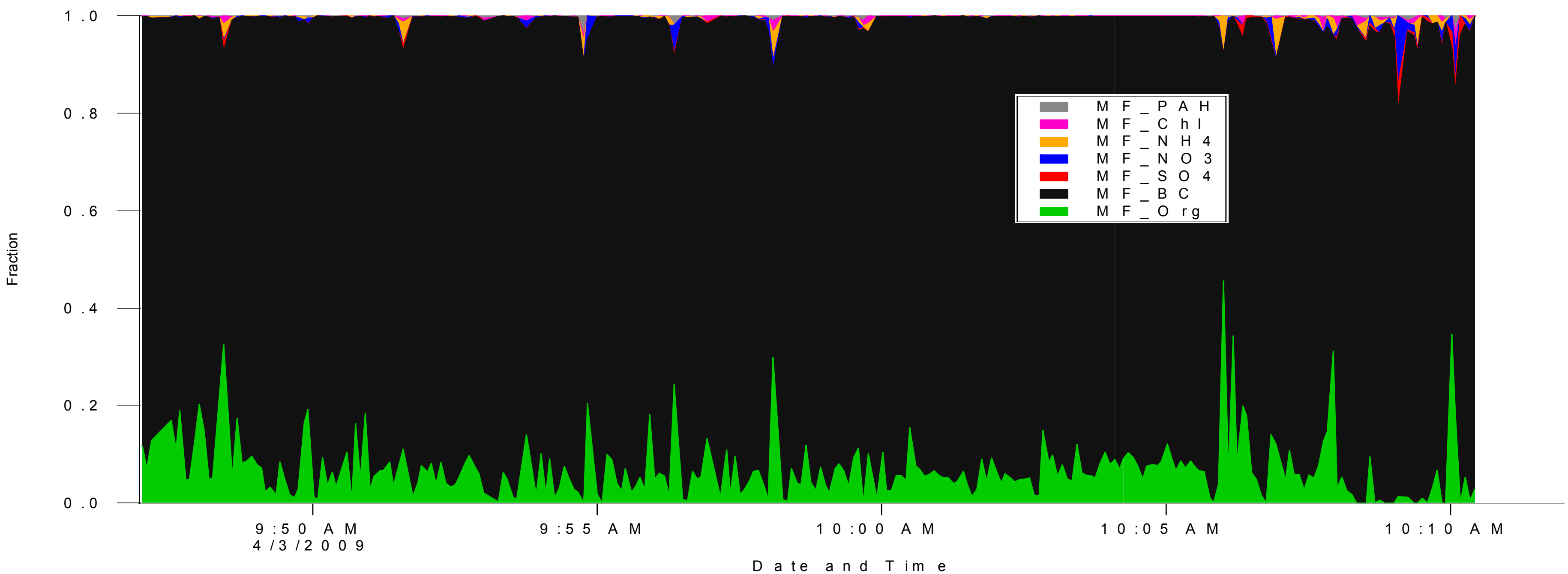
Inorganics-S.C.

60 km/h					
date_60	OM/BC	CO/NOx	CO/CO2	OM/(BC*CO2)	NO/NOx
110408	**0.413**	0.254652	0.00050322	0.004945473	0.982716109
71108	**0.397**	0.025746	0.00010761	0.005113857	0.899252778
211108	**0.18**	0.012236	3.1328E-05	0.00149138	0.922717961
70109	0.201	0.044092	0.00010491	0.001052584	0.938656715
90408	**1.2612**	0.691773	0.00152673	0.019011913	0.954776135
51108	**0.5089**		0.00078636		
Idle					
date_idle	OM/BC_idle	CO/Nox_idle	CO/CO2_idle	OM/(BC*CO2)_idle	NO/NOx_idle
100308	0.176	0.275182	0.00271439	0.003667389	0.900077229
40408	0.304	0.249277	0.00247813	0.00452191	0.904475671
171108	0.102	0.232615	0.00248073	0.002273959	0.940398773

HDDV

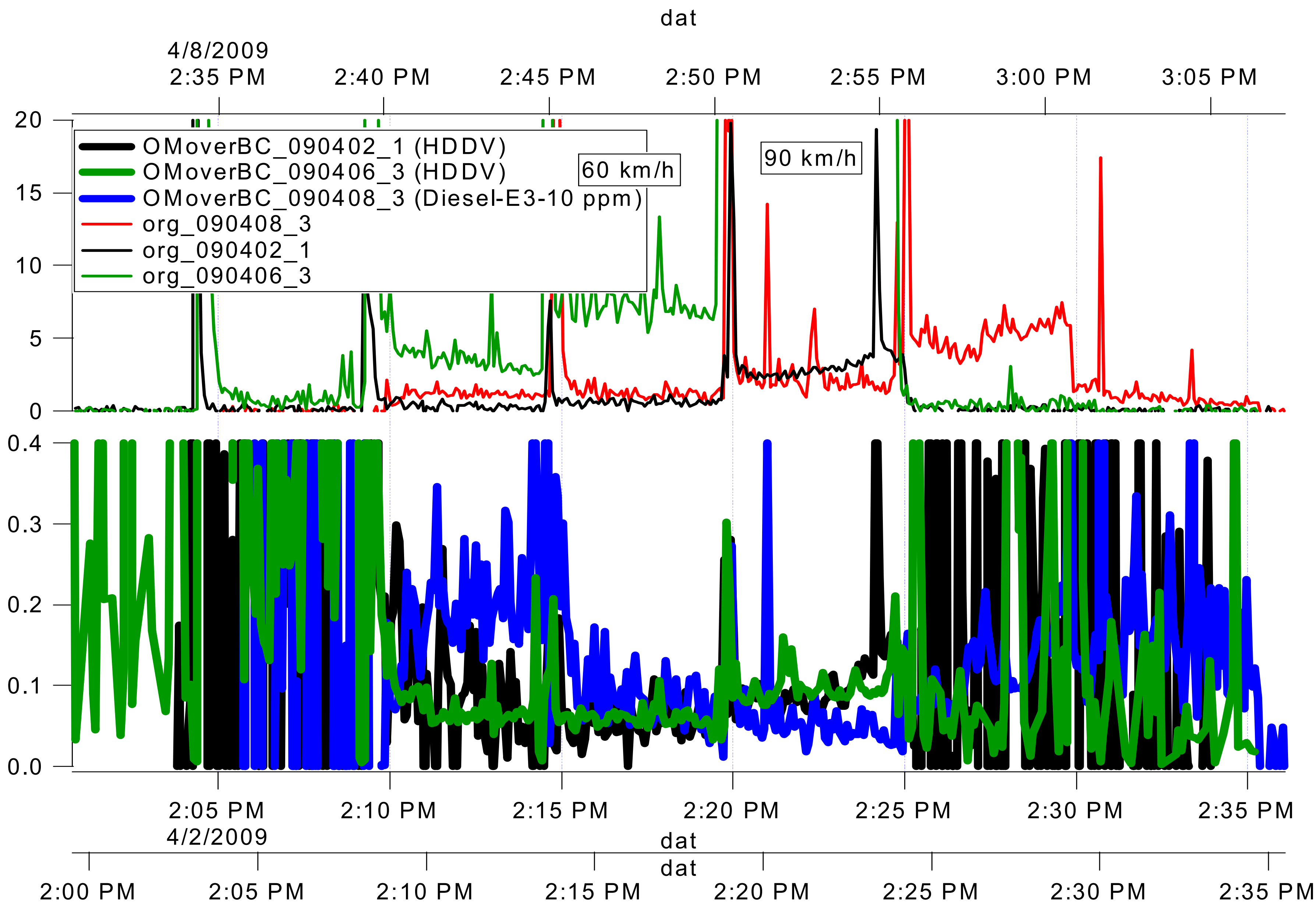


0 .4
0 .2
0 .0
OM/BC
1 0 0
8 0
6 0
4 0
2 0
0
org
5 0 0
4 0 0
3 0 0
2 0 0
1 0 0
0
BC
9 :4 5 A M
4 /3 /2 0 0 9
9 : 5 0 A M
9 : 5 5 A M
1 0 : 0 0 A M
1 0 : 0 5 A M
1 0 : 1 0 A M
d a t



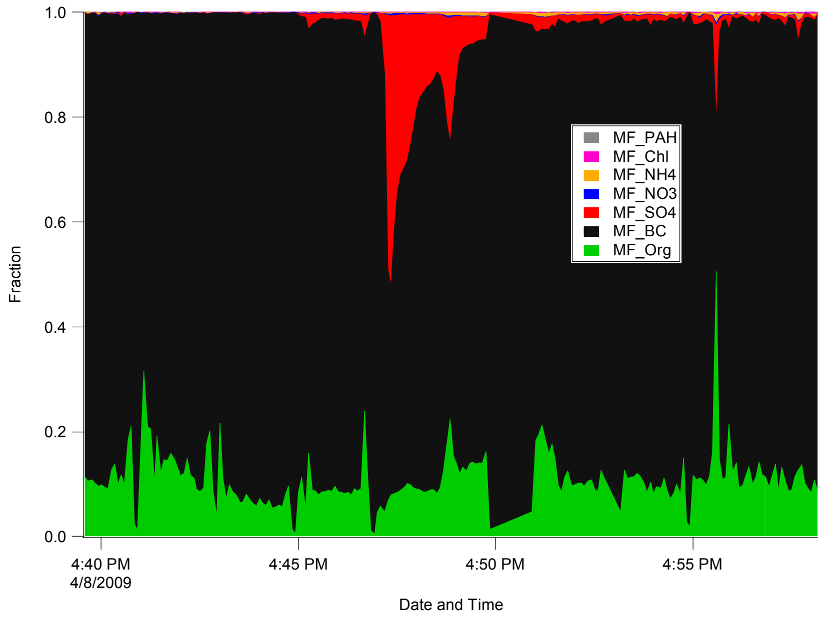
1 .0
0 .8
0 .6
0 .4
0 .2
0 .0
Fraction
M F _ P A H
M F _ C h l
M F _ N H 4
M F _ N O 3
M F _ S O 4
M F _ B C
M F _ O rg
9 : 5 0 A M
4 /3 /2 0 0 9
9 : 5 5 A M
1 0 : 0 0 A M
1 0 : 0 5 A M
1 0 : 1 0 A M
D a te a n d T im e

HDDV vs Diesel E3 passenger car

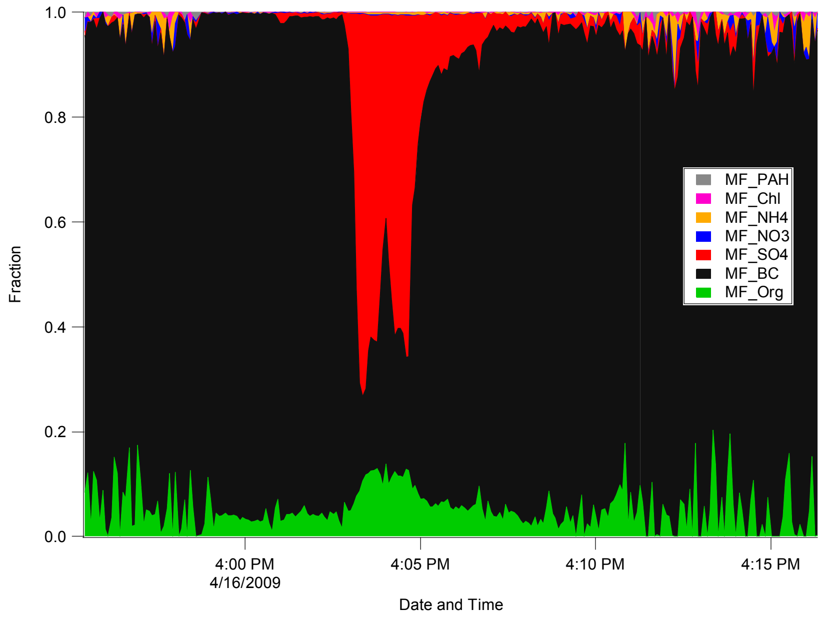


DPM composition

Diesel Euro 3



Diesel Euro 4



E4 gasoline car