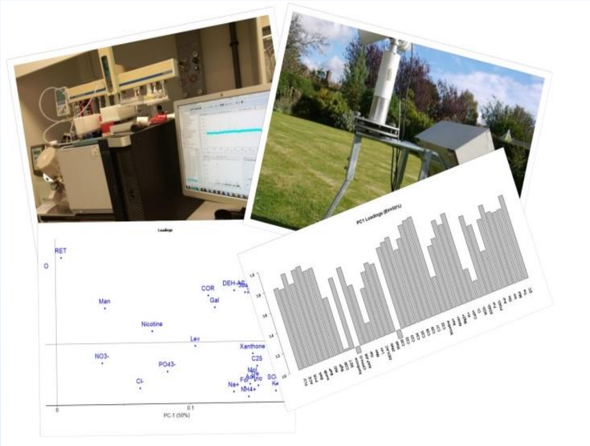
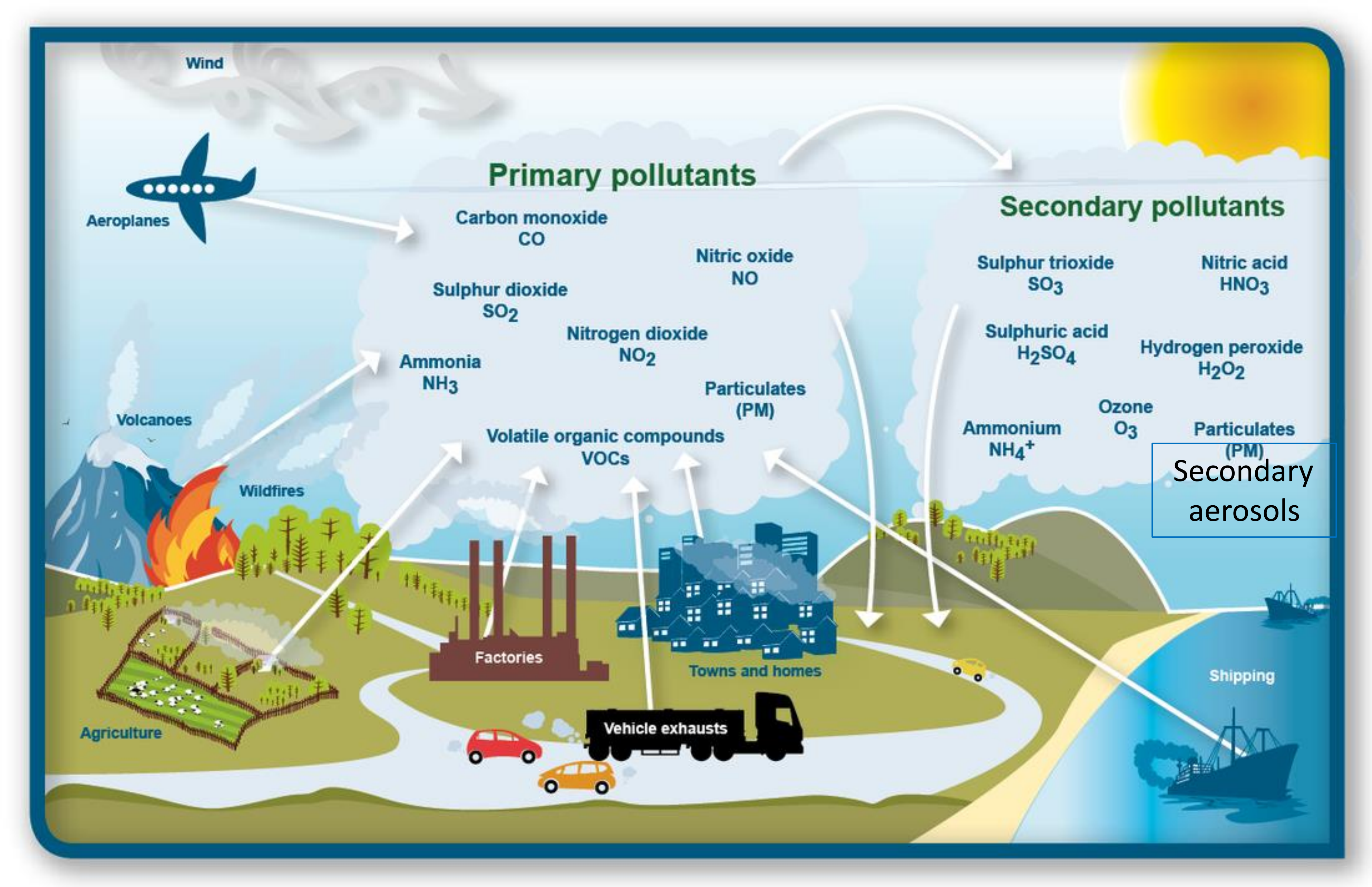


Aerosol properties, dynamics, chemistry and microphysics

Dr. Olga Popovicheva

Moscow State University , Moscow

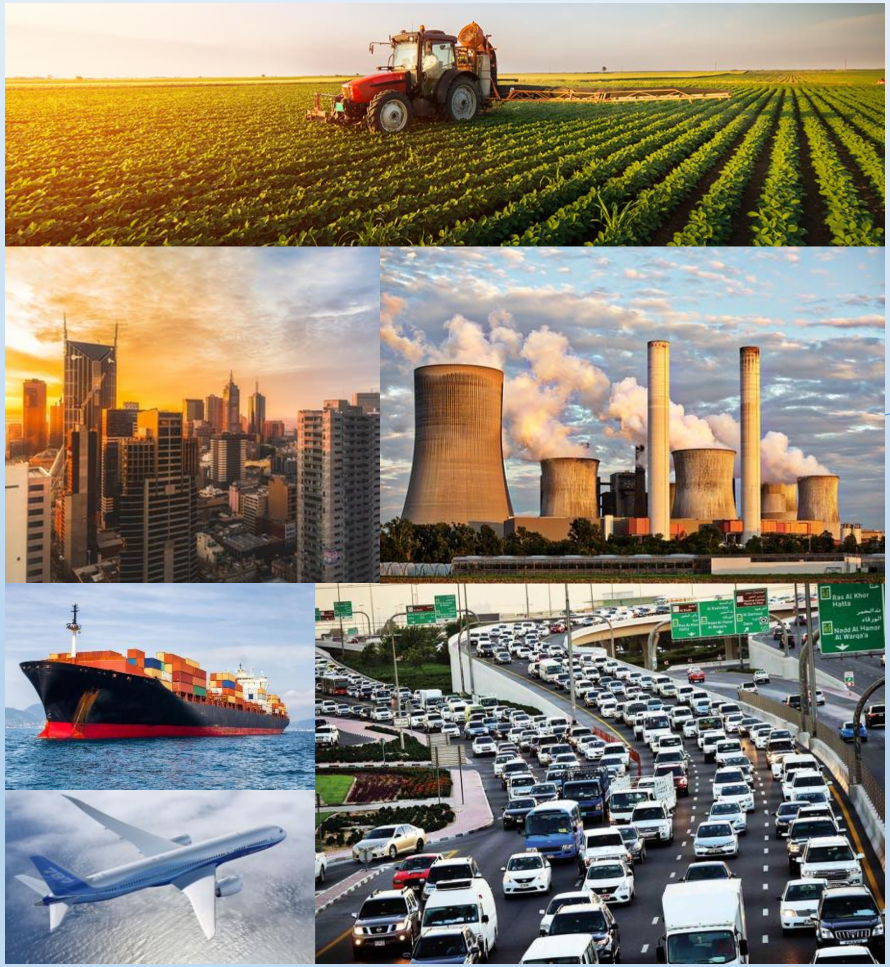
Primary and secondary pollutants in atmosphere



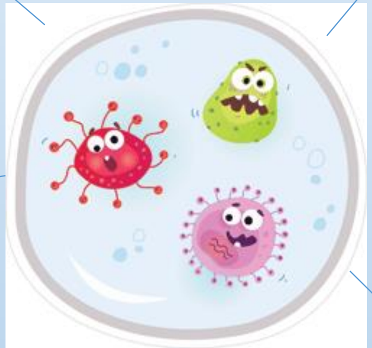
AEROSOL SOURCE

ANTROPHOGENIC SOURCES

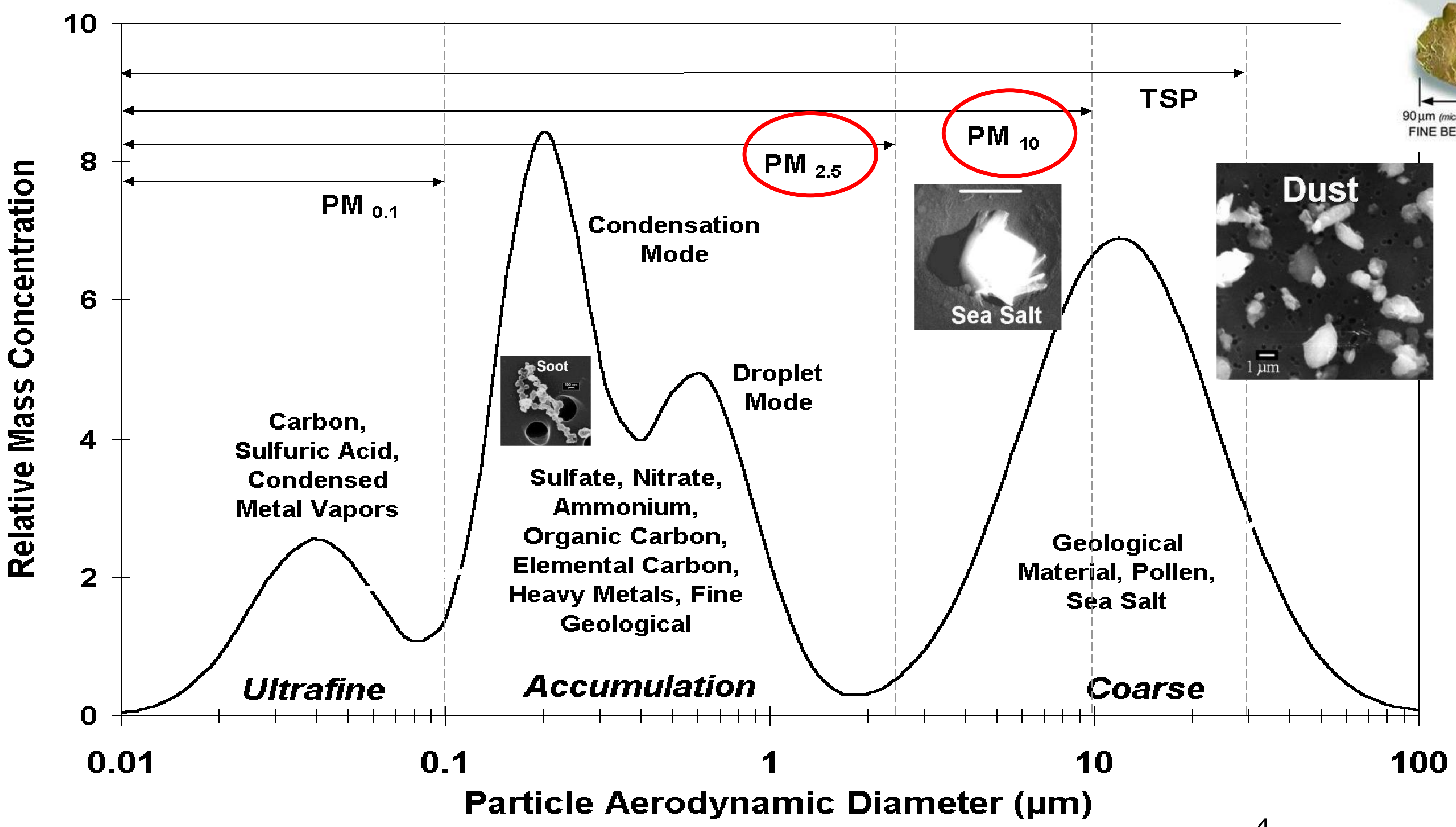
NATURAL sources

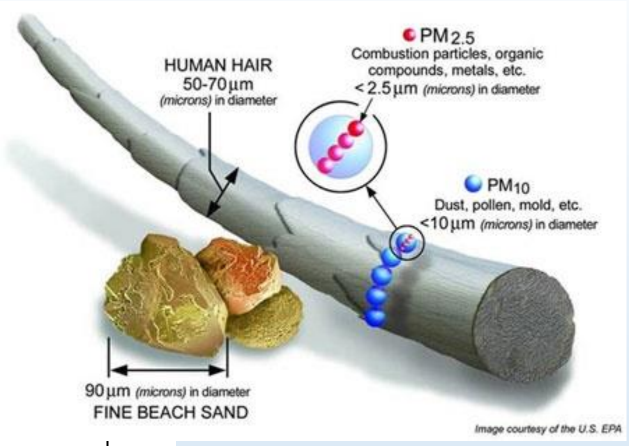


mixed aerosol

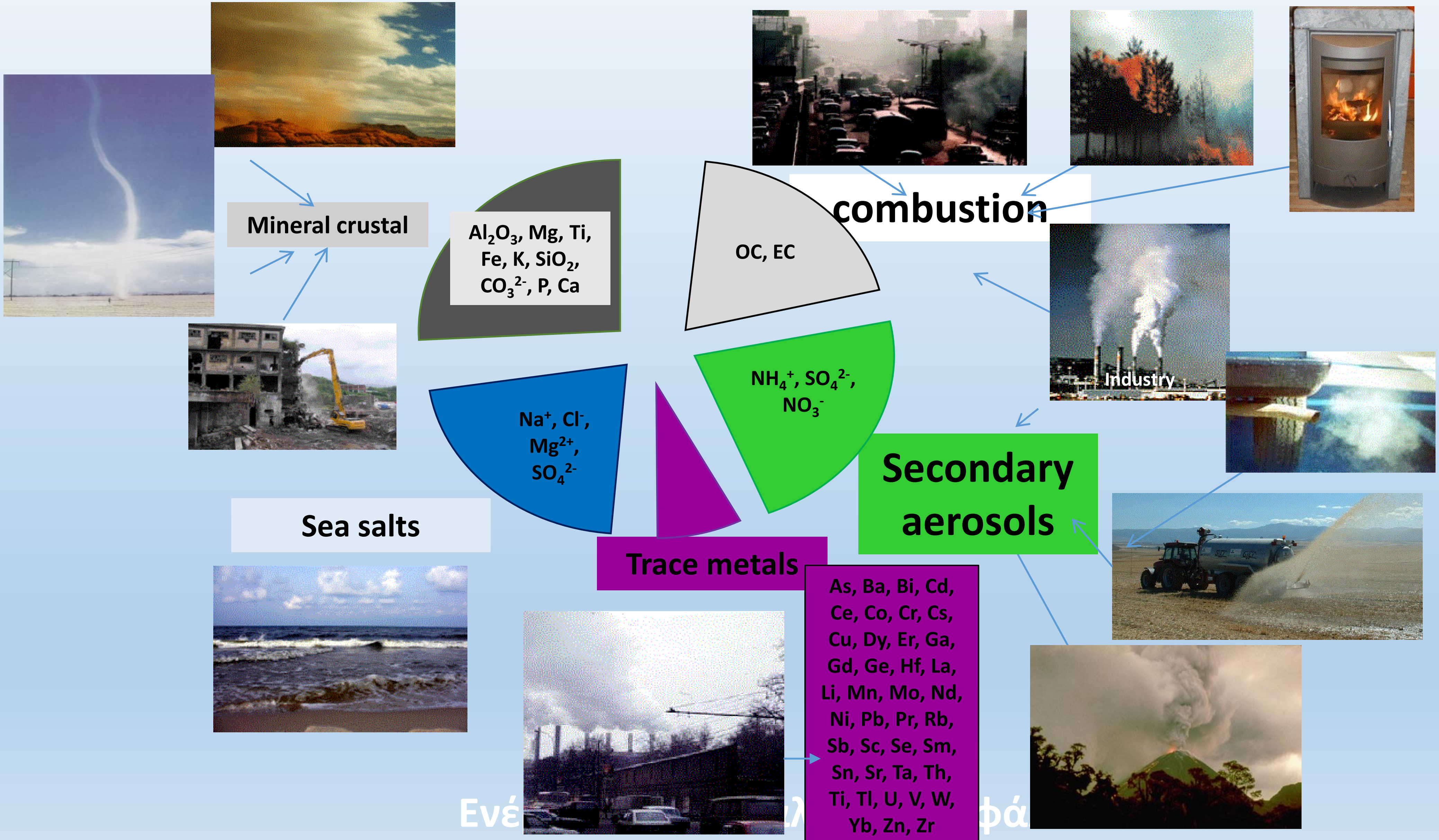


Aerosol size distribution

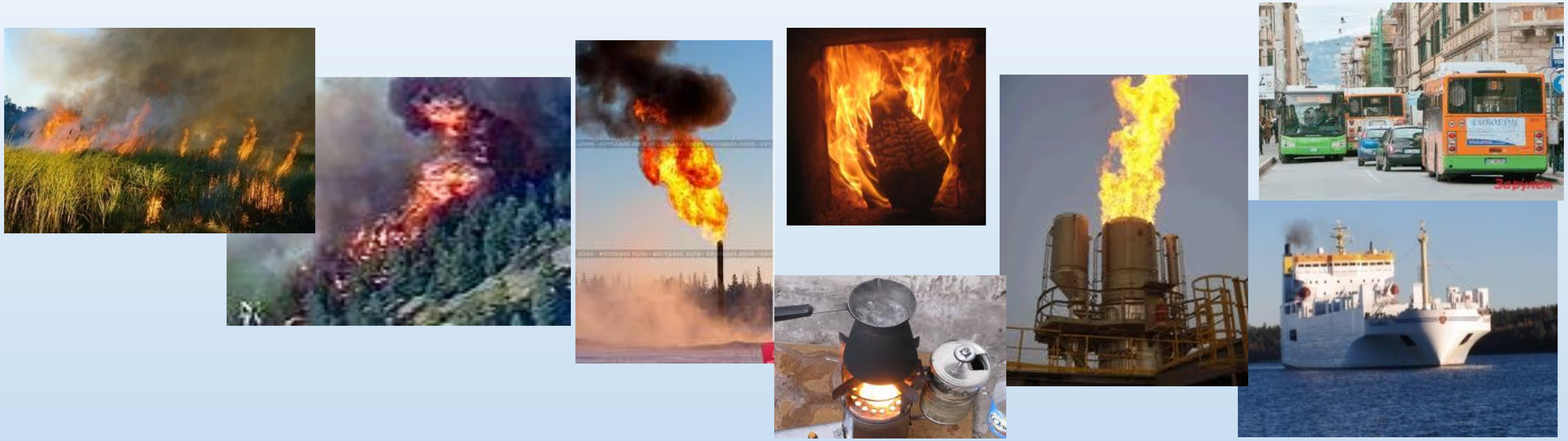




Aerosol chemical composition relates to a source



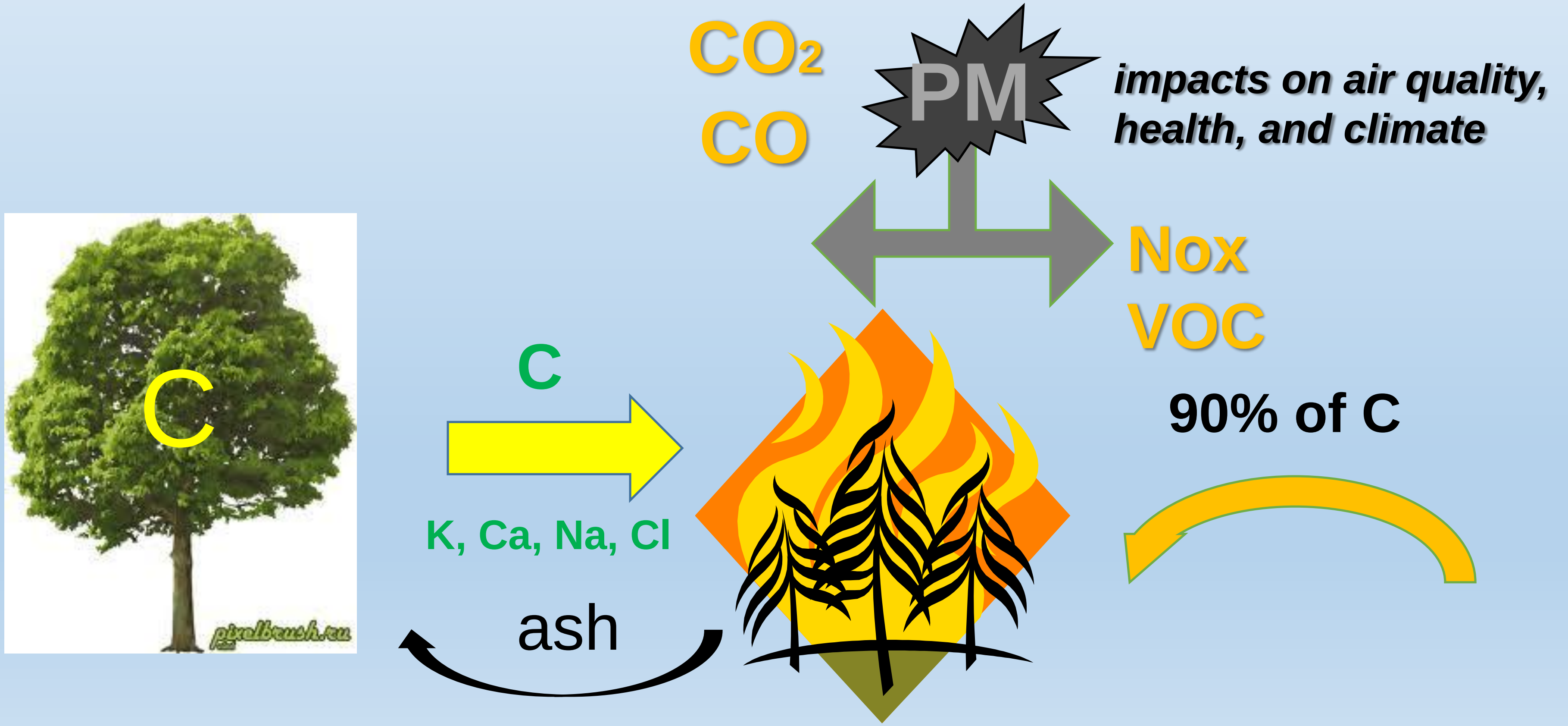
Aerosol/ BC: Contributing global scale challenges



- Globally BC emissions
- Transport contributes ~25% of total anthropogenic emission

Biomass burning and particulate matter

Open biomass burning (BB) relating to deforestation, grass burning, and vegetation fires
contributes **up 42%** to combustion emission global inventory.



Biomass Burning Activities – Global

Classification of Fires

NATURAL (~ 10%)

Wildfires (Forests)
Savannah and grass burning

ANTHROPOGENIC (~ 90%)

Land-clearing / slash & burn agriculture
Residential biofuel combustion

Biomass Burning Activities – Global

Classification of Fires

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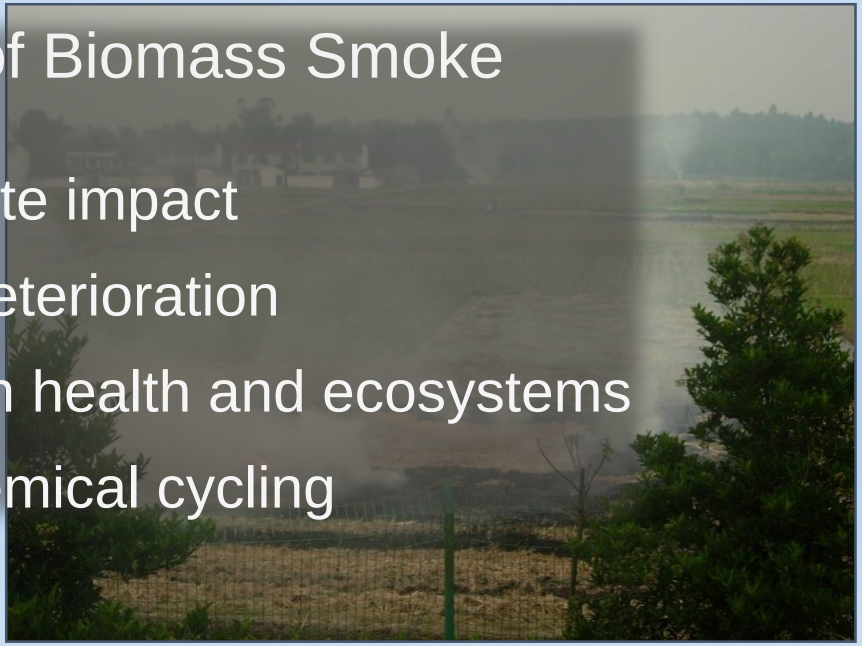


Environmental Impacts of Biomass Smoke

- Global and regional climate impact
- Air Quality and visibility deterioration
- Adverse effects on human health and ecosystems
- Disturbance of biogeochemical cycling

Biomass Burning Activities in Russia

- **52% of Russia is covered by forests; 3% is burned annually!**

Types of Fires

PEATLAND FIRES

Siberia
European part of Russia

AGRICULTURAL RESIDUE BURNING

FOREST FIRES

Siberia

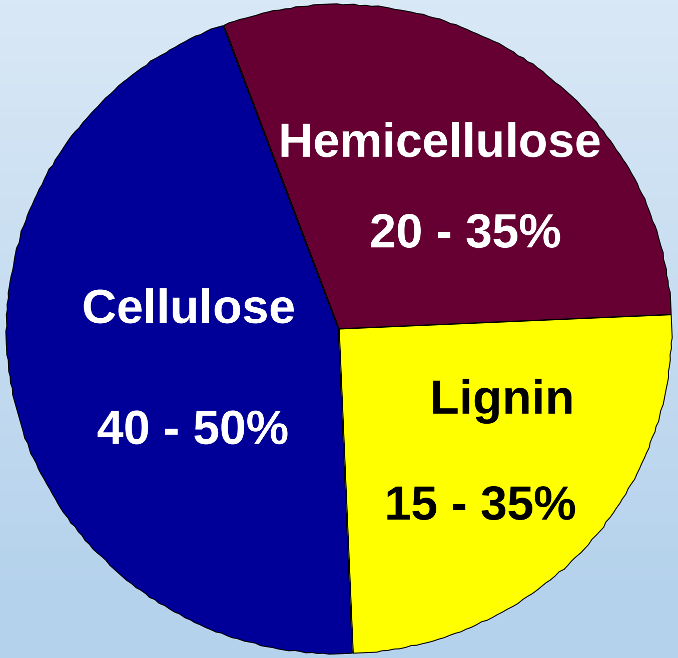
Peat Burning vs. Forest Fires –
Smoldering vs. Flaming Combustion

Distinct Peat Combustion Conditions

- Low-temperature combustion (< 600 °C)
- Incomplete form of combustion
- Deep smoldering is essentially independent of surface conditions (e.g., weather)
- Soils in peatlands smolder as ground fires
- Difficult to extinguish/control
- High vulnerability to burning
- Cross-biome similarities yet important differences

BIOMASS COMPOSITION

Average biomass composition



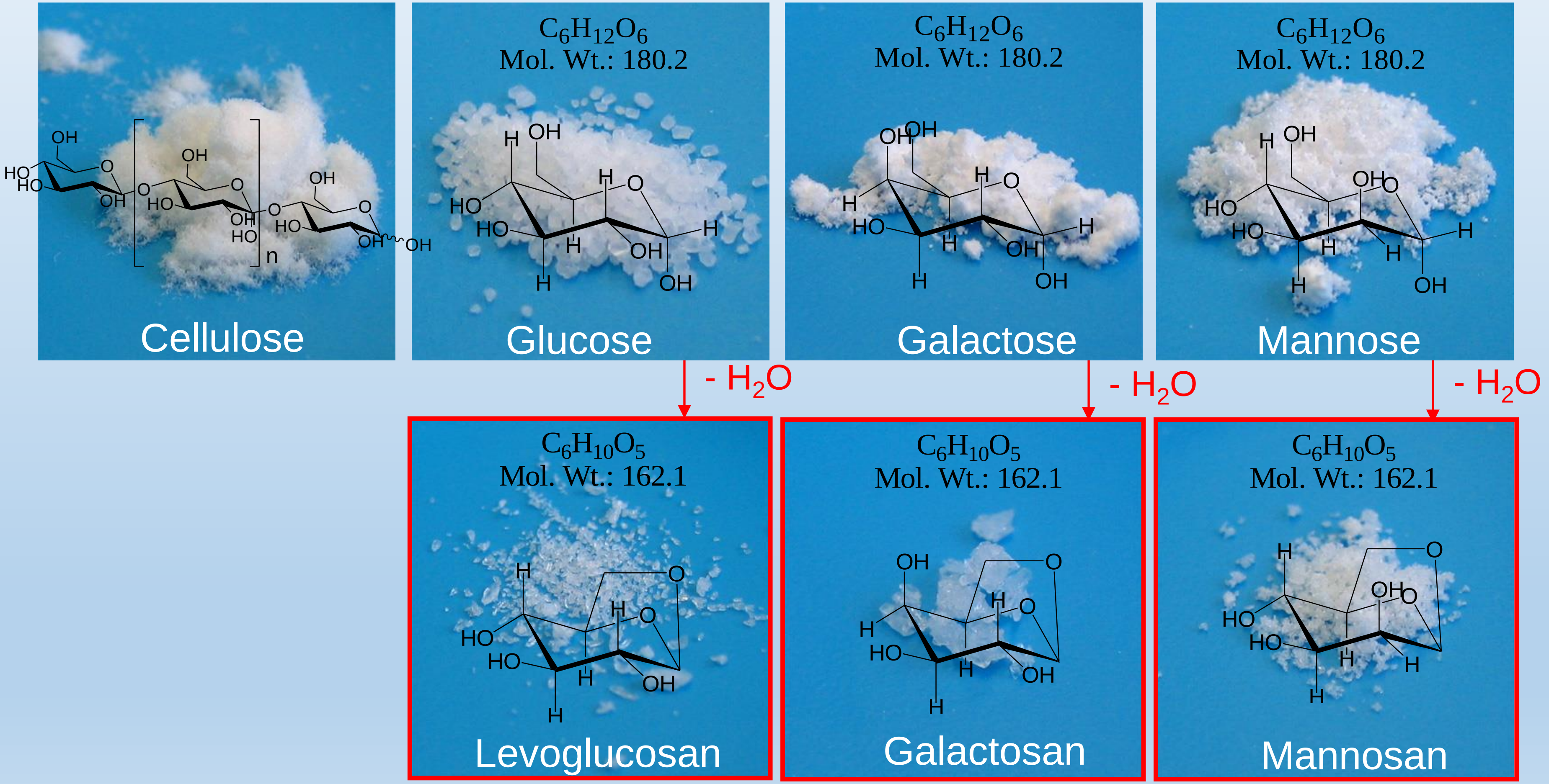
Cellulose: a linear polymer composed of 7000-12000 D-glucose monomers,

Hemicelluloses: consist of about 100-200 sugar monomers (glucose, mannose, galactose, arabinose, xylose, and a few sugar acids), and are less structured than cellulose molecules.

[Sergejewa, 1959; Petterson, 1984]

Biomass Burning Chemistry

Cellulose + Hemicellulose Composition and Breakdown



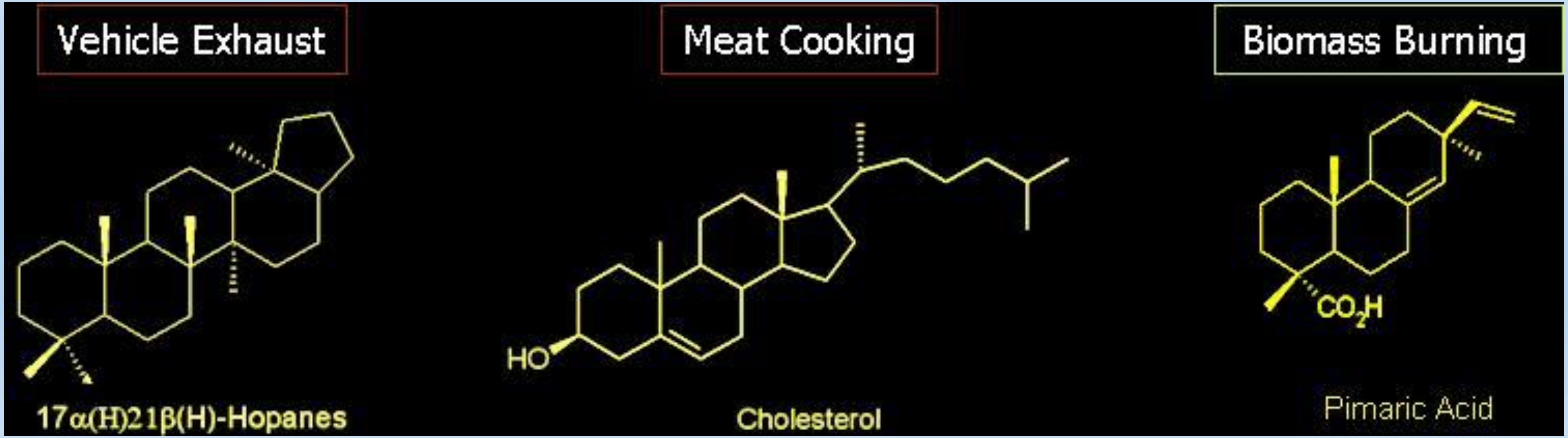
Courtesy of ***Y. Iinuma***

Source Apportionment

Molecular Tracer/Marker Methods

- “Compounds with unique properties that by their pure existence allow for a conclusion about their sources or formation.” (*Rudich et al., Ann. Rev. Phys. Chem., 2007*)
  - Specific emission from one source type
  - Conservation of tracers (i.e., sufficient stability during atmospheric lifetime of tracer species)
  - Availability of sensitive and accurate analytical methods

Molecular Source Tracer Examples:

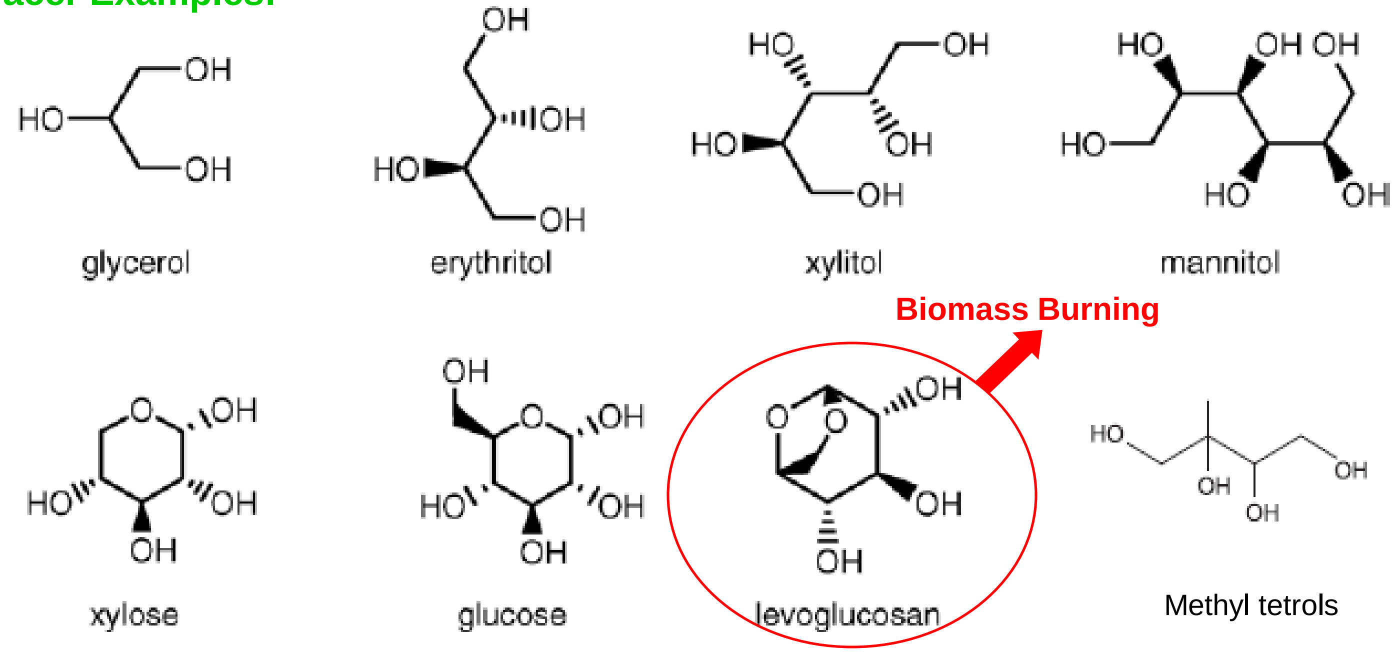


Biogenic & Biomass Smoke Aerosols

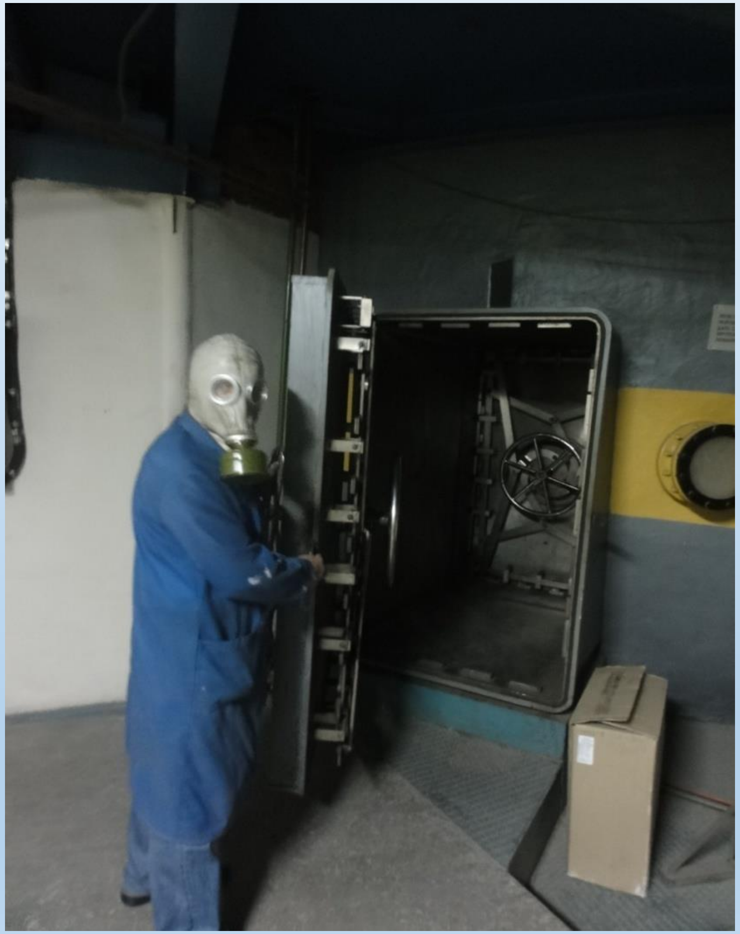
Sources + Selected Products/Tracers

- **Primary Biogenic Aerosol**
  - Leaf abrasion
  - Plant detritus
  - Microbial processes
- **Biogenic SOA**
  - Terpene oxidation
  - Isoprene oxidation
  - Other BVOCs
- **Biomass Burning**
  - Agricultural residues
  - Wildland fires
  - Biofuel use (residential)

Tracer Examples:



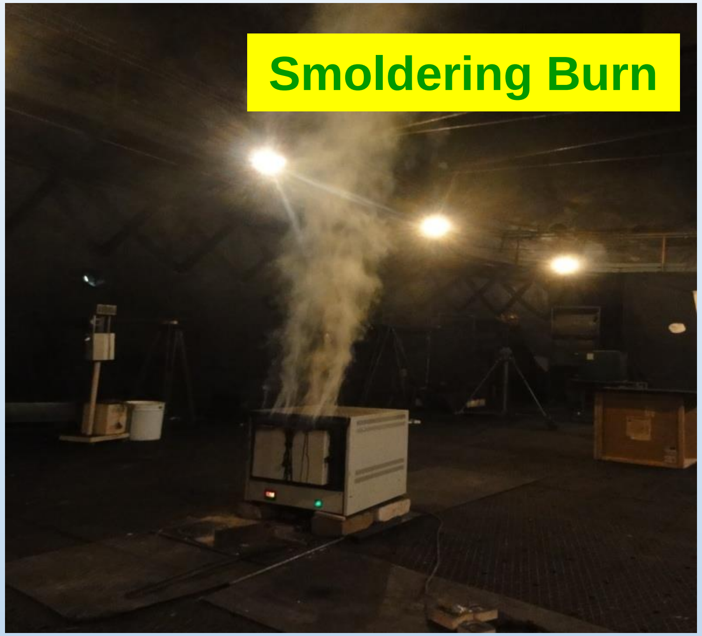
Laboratory simulations of wildfire biomass burning are performed in a Large Aerosol Chamber of 1800 m^3 to assess microstructure, optical, and chemical aerosol properties.



IAO, Tomsk

Chamber Combustion of Siberian Forest Fuels

LARGE AEROSOL CHAMBER



T smoldering ≈ 400C

T flaming ≈ 700C

Siberian pine

Debris

- SEM/EDX
- thermo-optics
- FTIR
- GC-MS
- HPAEC

PM Speciation

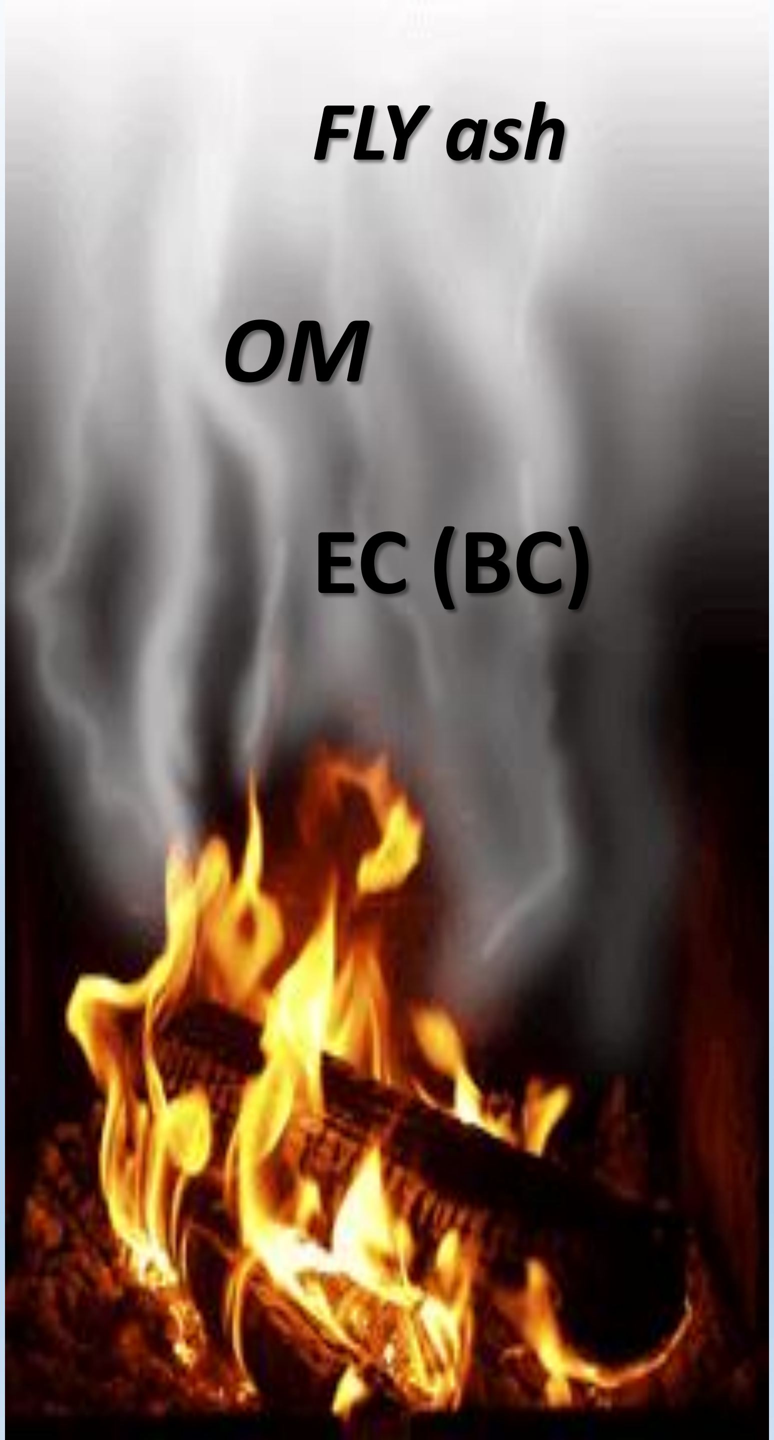
INDIVIDUAL PARTICLE ANALYSIS

- **Morphology, shape, size, composition**

COMPOSITION BULK ANALYSIS

- **Organic Carbon (OC), Elemental Carbon (EC), Carbonate Carbon (CC)**
  - *thermo-optical transmission*
- **Water-soluble organic carbon (WSOC)**
  - *total organic carbon (TOC) analyzer*
- **Inorganic ions**
  - *ion chromatography*
- **Organic/inorganic functionalities**
  - *FTIR spectroscopy*
- **Polar organic compounds (acids and others)**

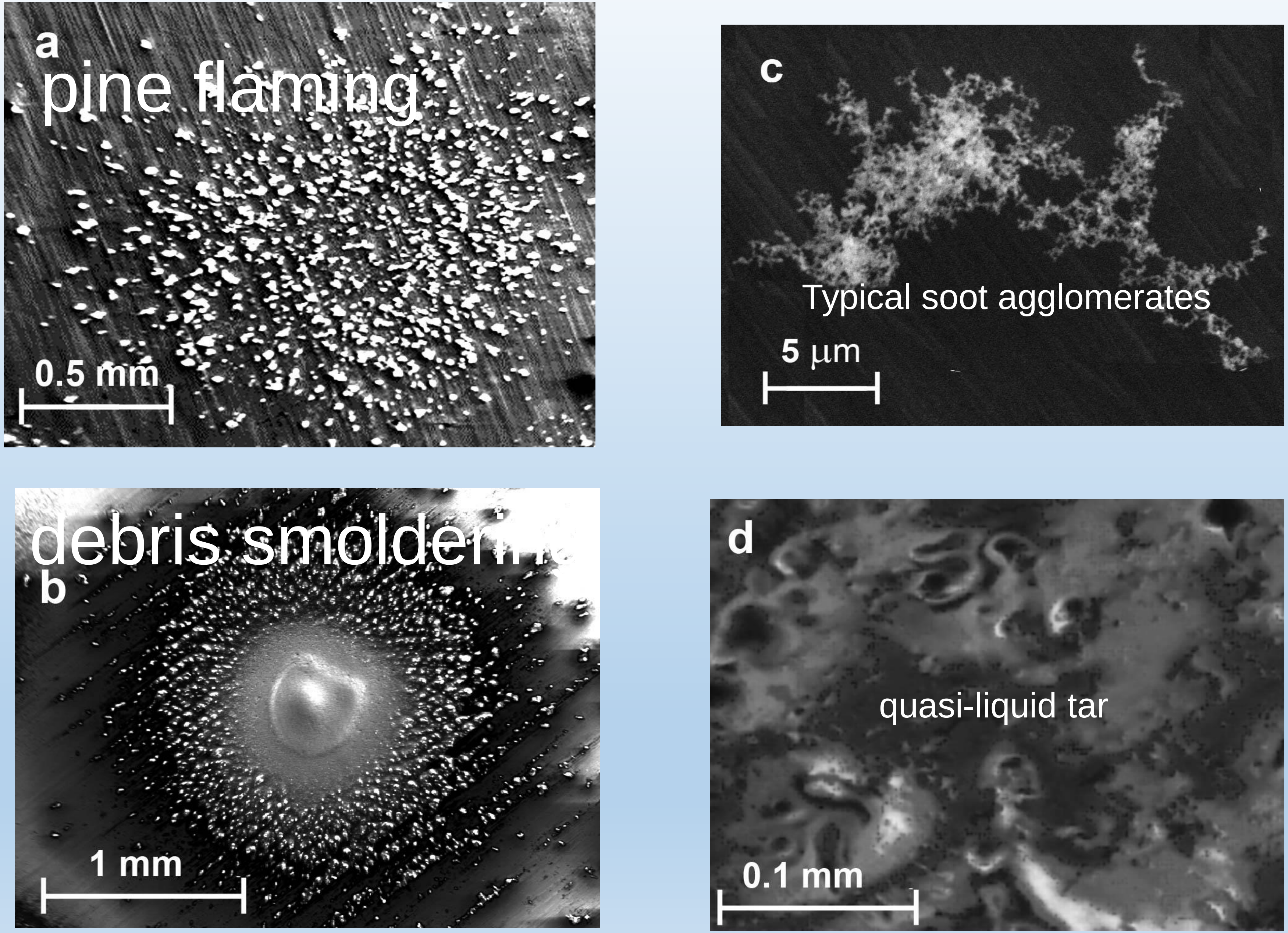
- **Molecular tracers for biomass burning –**
  - *HPAEC-PAD*



INDIVIDUAL PARTICLE ANALYSIS

SEM/EDX Microscopy

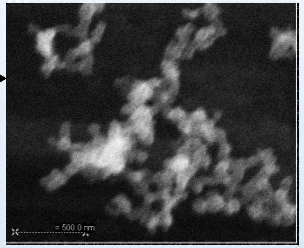
SEM. Panorama of an impaction spot

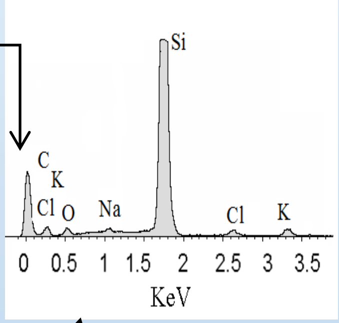


INDIVIDUAL PARTICLE ANALYSIS

SEM/EDX

sampling on foil





100 nm < particle size < 3 µm

morphology and elemental composition of ~500 individual particles

Expert analysis

Data matrix

C	O	F	Na	Al	Si	K	Ca	Ba
24,75	16,67	48,05	2,72	1,05	6,76	0	0	0
15,58	35,88	23,5	3,55	2,19	17,71	1,05	0,53	0
7,54	33,92	21,08	4,91	2,44	23,16	2,08	0,98	3,89
27,96	8	56,83	1,6	0,5	4,68	0,43	0	0
13,72	30,17	32,3	3,9	1,87	16,29	1,05	0,7	0
3,64	45,07	8,03	3,9	3,23	29,18	1,63	1,06	4,26
18,84	21,82	25,49	3,59	2,08	20,64	2,14	1,2	4,19

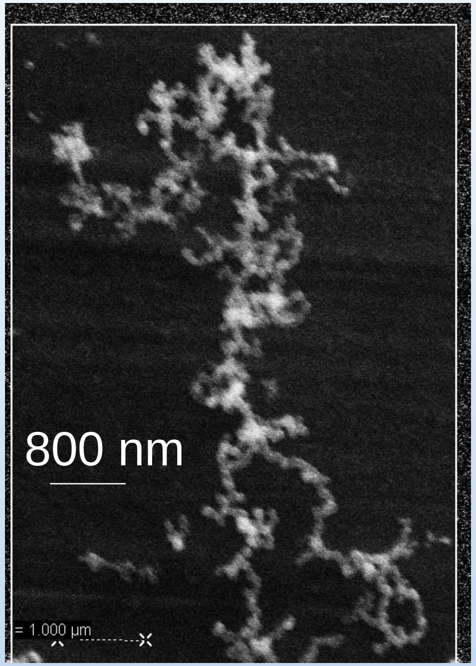
Cluster analysis

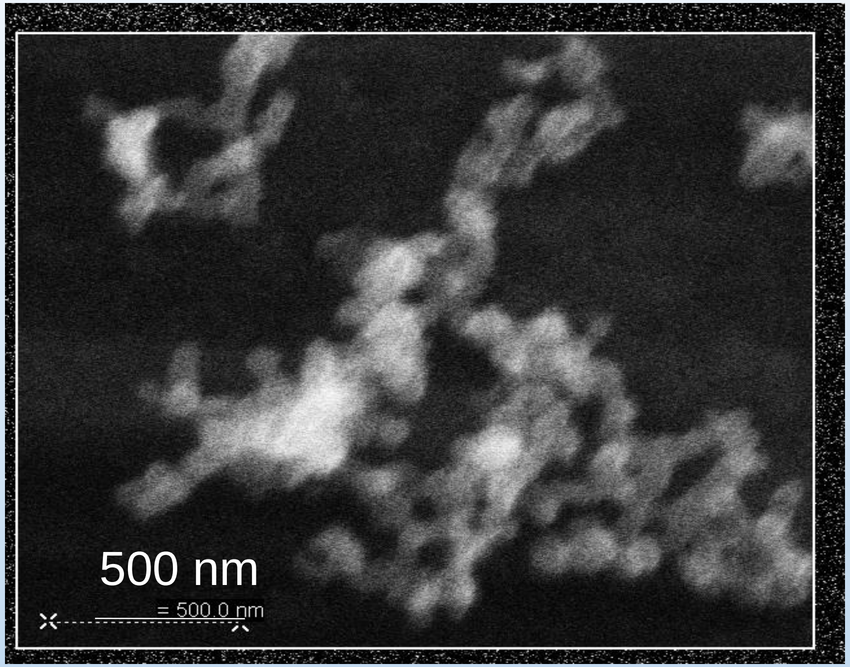
Groups of pine and debris carbonaceous/fly ash particles and their abundance in PM2.5 smoke particles

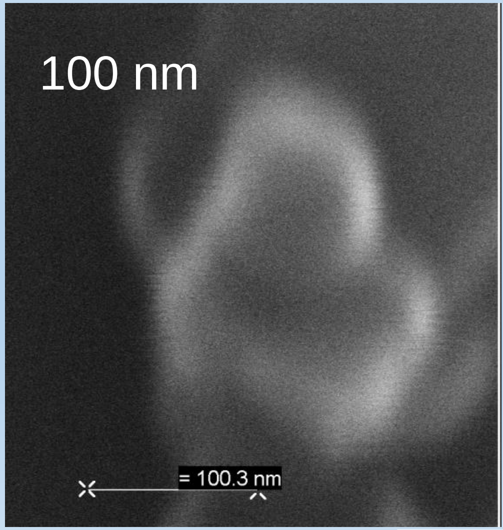
Groups	pine flaming	debris flaming	pine smoldering	debris smoldering
Soot/ Organic	$C_{95}O_4$(87)	$C_{97}O_3$(93)	$C_{85}O_{15}$(57)	$C_{89}O_{11}$(69)
Ca-rich	$C_{51}O_{30}Ca_{17}$ Mg_1(5.6)	$C_{67}O_{17}Ca_{14}$(1.4)	$C_{49}O_{30}Ca_{19}$(15)	$C_{76}O_{16}Ca_7$(11)
Si-rich	$C_{45}O_{30}Si_{11}Al_5Fe_4Ni_2$(3.6)	$C_{39}O_{30}Si_{18}$ Al_7 K_1Fe_2(5.5)	$C_{34}O_{31}Si_{16}Al_{13}$ K_2(19)	$C_{57}O_{24}Si_{10}K_1$ Al_6 (14)
S-rich N-rich	$C_{62}O_{22}S_{14}$ (3.8)		$C_{58}O_{11}S_{27}$ (8.3)	$C_{48}O_{17}S_{35}$ (1.5) $C_{67}O_9N_{24}$(1.8)
Fe-rich			C_{42} O_{28} $Fe_{17}Mg_2Al_3Si_5$ Ca_4 (1.4)	$C_{25}Fe_{23}O_{31}Si_{12}Mg_5$ Al_3K_1(2.2)

FLAMING

open fire
pine wood







Group 1. TYPICAL SOOT

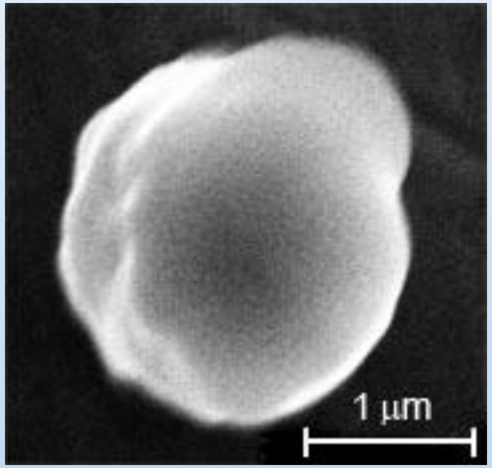
on average 95% C and 4% O

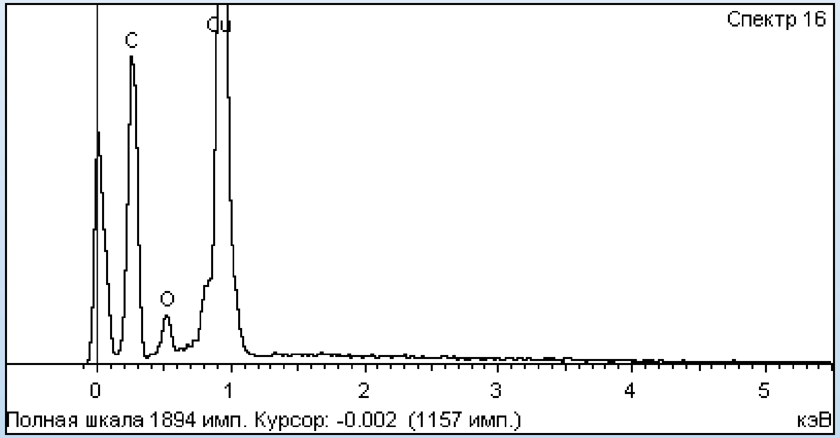
~25% of particles contain 100% of C
in correlation with OC/EC ~ 0.3-0.5

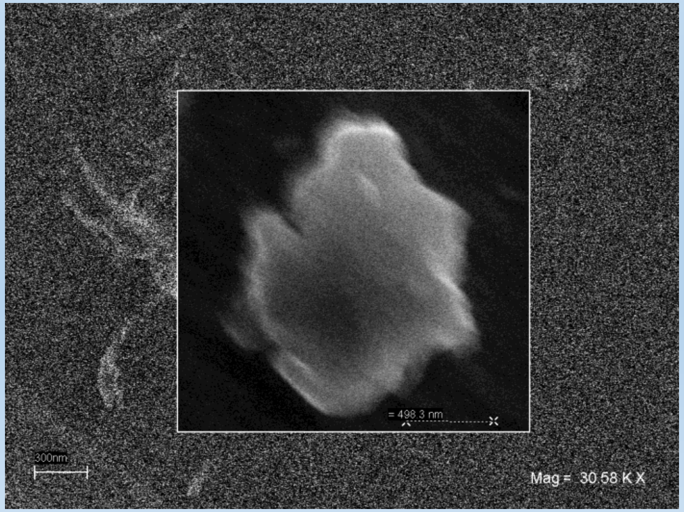
SMOLDERING

smoldering
pine

Gas-to particle condensation





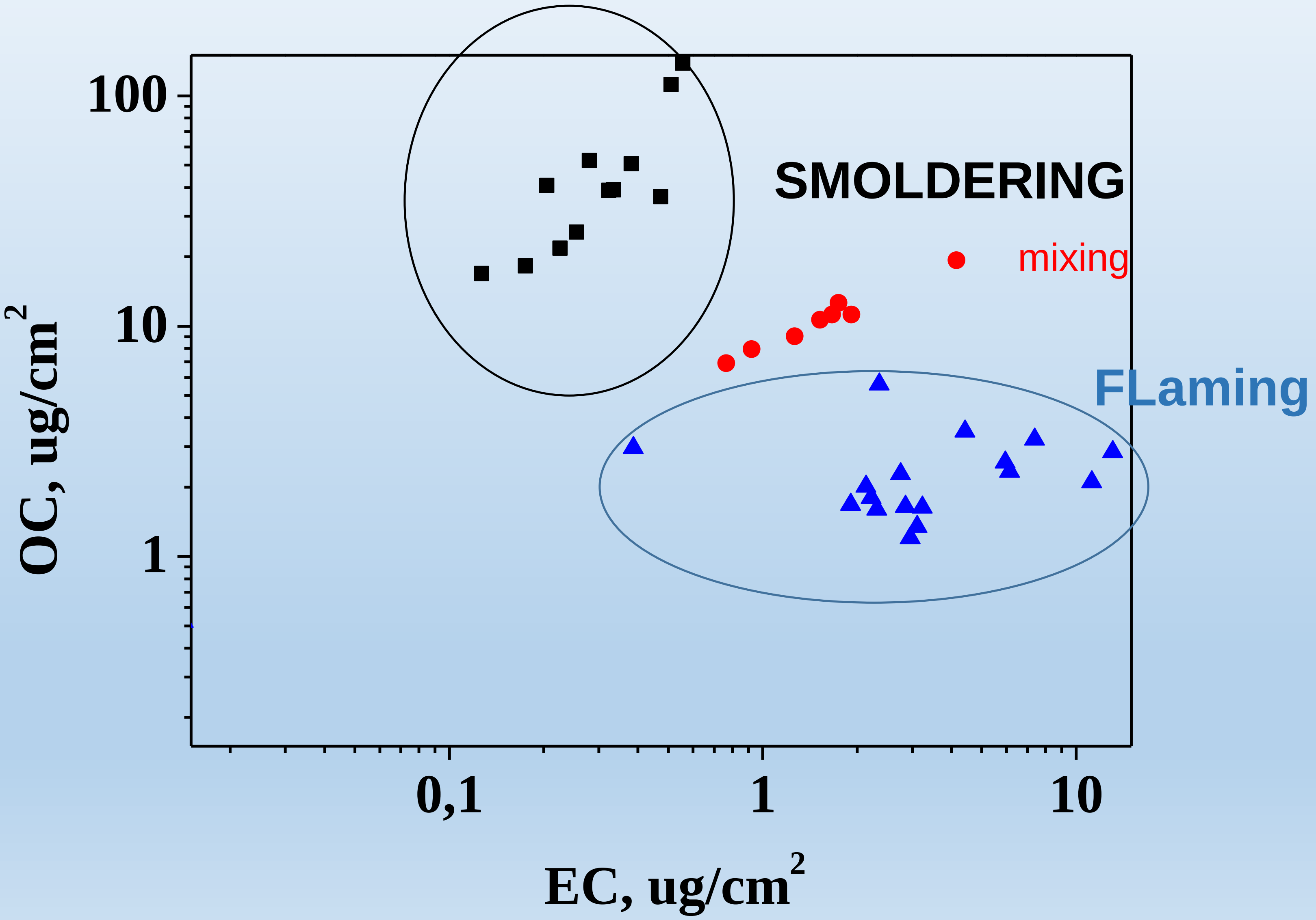


Group 1. Organics

on average 85% C and 15% O

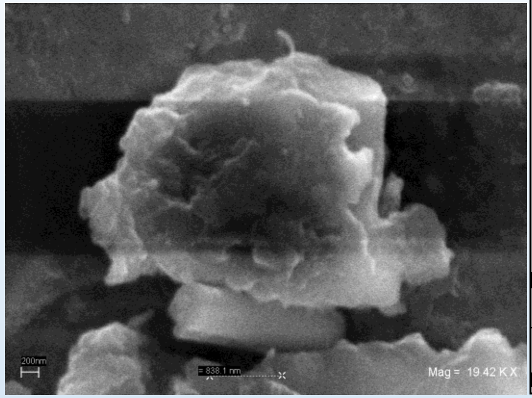
not soot, OC/EC ratio of 34-194
no EC particles

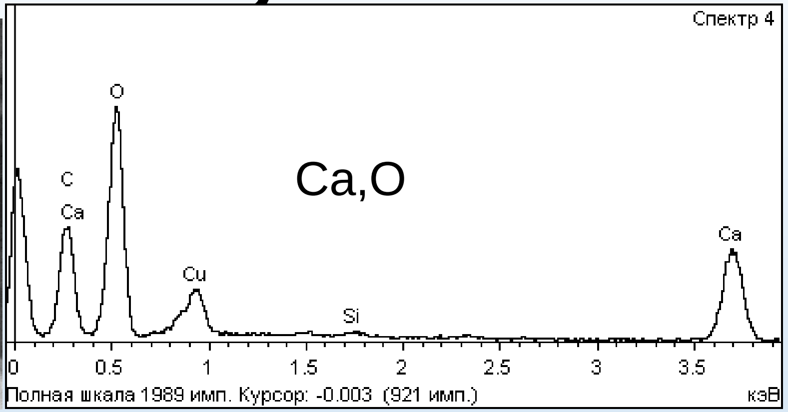
Organic carbon (OC) / Elemental carbon (EC) from pine and debris flaming and smoldering



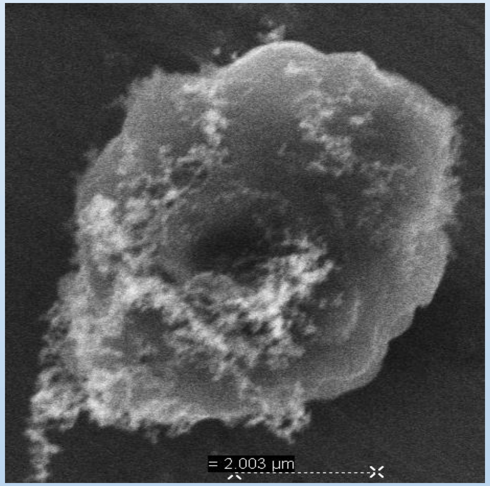
Group 2. Ca-rich in fly ash and dust

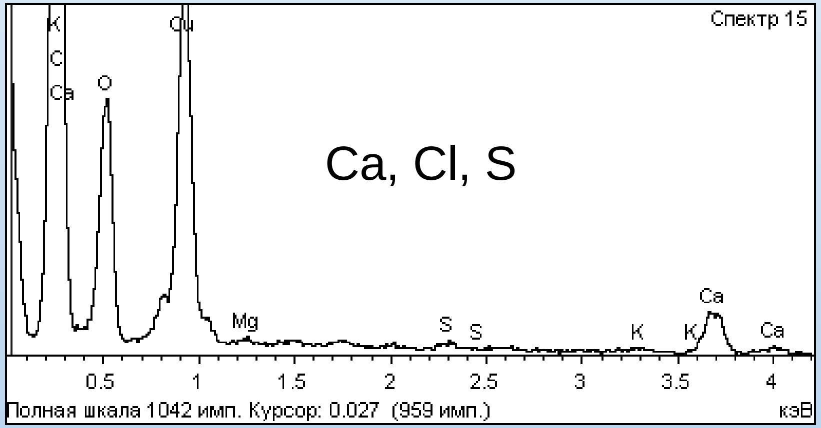
FLAMING





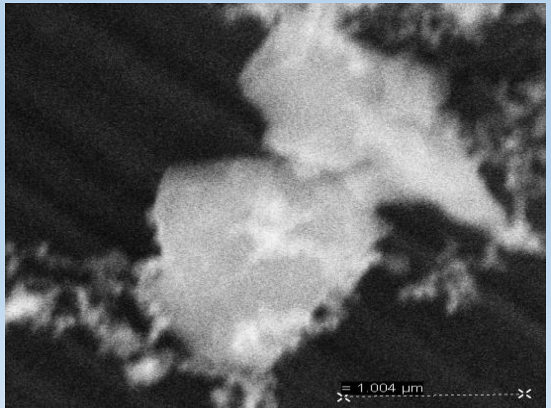
CaO/CaCO3

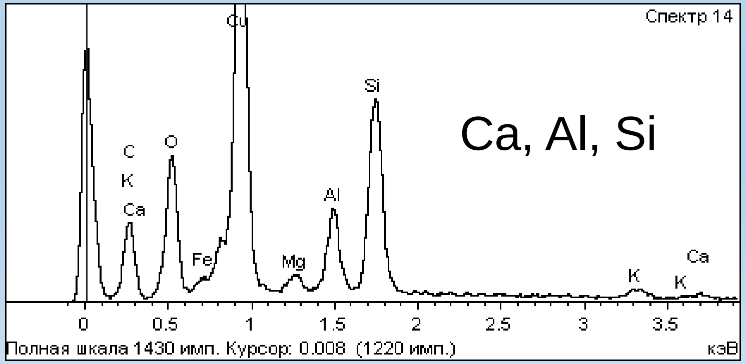




CaSO4, CaCl2

SO_4^{-2}, Ca_2^+, Cl^-,
in good correlation
with ion measurements

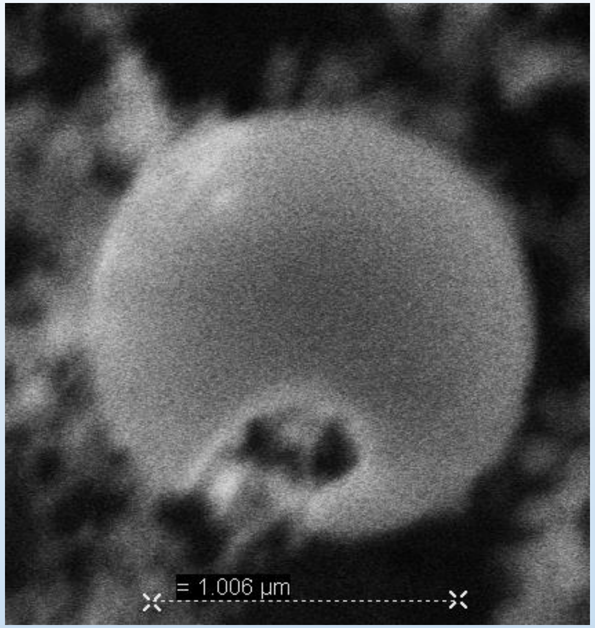


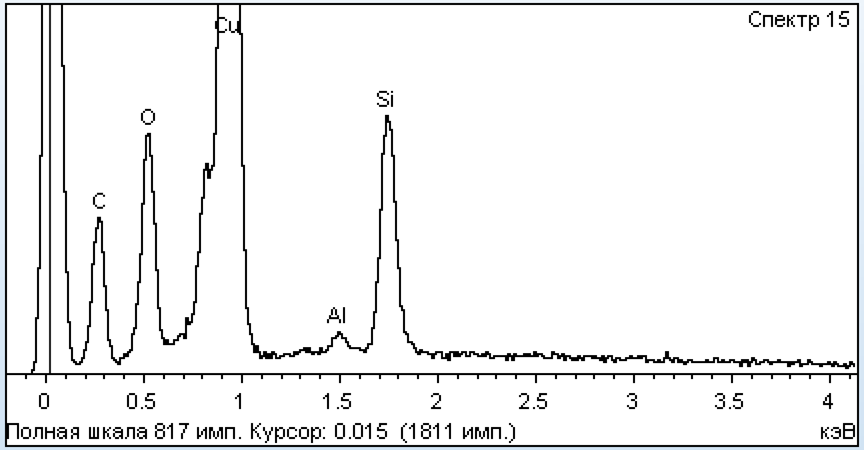


Ca-dominated
aluminosilicates
such as
anorthite $Ca[Al_2Si_2O_8]$

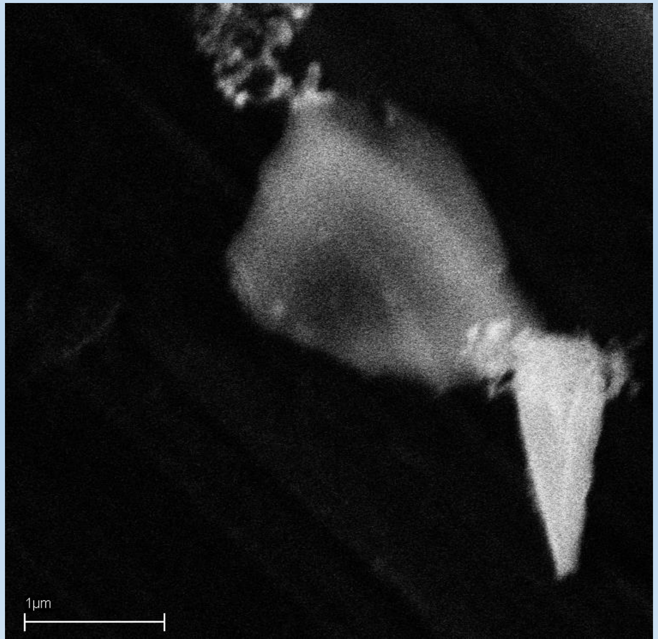
Group 3. Si-rich

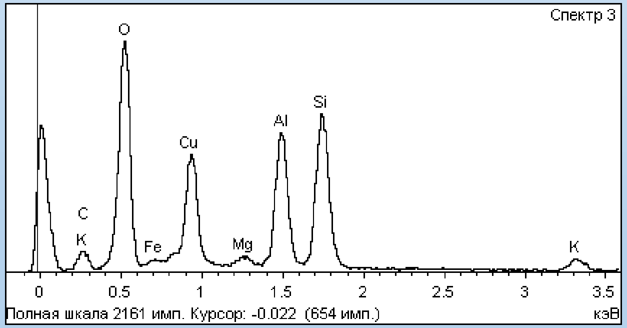
FLAMING





Si-Al   aluminum silicates

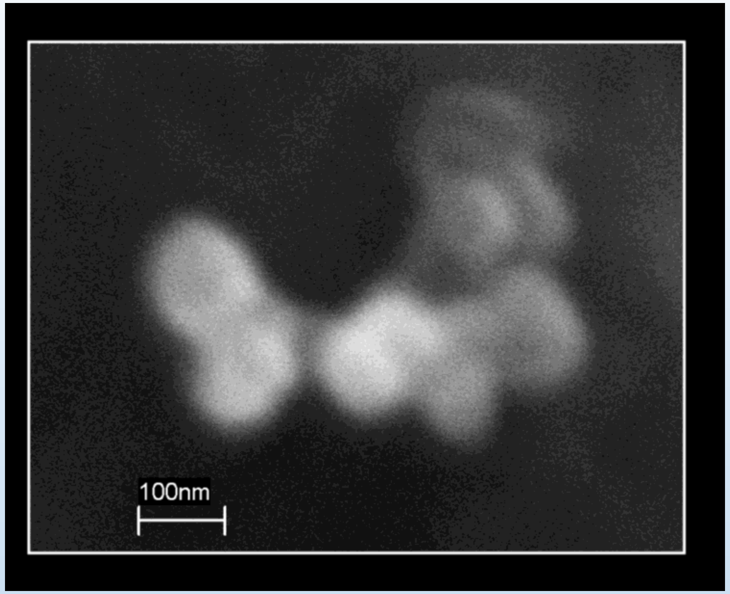


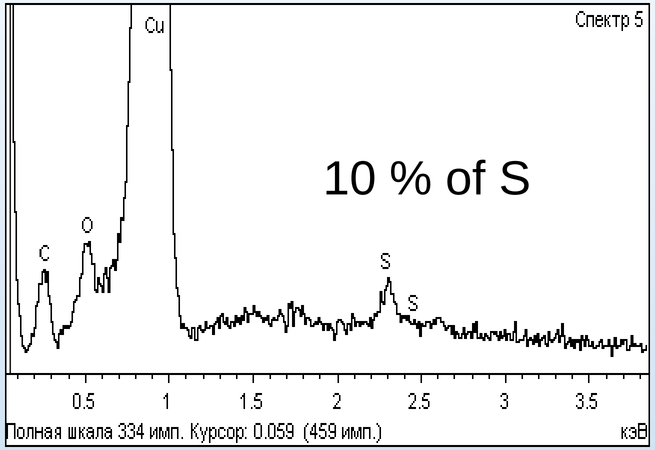


Si-rich Al-Si-K (Fe, Mg)
aluminosilicates such as sanidine $[KAlSi_3O_8]_4$
in debris flame

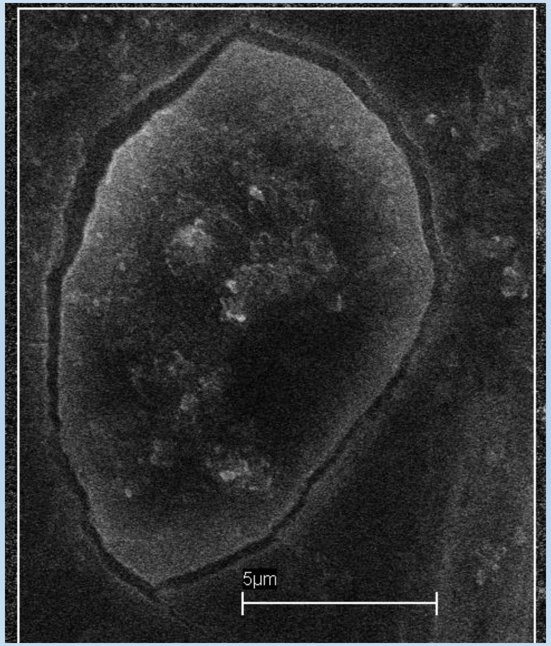
Group 4. S-rich

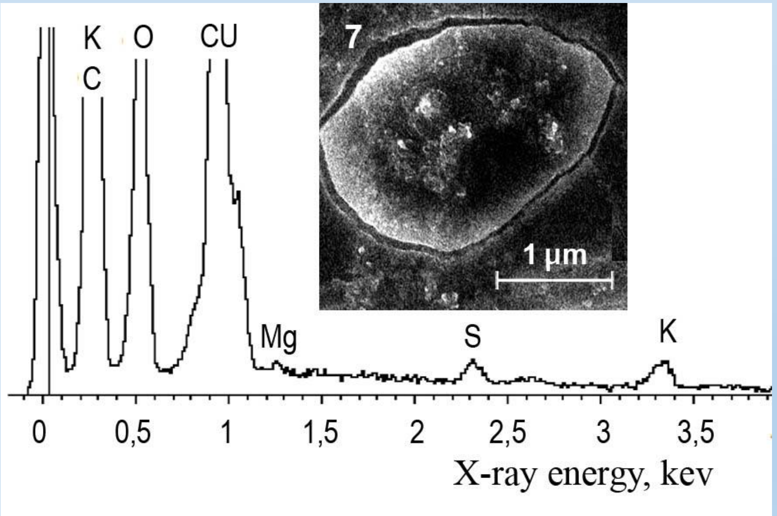
FLAMING





in sulfates of sulfuric acids

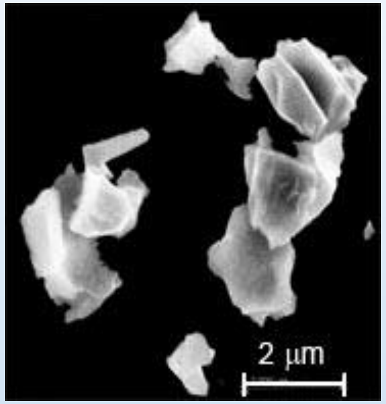


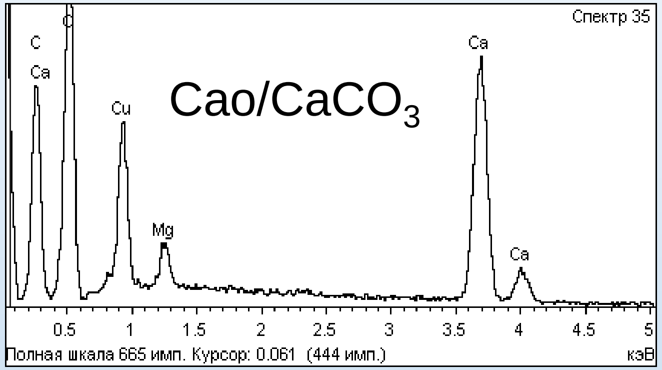


In potassium sulfates, in accordance with K^+ and SO_4^{2-}.

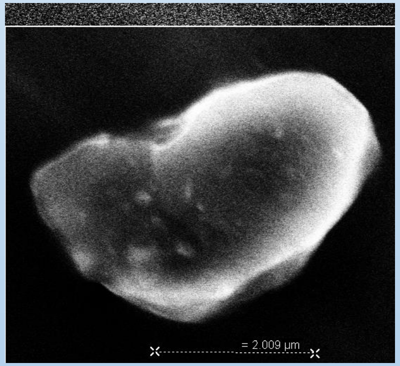
SMOLDERING

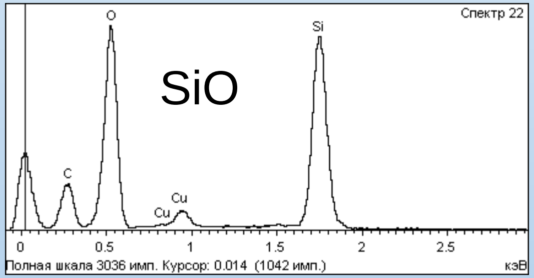
Group 2. Ca-rich





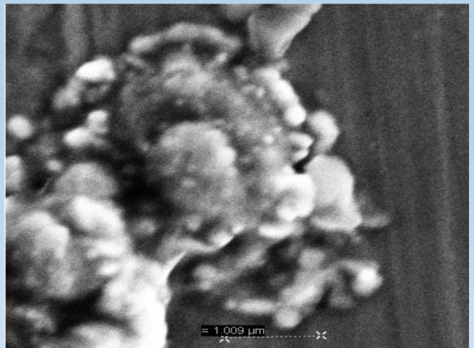
Group 3. Si-rich

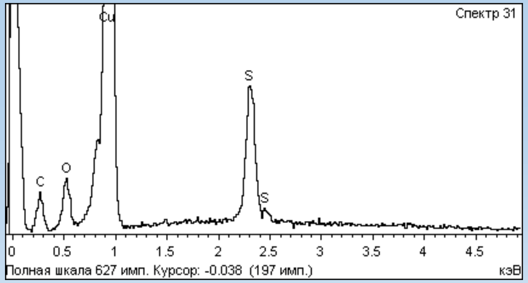




Low temperature combustion
- No condensation of inorganic compounds
- in correlation with low ions

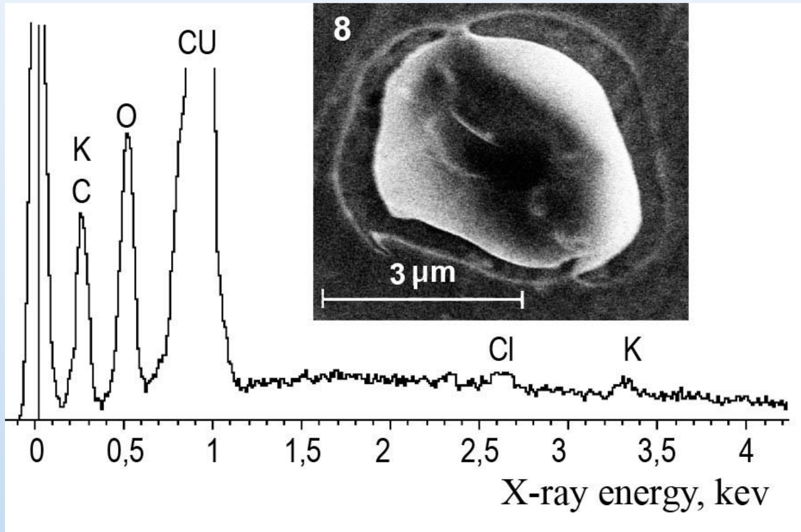
Group 4: S-rich





Aging of smoke microstructure

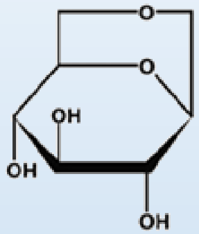
Group	Pine flaming $PM_{2.5}$	Pine flaming $PM_{2.5}$
Soot/ Organic	$C_{95}O_4$(87)	$C_{92}O_8$(61)
Ca-rich	$C_{51}O_{30}Ca_{17}$(5.6)	$C_{47}O_{30}Ca_{18}S_2$(3.2)
Si-rich	$C_{45}O_{30}Si_{11}Al_5Fe_4Ni_2$(3.6)	$C_{24}O_{44}Al_6Si_{21}K_2$(2.2)
S-rich	$C_{62}O_{22}S_{14}Cl_2$(3.8)	$C_{51}O_{22}S_2Cl_2$(26)
Fe-rich		
K,Cl-rich		$C_{51}O_{42}K_3Cl_5$(7)



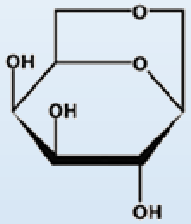
During time evolution of smoke volatile inorganic compounds condensed as potassium chlorides and sulfates

Molecular markers from Siberian biomass burning

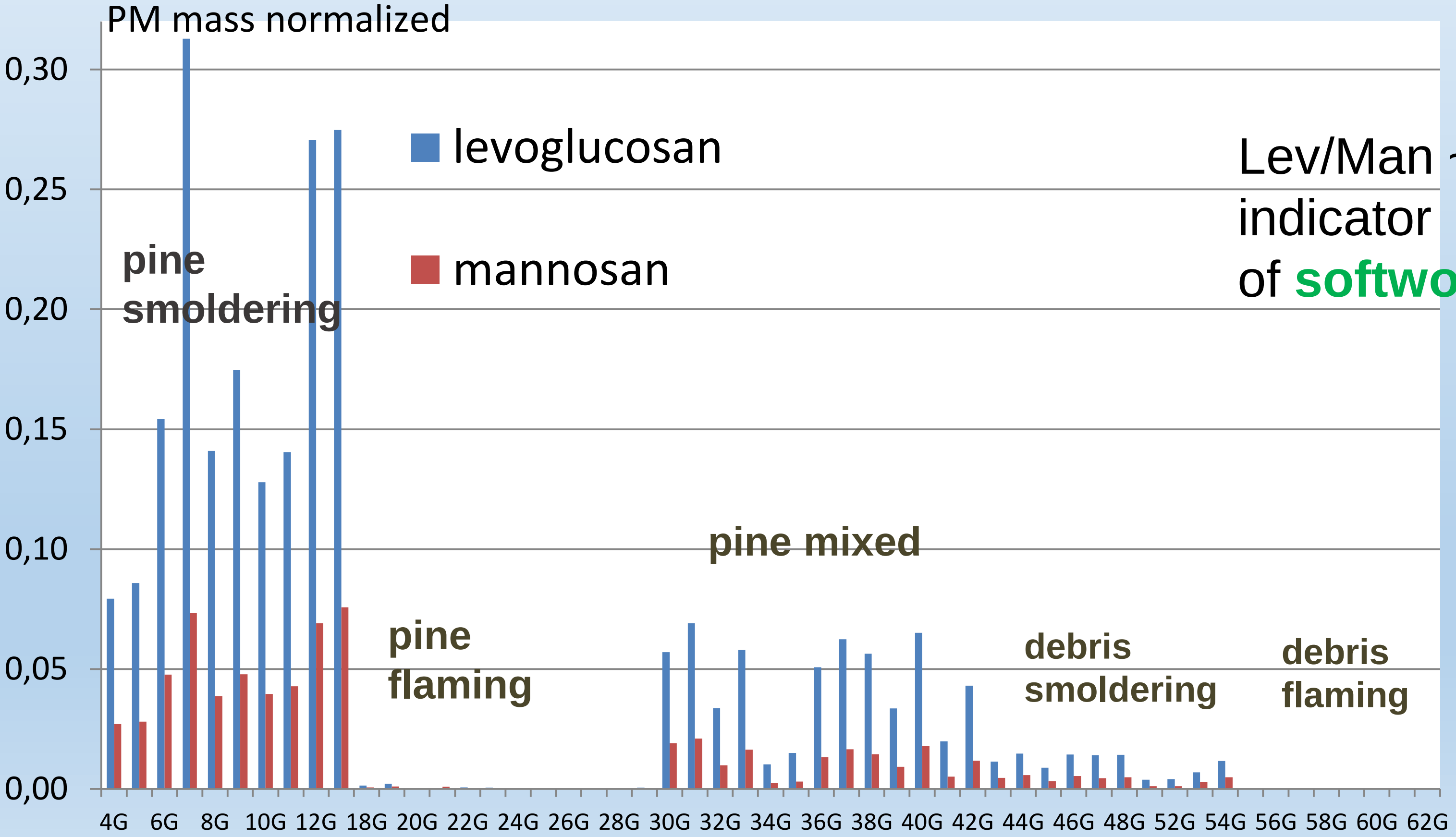
Levoglucosan



Mannosan



Anhydrosugars
as markers for wood
smoldering combustion
Up to 30% of PM!



Lev/Man ~ 2-4
indicator
of softwood burning

Biomass Burning Activities – Siberia

Fire activity in Siberia observed on 30 July, 2012

Biomass Burning Activities – Siberia

Air quality in Tomsk, Siberia, observed between 27 and 28 July, 2012

Biomass Burning Activities – Siberia

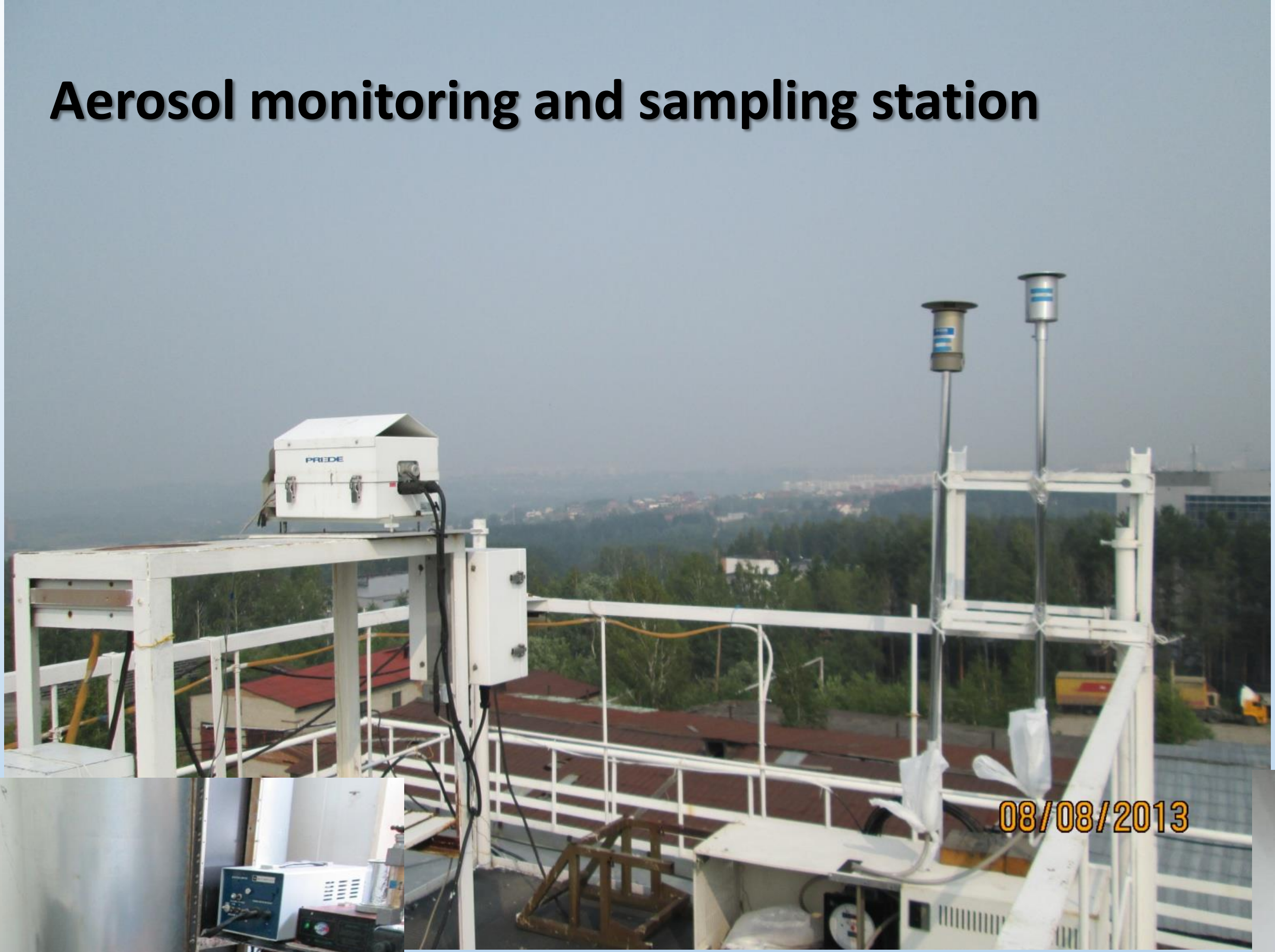
Air quality in Tomsk, Siberia, observed on 30 July, 2013

Aerosol monitoring and sampling station

IAO, Tomsk

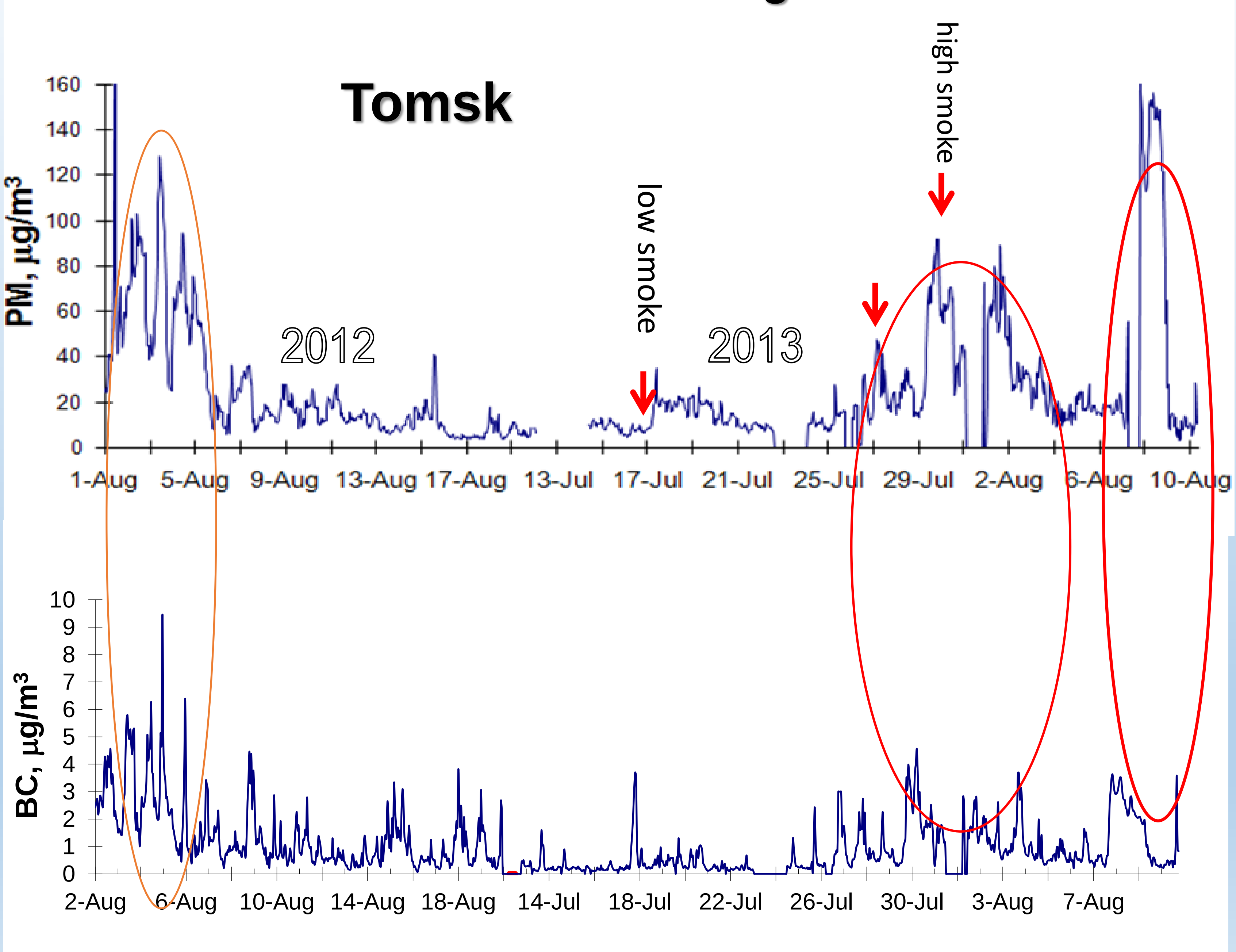
56.5° N, 85.1°E

Summer 2013



Nephelometer – aerosol scattering
Aethalometer – aerosol absorption -> BC
Absorption Photometer MAAP
PM10 and PM2.5 filter sampling

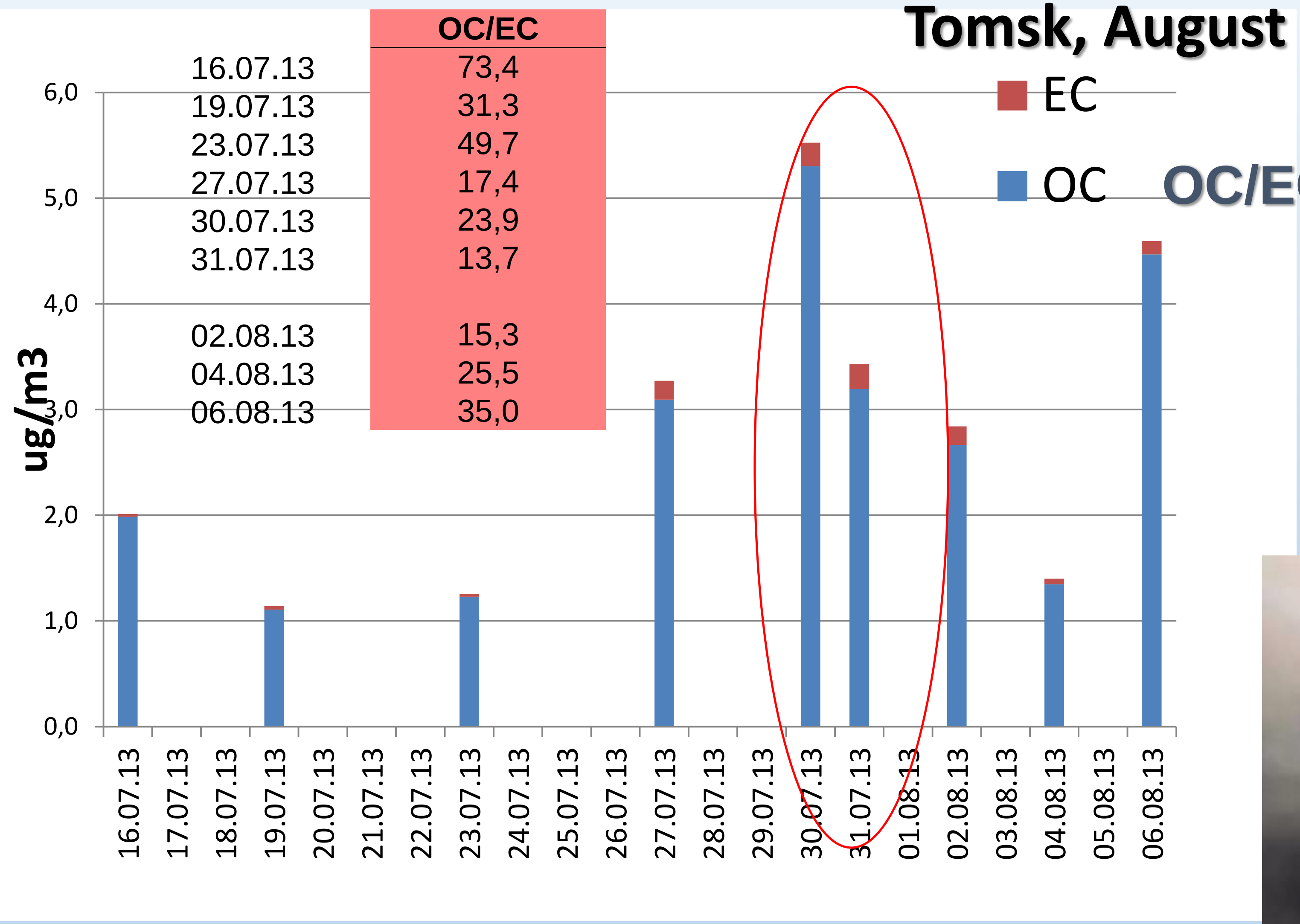
PM and BC Concentrations during wildfires in Siberia



OC and EC Concentrations during wildfires in Siberia

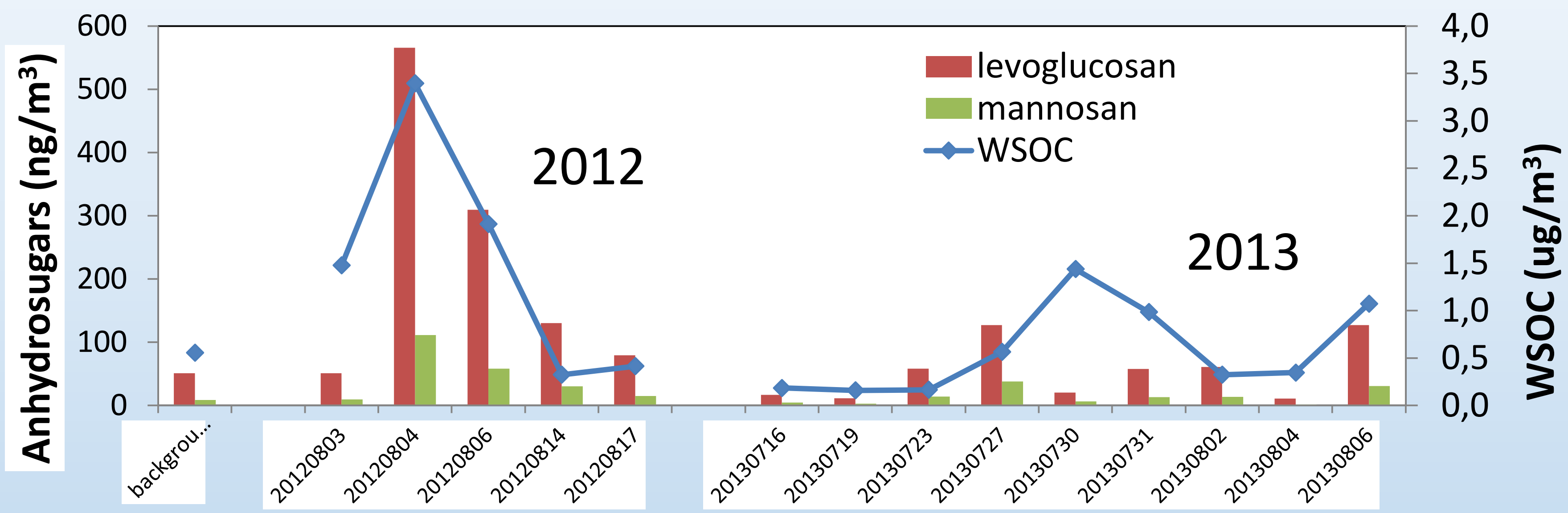
Tomsk, August 2013

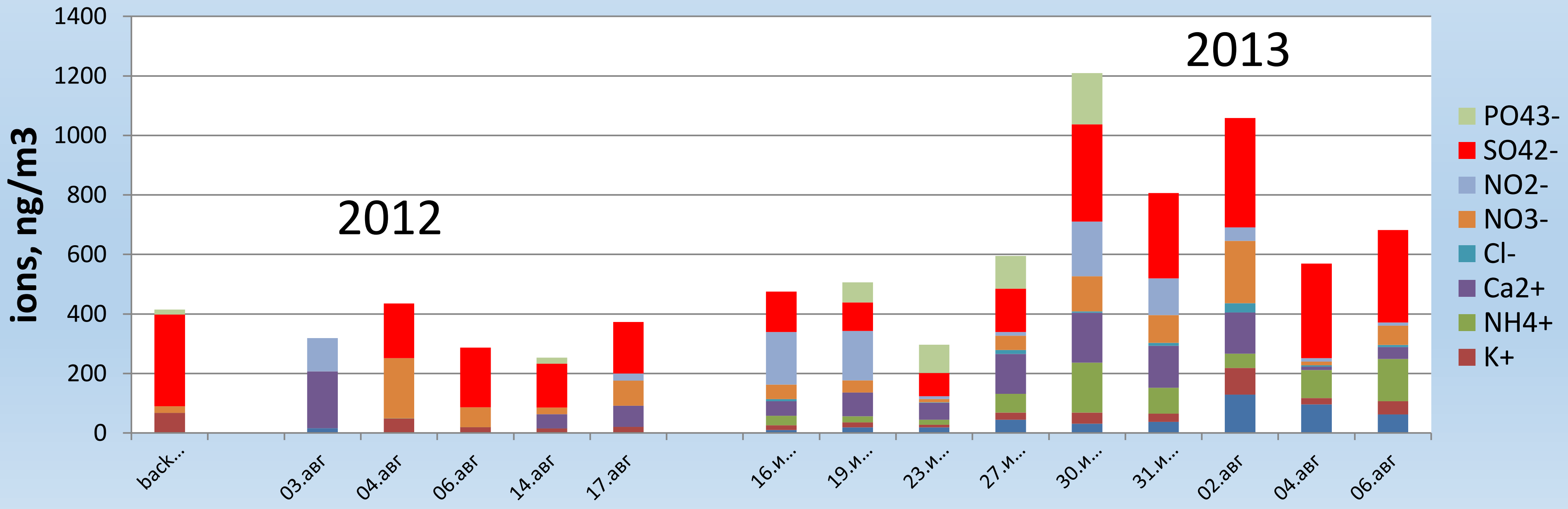
OC/EC ~ 15-75



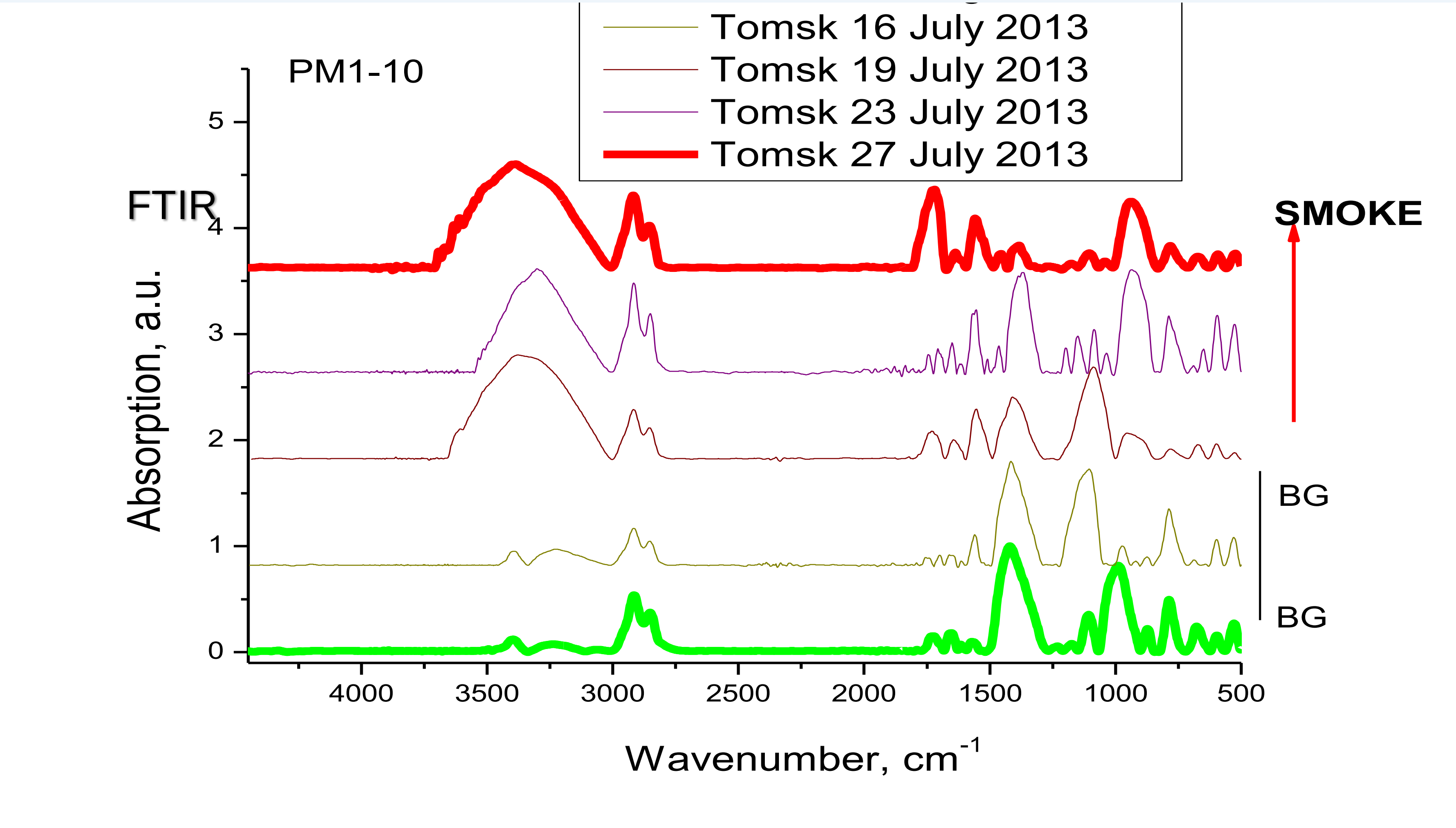
	OC/EC
16.07.13	73,4
19.07.13	31,3
23.07.13	49,7
27.07.13	17,4
30.07.13	23,9
31.07.13	13,7
02.08.13	15,3
04.08.13	25,5
06.08.13	35,0

PM Composition during wildfires in Siberia





Functional Groups during wildfires in Siberia



Smoke during wildfires enhances ambient levels in Tomsk of:

- sulfates, ammonium, nitrates
- **acid carbonyl** groups
  - → indication of photochemical aging
- carbonates due to soil dust emissions during large wildfires

Conclusions:

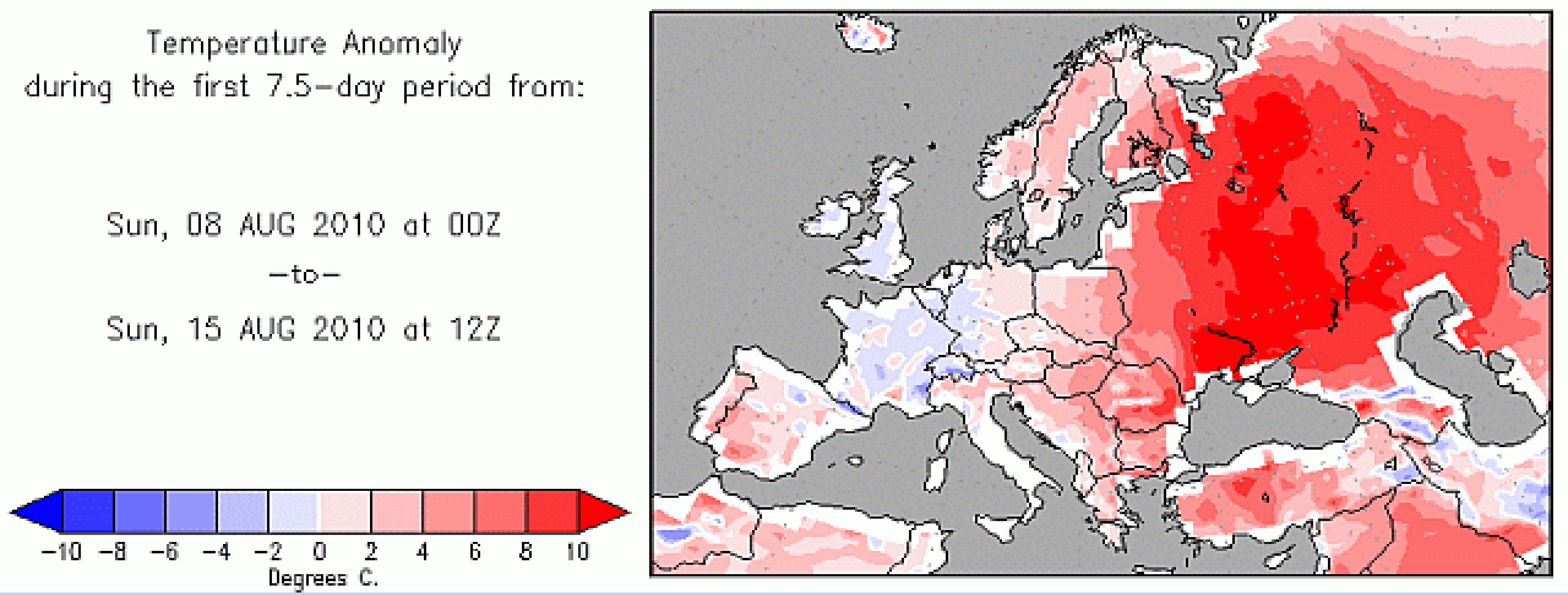
Microphysical and chemical properties of aerosol emissions from combustion of Siberian boreal forest plant species

• High temperature burning in open **flaming** fires of plants significantly influences the particle formation and composition, producing soot and fly ash.
→ Soot is a micromarker of Siberain BB.
• Fraction of EC and OC, non-acid and nitro compounds are dominant.

• Formation of quasi-liquid tar, organic and fly ash particles at low temperature in **smoldering** is significant.
• Fraction of OC, acid and non acid, levoglucozane,n - alkane compounds are dominant.

Anhydrosugars are good markers of Siberian wood burning in smoldering phase.

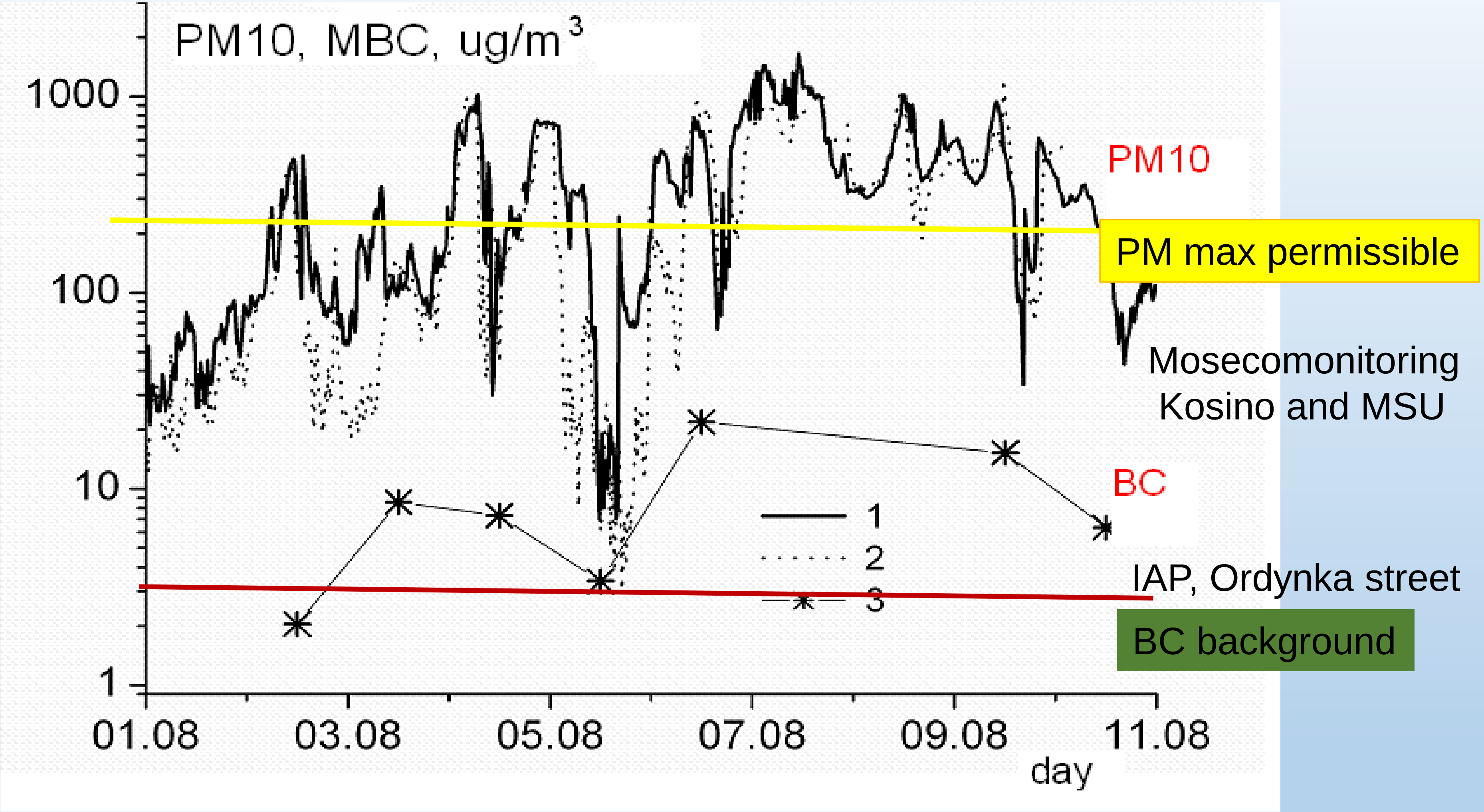
Characterization of smoke aerosols of extreme wildfire event, August 2010



Summer 2010 brought an unusual heat into Eastern Europe, temperatures in Moscow during July and August were from +18°C above normal

Heat and dry conditions provoked numerous **wildfires of forest, and peat bogs**

Moscow extreme smoke event, August 2010: PM10 and BC mass concentrations



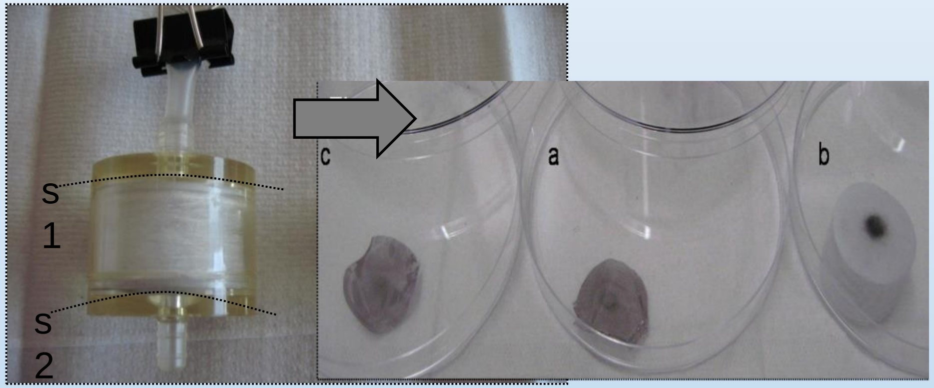
Starting with 6 August 2010 Moscow megacity was covered with a thick haze considerably affecting the air quality

Moscow smoke sampling

Week sampling

- at suburb site , 20 km to the north of Moscow

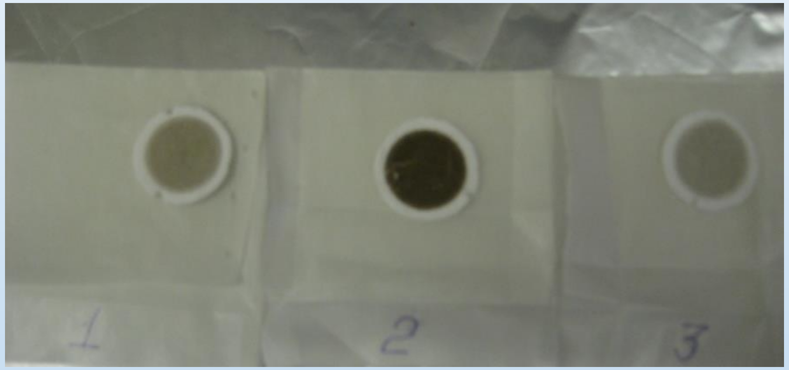
from 7 to 14 August 2010, 5 to 16 August 2011



Daily sampling

- in Moscow center, Ordynka street,

from 4 to 17 August 2010,
5 to 16 August 2011



and characterization

- **Total carbon (TC), OC, and EC, and carbonate carbon (CC)** by thermo-optical method, Sunset off-line Analyzer,
- **Organic/inorganic functionalities** by FTIR Prestige-21 spectrometer,
- **anhydrosugars (levoglucosan, mannosan and galactosan)** by HP liquid chromatography ,
- **inorganic ions** by HPLC system,
- **individual particles analysis** by SEM/EDX, by cluster analysis

Analyses of composition indicates aerosols in Moscow were affected by open fires in those days of intensive smoke.

Total carbon 10 times higher than 2011
EC and CC 2 times higher
OC/EC up to 28 - smoldering fires
LG 100 times higher
K+/EC is tracer of biomass burning

Inorganic ions

Ca^{2+}, SO_4^{2-}, NO_3^-, NH_4^+ are dominant in Moscow smoke,

K^+ is marker of biomass burning


Thanks for the nice air quality !