Water interactions with combustion particles in atmosphere

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Introduction. The fate of combustion– generated nanoparticles in the humid atmosphere is strongly related with ability to interact with water. The indirect climate forcing is caused by the potential ability of soot aerosols to act as cloud condensation nuclei (CCN) and ice nuclei (IN), which is a quantitative indicator of the ability of a combustion aerosol to become involved in atmospheric removal by nucleation scavenging. A lack of airborne observations of the water/soot interactions means that emission of combustion particles from various transport systems, industry, domestic heating and biomass burning has become a significant source of uncertainty in current environmental assessment studies.

It is recently concluded that soot particle may be important aerosol impacting ice clouds formation in the troposphere. Numerous observations and modeling studies prove that aircraft-generated soot facilitates the contrail and cirrus formation. If soot aerosols act as effective IN they may change the mechanism of the cirrus formation from homogeneous nucleation due to background aerosols to heterogeneous nucleation. However, sparse documentation exists on the ice nucleation activity of soot particles measured at contrail and cirrus level. The lack of experimental data on hygroscopicity of original soot from aircraft engines led investigators to an assumption about initial hydrophobicity of emitted soot and its activation by plume processing. But recent laboratory studies of aircraft engine-generated soot proved the significant role playing by surface sulfates and organic compounds in original soot hydrophilicity and CCN activity. Finally, global climate models predict the significant aviation impact on cloudiness and climate assuming the high CCN/IN activity of aircraft-generated soot leaving the problem of a great uncertainty for future studies.

This review presents a comprehensive analysis of water interaction with transport engine- generated and wood burning particles at atmospheric conditions. The purpose is a definition of a *quantification measure* for the separation between hygroscopic and non-hygroscopic soots and for the identification hydrophilic and hydrophobic particles between non-hygroscopic atmospheric aerosols. A few classical water adsorption models are applied for parameterization and quantitative comparison.

Water uptake. Gravimetrical measurements of water uptake coupled with chemical composition and porosity analysis clarifies the mechanism of water interaction with aircraft engine soot, ship exhaust residuals and wood burning particles in the wide range of relative humidites, up to condensation regime, and temperatures down upper tropospheric ones. Soot is complex material composed from elemental carbon covered by organic/inorganic compounds. In the general case two mechanisms of water interaction, namely the bulk dissolution into water soluble coverage (a*b*sorption mechanism) and the water molecule adsorption on active sites (a*d*sorption mechanism) govern the water-soot interaction.

Concept of quantification. Comparative analysis of water uptake on soots of various compositions, from elemental carbons to complex composites with large water-soluble fraction, allows us the suggesting a *concept of quantification* (Popovicheva et al., 2008). The isotherm for a water film extended over the surface is proposed as a *quantification measure* which separates hygroscopic from non-hygroscopic soot. Water uptake on hygroscopic soot significantly exceeds the surface water film formation and may reach tens water monolayers. If soot particles made mostly from EC and/or the organic coverage is totally water insoluble we assume non-hygroscopic

soot with water uptake less (hydrophobic soot) or approaching (hydrophilic soot) the surface water film formation.

Water uptake measurements accompanied by comprehensive soot characterization have shown that aircraft engine combustor soot is the representative of hygroscopic soots due to high water soluble fraction leading to multilayer water uptake. Spark discharge Palas soot is hydrophobic black carbon because of the chemically-pure surface which supports just low water adsorption on a few active sites. While laboratory-produced TC1 kerosene flame and CAST burner soots may be classified as hydrophilic between non-hygroscopic soots because of the present of some water soluble compounds and functionalities on their surface leading to the cluster formation and confluence into the water film extended over the surface.

Classical models of water adsorption may be applied for parameterization of experimental data in some ranges of relative pressures. The more adsorbate-adsorbate interactions are developed in the model the better is its application. But the single model which may be universally applied for water uptake on soot of any extend of hydrohilicity is absent.

The concept of quantification of water uptake by soot particles developed in this study is proposed to be useful for connection between the isotherm data and the cloud condensation soot activity (CCN data). It may allow defining which combustion soot may be activated in respect to the Kelvin barrier overcome. The formation of the water film extended over hydrophilic surface is assumed to be needed for wetting that soot particle which becomes "Kelvin activated" at water supersaturations. Achievement of this condition may be concluded from the adsorption data. In other case of hydrophobic soot the low adsorption just on the few active sites is not a good requisite for the CCN activation; such kind of soot will ask really high supersaturations to become Kelvin activated. The further measurements to prove this conclusion are required.

The concept of quantification of water uptake is assumed to be useful for understanding ice nucleation on soot particles since water-soot interaction is the first step before freezing in any atmospheric systems, whenever in the cooling plume or the background atmosphere. The amount of water on soot particles and freezing of adsorbed water may depend on temperature. But if surface water is remaining unfrozen at low temperatures the mechanism of water uptake and water distribution over the surface may be concluded from the concept of quantification resulting in the assumption what extend of soot hydrophilicity is preferable for ice nucleation.

References.
O B Popovicheva, N.M. Persiantseva, V. Tishkova, N.K. Shonija, N.A. Zubareva Quantification of water uptake by soot particles. 2008 Environ. Res. Lett. 3 025009 (12pp), doi: 10.1088/1748-9326/3/2/025009.

WATER INTERACTIONS with COMBUSTION PARTICLES

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**Soot is a product of incomplete burning of hydrocarbons**

EC, OC + inorganics

morphology
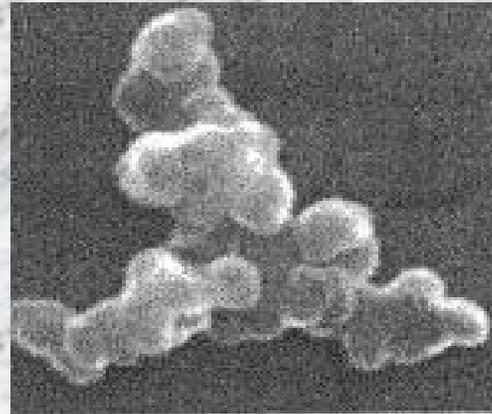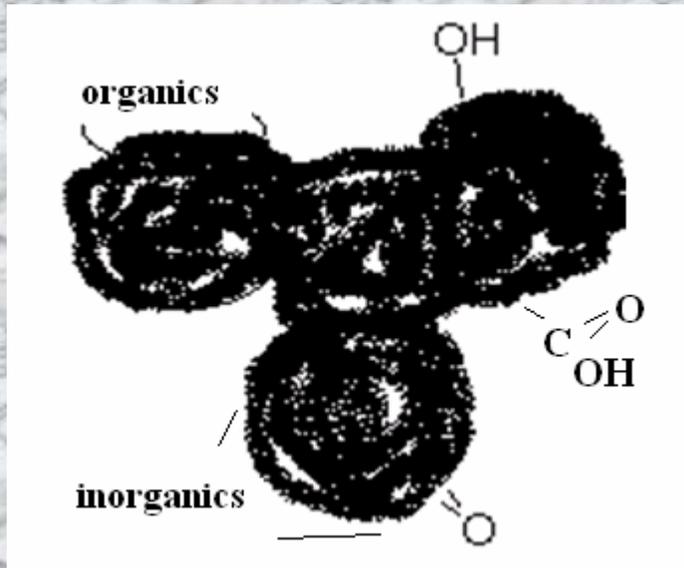
soot agglomerates of primary particles 35-50 нм

100nm

Mag = 92.87 K X
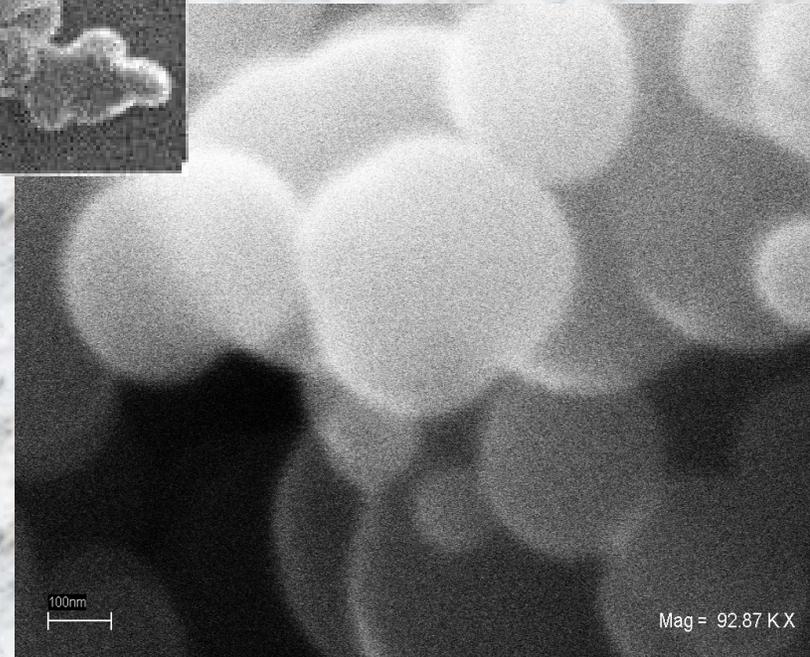
Combustion particles in atmosphere:
## typical features

microstructure
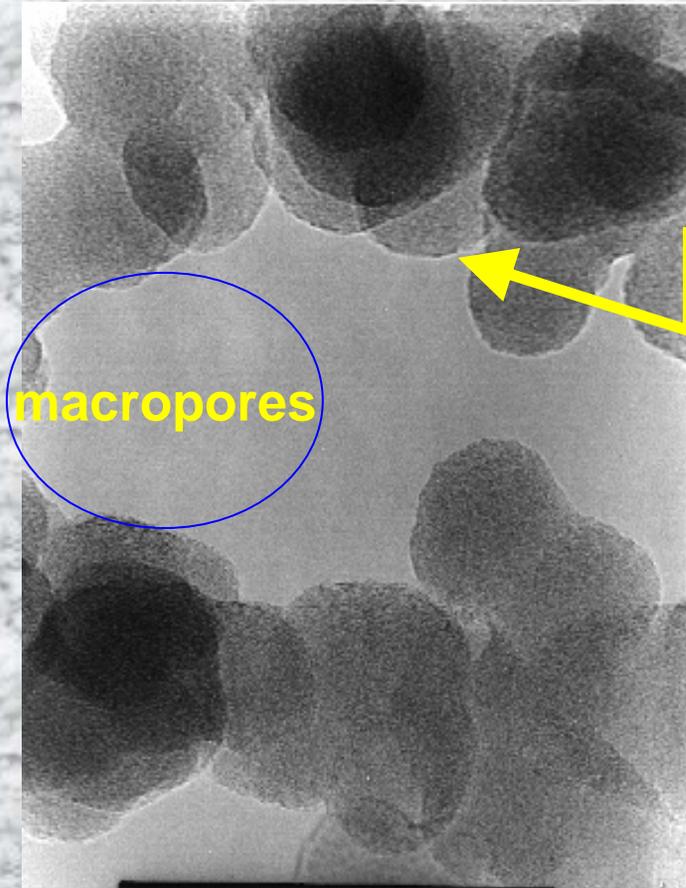
macropores

mesopores

micropores

0,142 nm

~ 0,35 nm
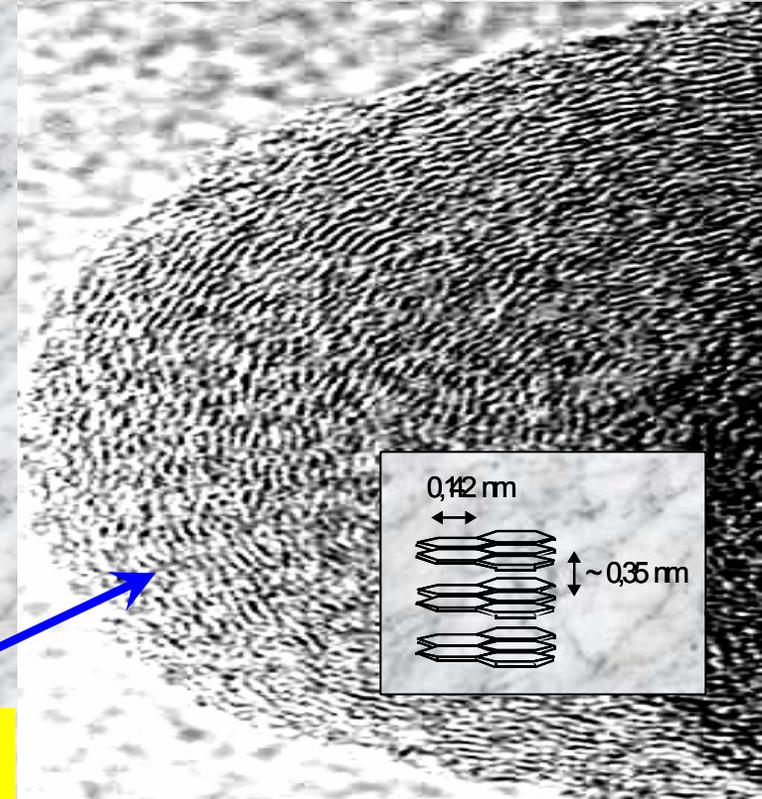
microcrystalline of graphite

Fundamentals of water adsorption on soot
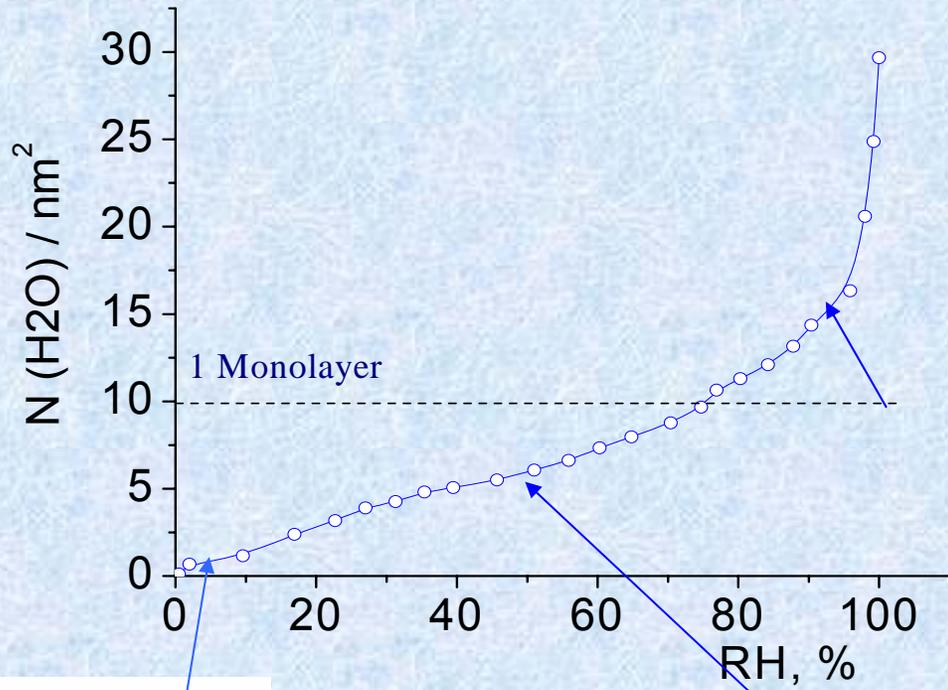
- **first water molecules adsorb on active sites**
- **adsorbed molecules act as secondary sites for further adsorption : cluster formation**
- **fluid-fluid cooperative effect is unique for black carbons**

N (H2O) / nm^2 vs RH, %

1 Monolayer

active site

OH

O = C
OH

C = O
OH
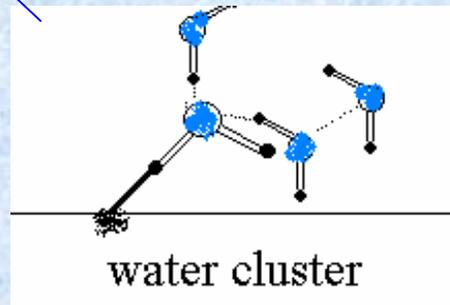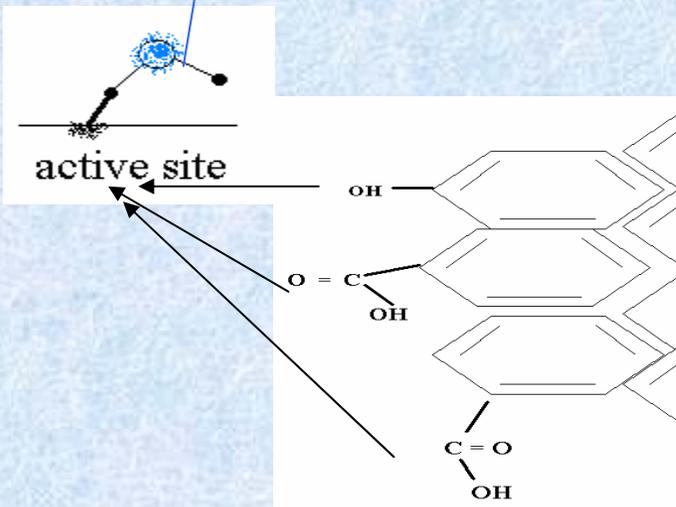
water cluster

Fundamentals of water adsorption on microporous soot

supermicropores

micropore

2 nm

0.4 nm

1 Monolayer

N(H20) / nm²

RH, %
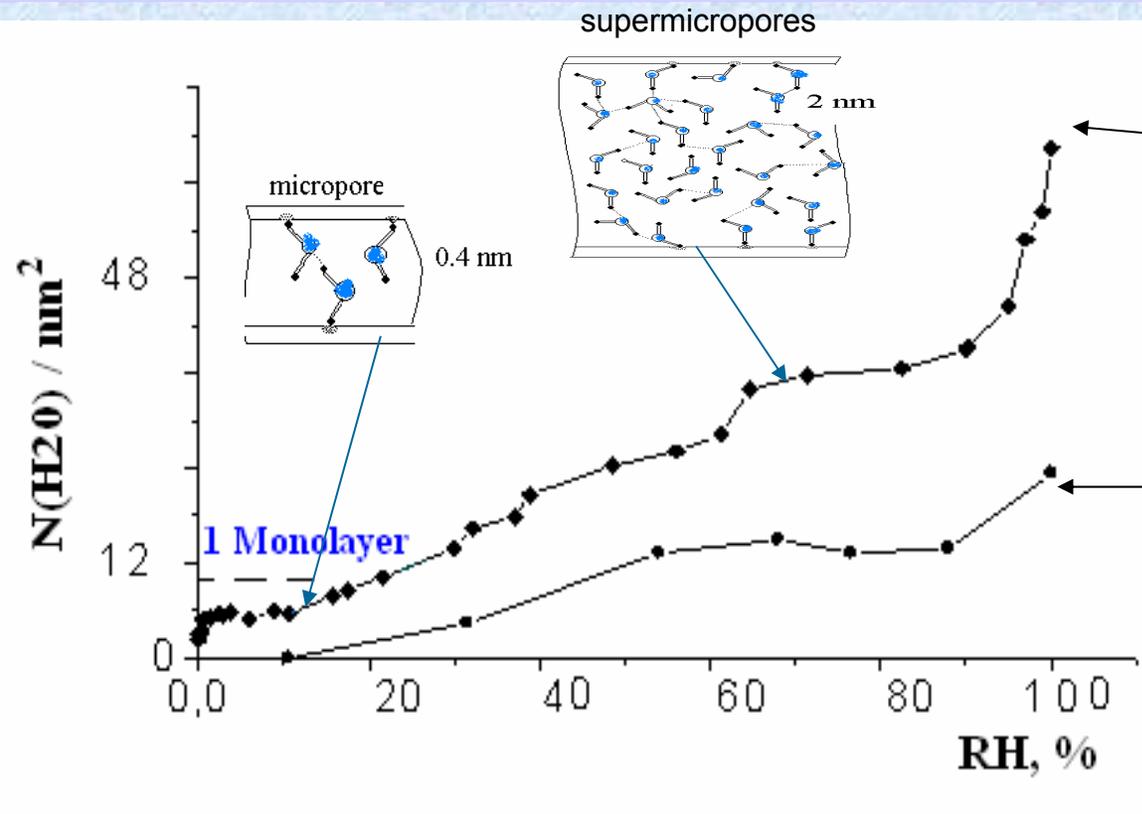
Microporous soot: cleaning procedure:

200⁰C, 10h, 10⁻³ torr

Non- microporous soot
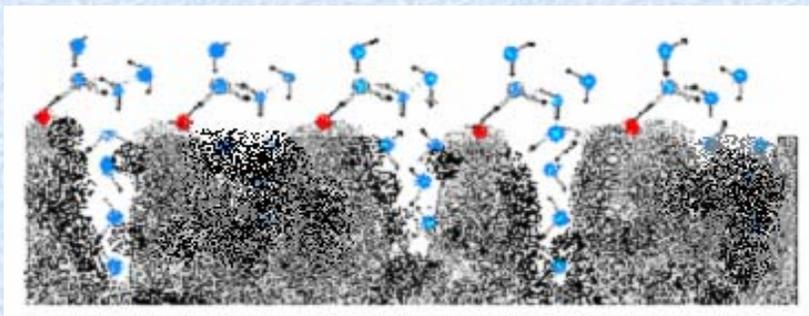
micropore filling increases the water adsorption

Cluster confluence

r=50 nm

**water film
extended over surface**

r =10 nm

active site
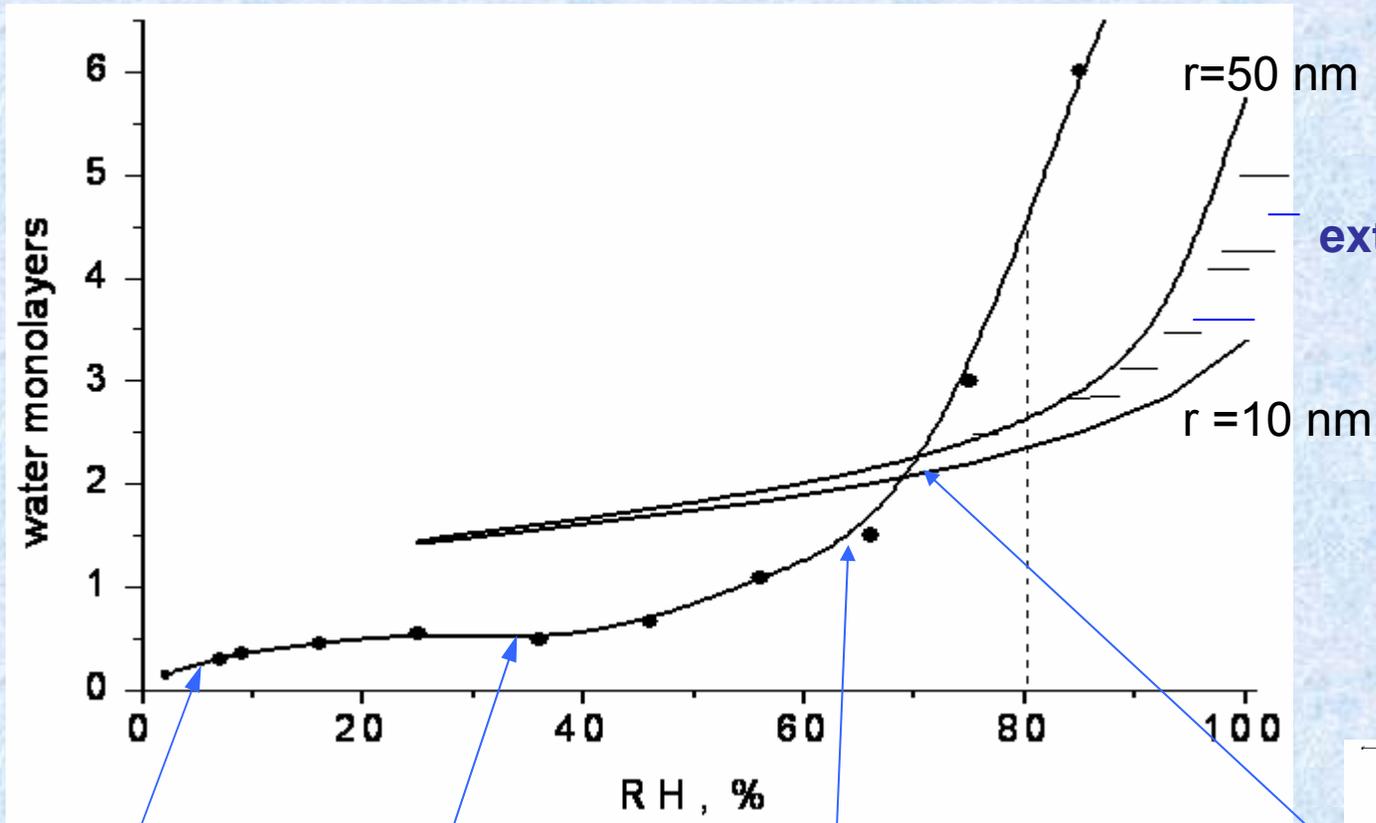
water cluster

water cluster confluence

water film extended over surface

Water film extended over surface

Thermodynamics of thin film on the surface:
Helsi-Hill equation for curved surface

$$\ln(p_s / p) = b/\theta^3 - W/RT$$

θ - adsorption coverage (in monolayers),
W - bending energy,
b - constant defined as

$$b = 2.5 V \sigma / RTd,$$

V - mole volume
σ - surface tension,
d - diameter of adsorbate molecule.

Kelvin equation for convex surface,
W is presented as:

$$W = 2 \frac{V \sigma}{r}$$

For water film   Berezin et al, RCB, 1998

$$\ln(p_s / p) = 4.34/\theta^3 - 1.08/r(nm)$$

water monolayers

water monolayers

RH, %
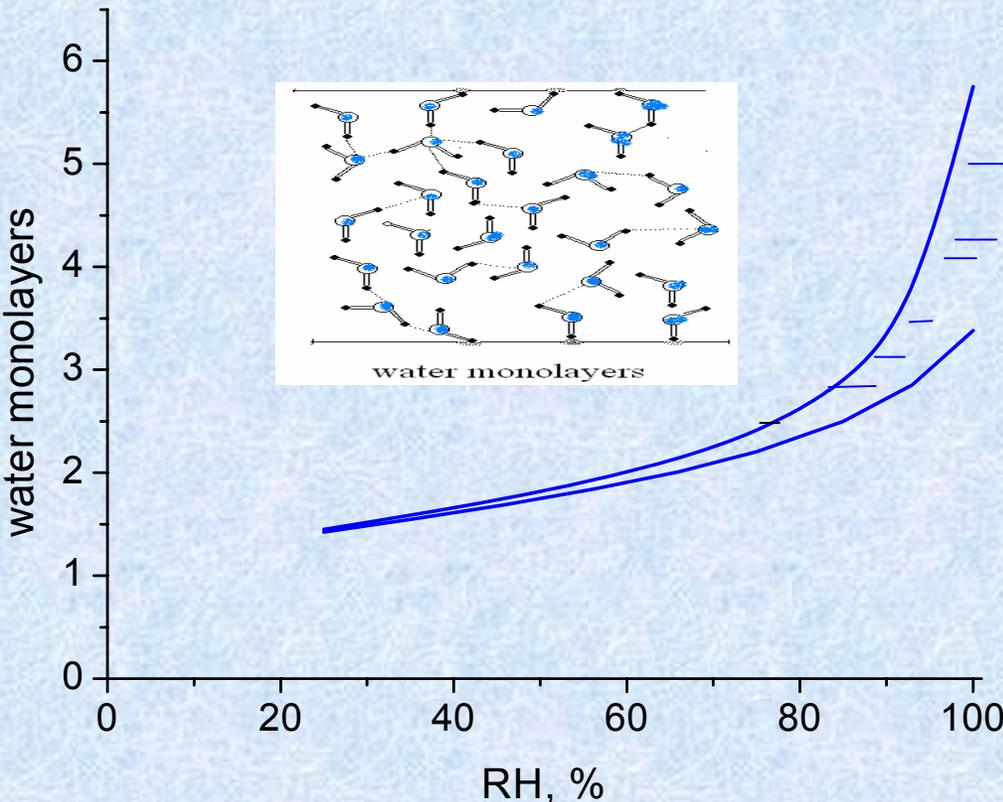
CONCEPT of QUANTIFICATION
of water uptake for non-hygroscopic soot

hydrophobic and hydrophilic soots
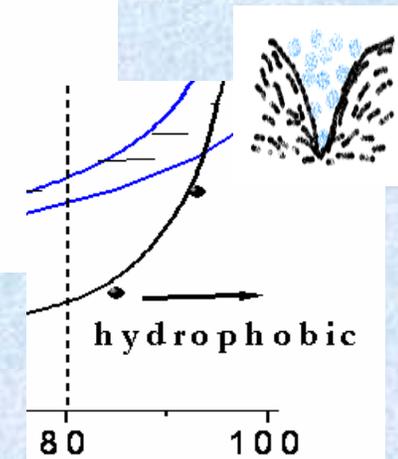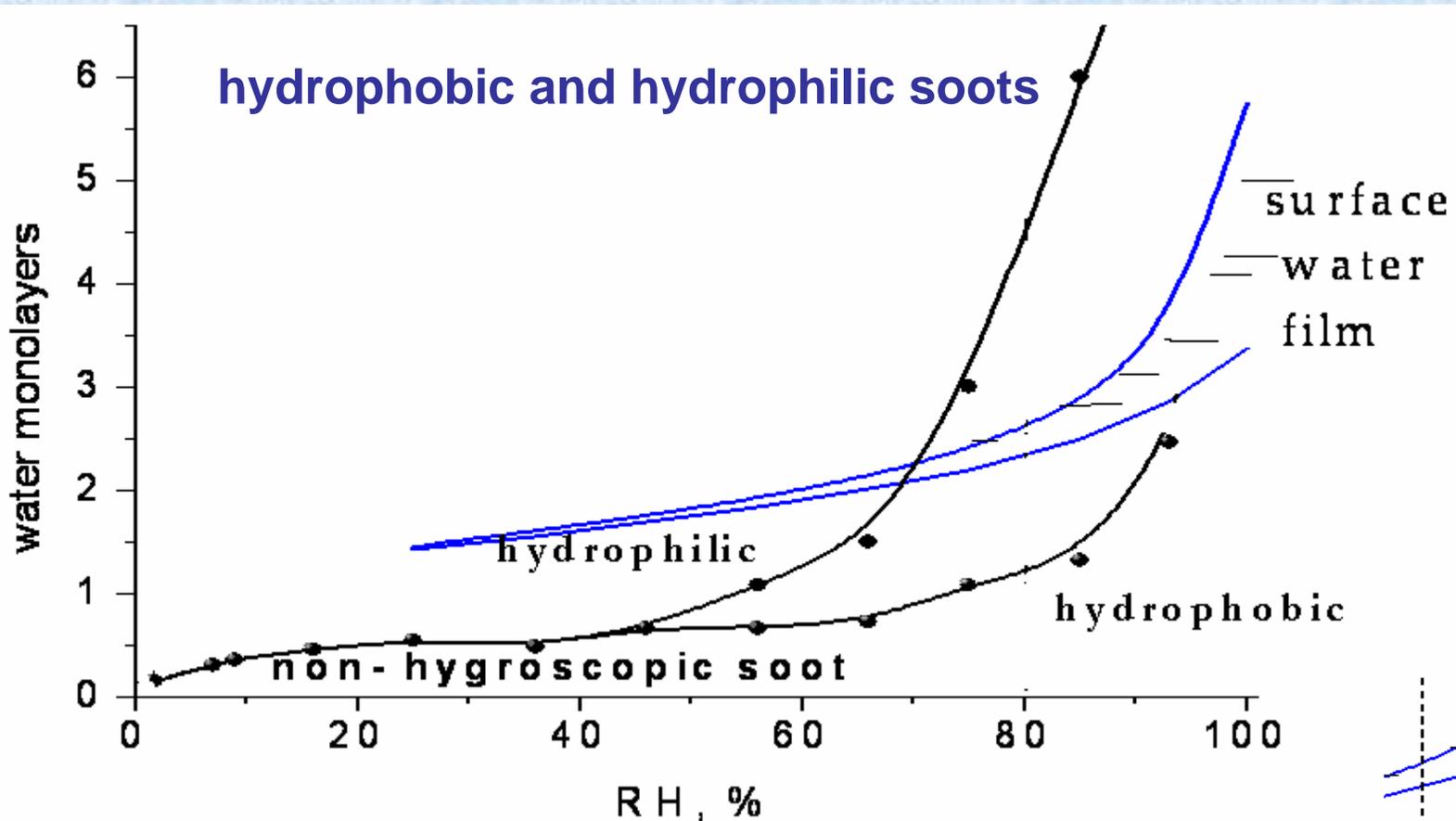
Fundamentals of water absorption on hygroscopic soot

Large water soluble fraction (WSF) on the surface
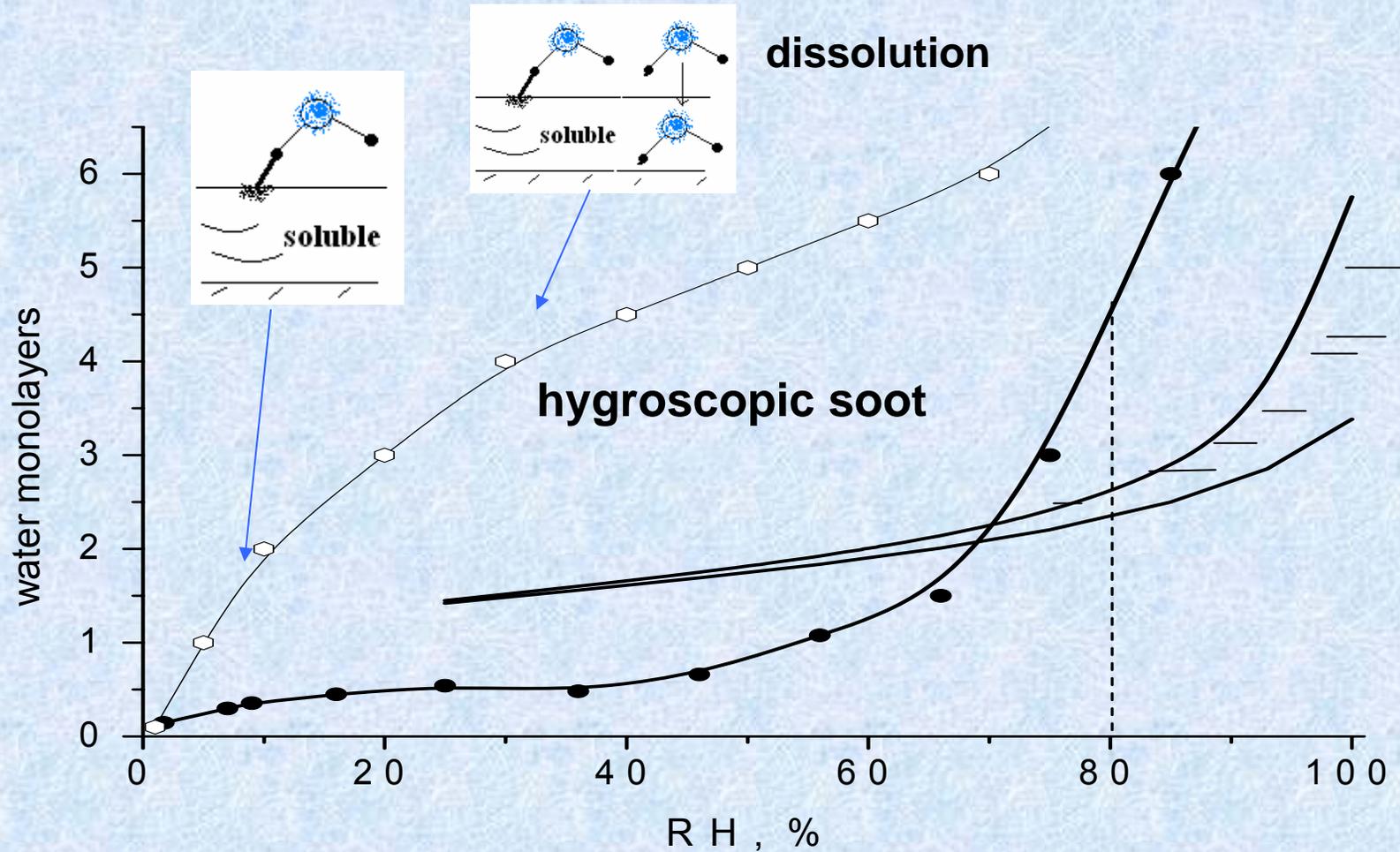
WATER UPTAKE on laboratory-made soots

commercial soots

artificial black carbon

hydrocarbon combustion
from different burners: diffusion and premixed flame

Gaseous fuel
•propane
•methane
•acetylene

Liquid fuel
•Hexane, octane, decane
•Lantern kerosene
• aviation kerosene : A-fuel, TC1
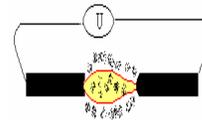
Spark discharge Palas soot

Combustion Aerosol STandard Soot CAST burner
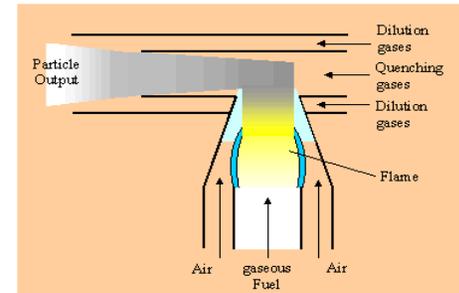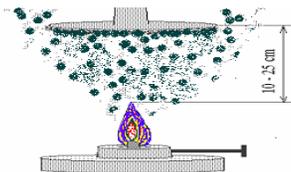
Methodic of water adsorption measurements

## Water uptake

gravimetry
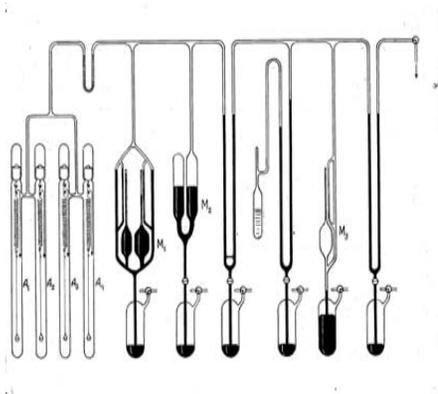
**Vacuum setup
McBein scales**
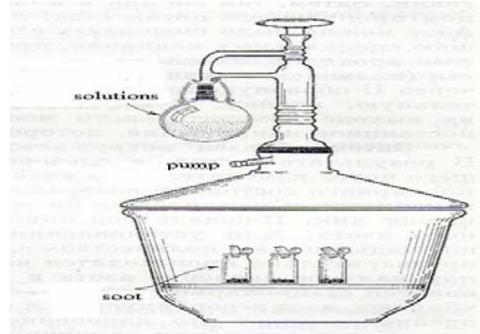
Exicator setup

Surface area

N$_2$ adsorption

Functional groups

FTIR
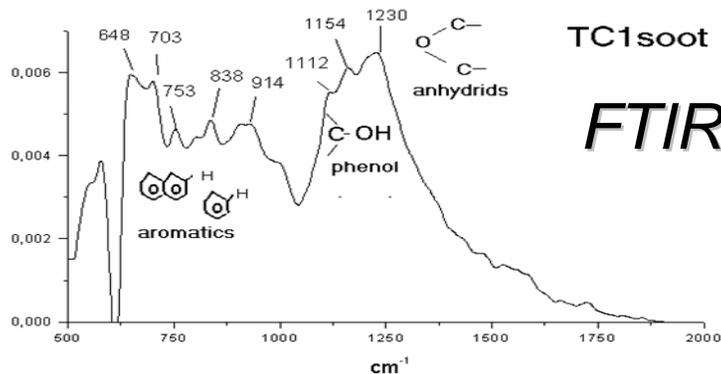
Water soluble fraction

water extract

Classification of laboratory-made soots

hydrophobic soots

_surface
water
film

Thermal soot
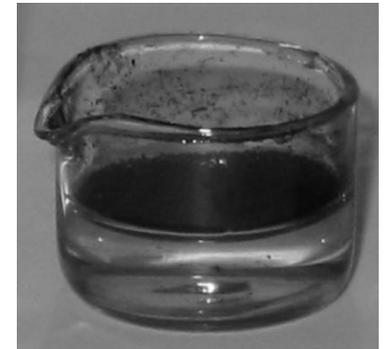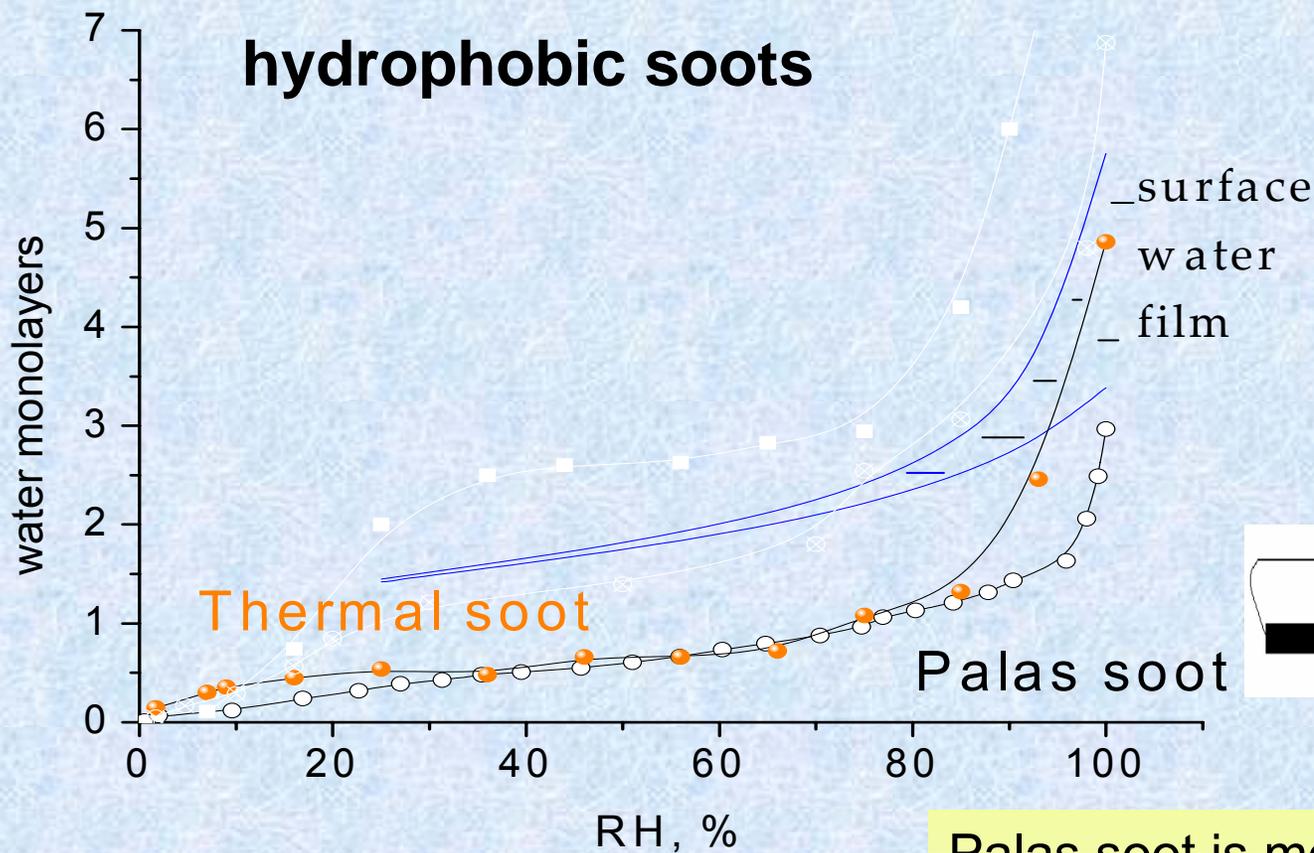
Palas soot

Palas soot is mostly EC with surface groups of carboxyl, carbonyl, phenols, polyaromatics and hydroxyl.
- negligible WSF.

Classification of laboratory-made soots

hydrophilic soots

water monolayers

C A S T , O C 2 7 %

C A S T , O C 4 %

s u r f a c e
w a t e r
f i l m

propane fuel

R H , %
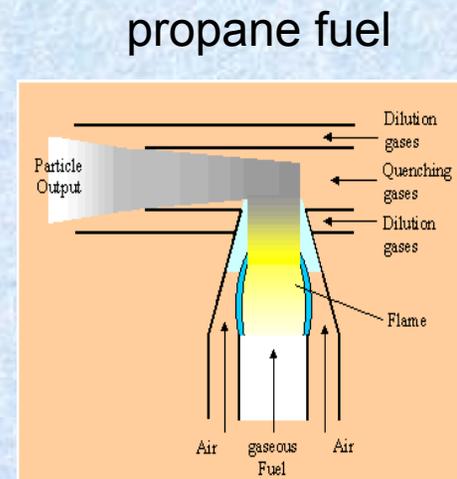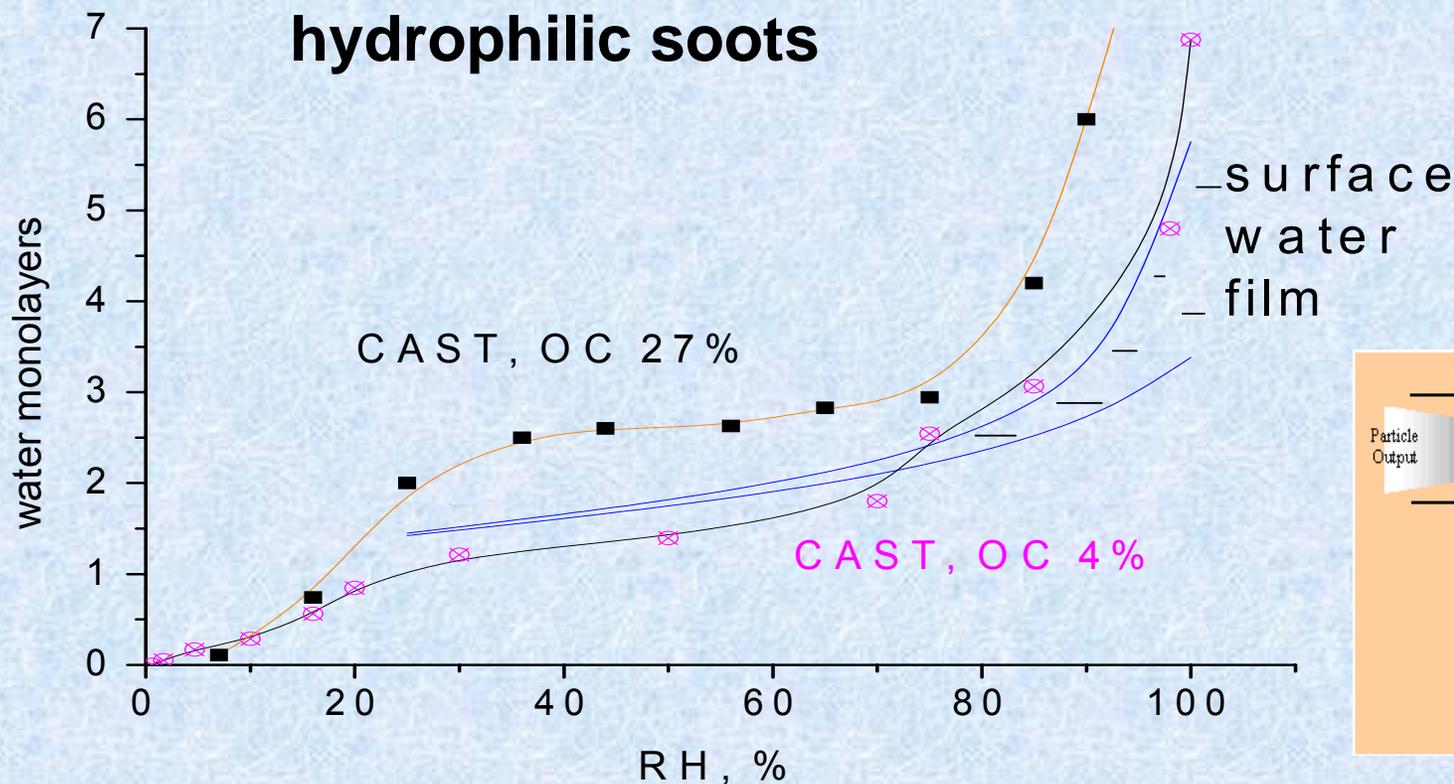
CAST soot with surface groups of carboxyl, carbonyl, and hydroxyl.
-   WSF ≈ 1%.

Classification of original soots

hygroscopic soot

Aircraft engine soot

**water monolayers** (y-axis): 2, 4, 6, 8, 10

RH, % (x-axis): 0, 20, 40, 60, 80, 100

surface water film
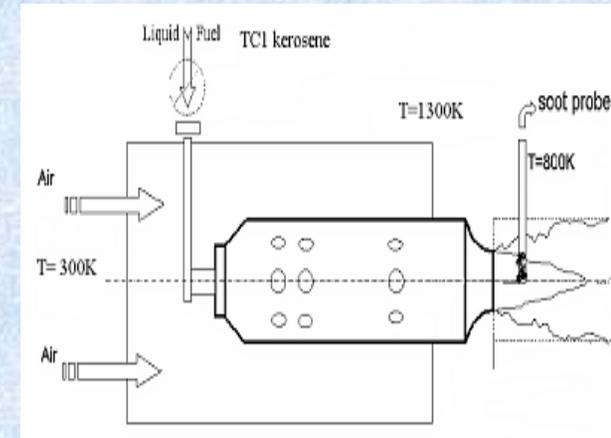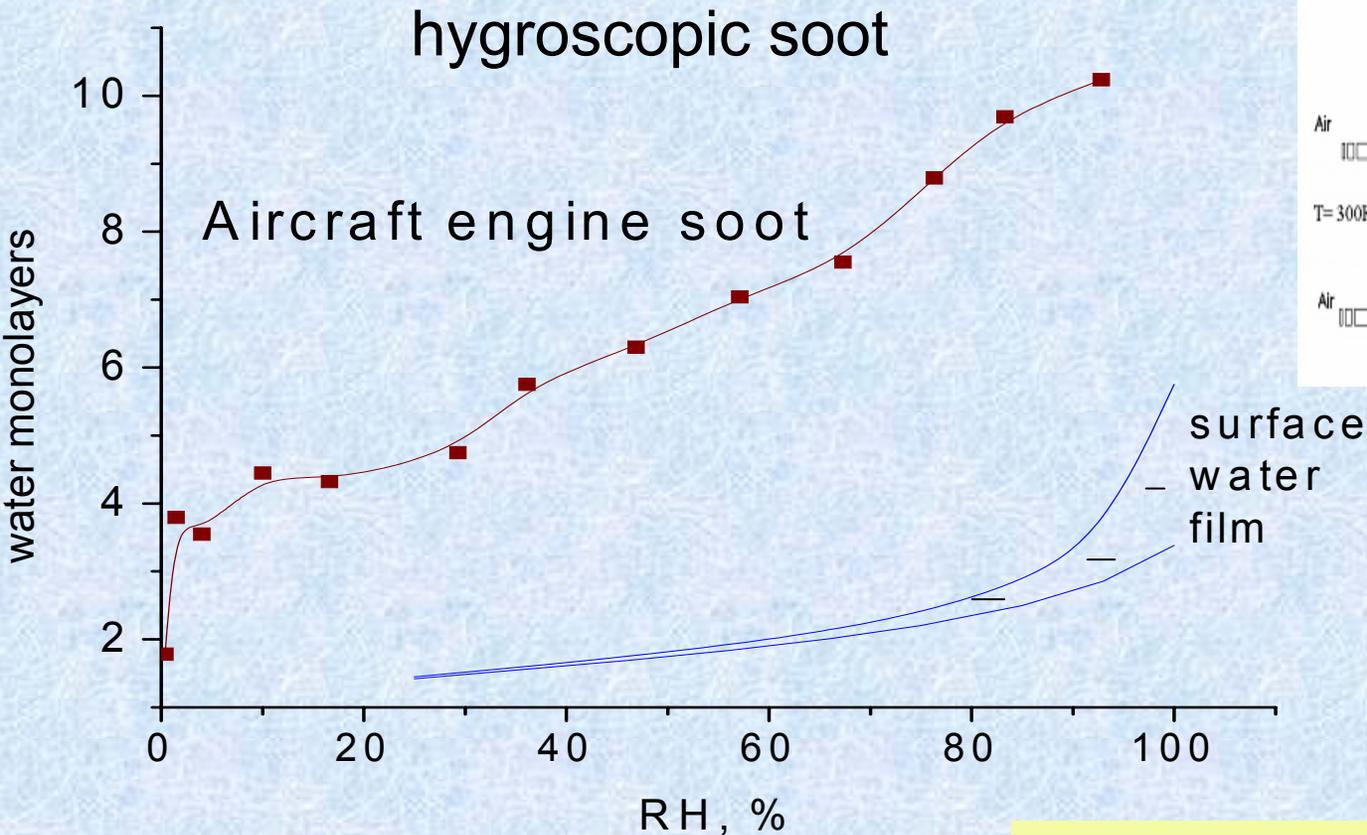
- gas turbine engine
- aviation TC1 kerosene
- cruise operation

AEC contains sulfate ion HSO4- surface functional groups
-13.5 wt% of water soluble compounds

hygroscopic soot

ship emission residuals

ship exhaust residuals

aircraft engine soot
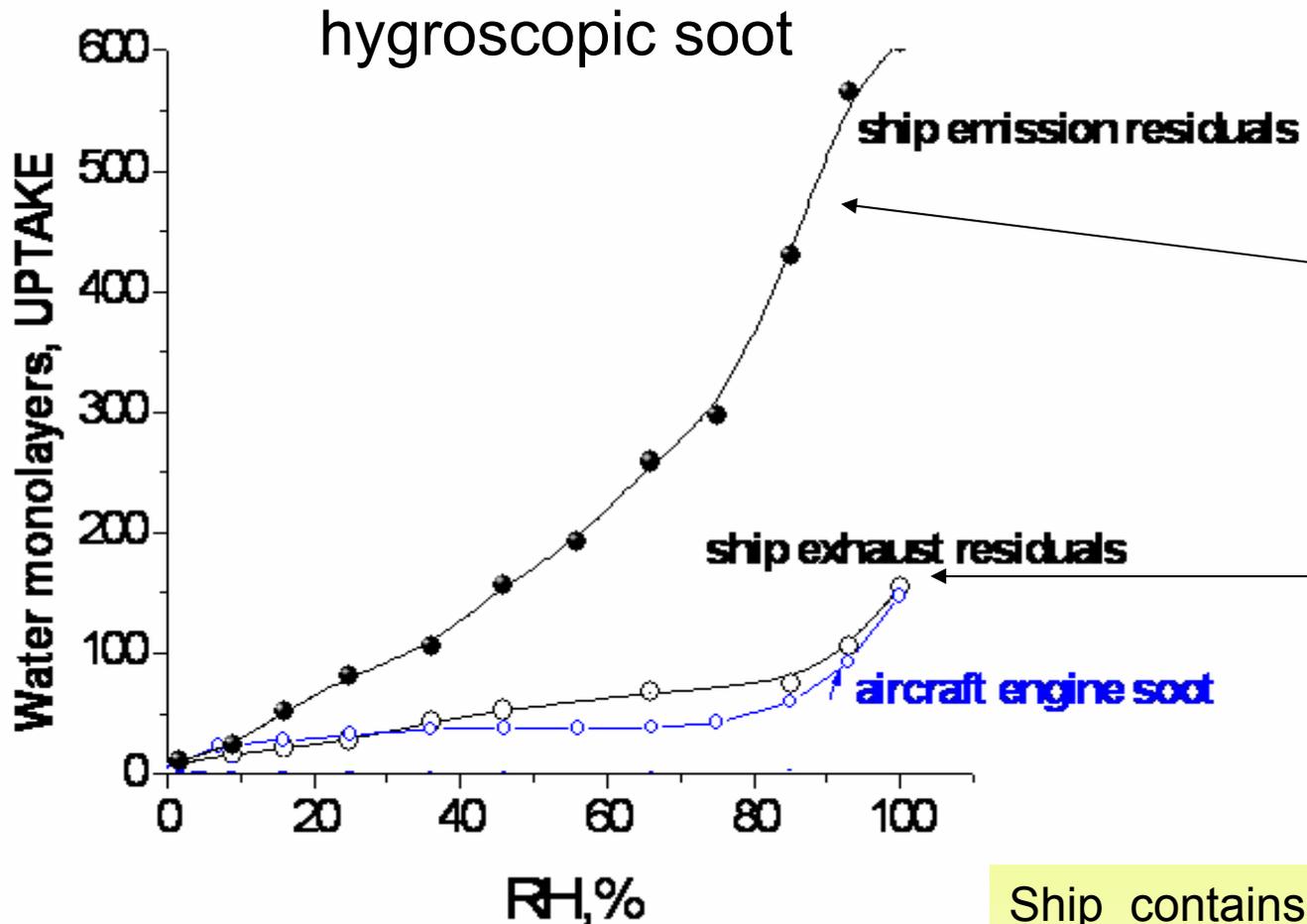
- heavy marine oil
- diesel engine

Ship contains organic sulfate surface functional groups
- up to 44 wt% water soluble
                                compounds

Conclusions:

❖ concept of quantification of water interaction
   with combustion particles is developed to separate
    hydrophobic, hydrophilic (non-hygroscopic)
                                        and hygroscopic soots.

❖ laboratory-made combustions soots are
                              almost hydrophobic/hydrophilic.

❖ original engine soots (gas turbine, diesel engine)
                                  are hygroscopic.

Quantification of water uptake by soot particles
O B Popovicheva *et al* 2008 *Environ. Res. Lett.* **3** 025009 (12pp)
doi: 10.1088/1748-9326/3/2/025009