

Quantification of water uptake by combustion (soot) particles

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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. Gravimetric 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 humidities, 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 (*absorption mechanism*) and the water molecule adsorption on active sites (*adsorption 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 to suggest 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 hydrophilicity 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.

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Quantification of water uptake by soot particles. 2008 Environ. Res. Lett. 3 025009
(12pp), doi: 10.1088/1748-9326/3/2/025009.

QUANTIFICATION OF WATER UPTAKE BY COMBUSTION (SOOT) PARTICLES

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Soot in atmospheric studies

Carbonaceous (soot) aerosols emission from transport systems, industry, biomass burning and its indirect effect on the atmosphere is currently acknowledged to be the largest source of uncertainties in understanding the anthropogenic aerosol impact on the global climate. The main reason is the significant role playing by soot aerosol in cloud formation, from one side, and a deep lack in the knowledge of water uptake by original soot particles, from the other side. It was recently concluded that soot appears to be the most important aerosol impacting clouds formation from aviation.

Soot particles emitted into atmosphere from a great variety of combustion sources have a wide range of a natural variability, including the ability to uptake water. Soot produced in urban regions is assumed to be hydrophobic, totally black carbon (BC), and present in an external mixture until their hygroscopic quality change due to the condensation of water-soluble material in the atmosphere. The assumption about initial hydrophobic nature of aircraft engine-generated soot was also accepted between modelers but recent experimental studies of engine combustor particles proved the significant role of organic matter and sulfates in original soot hygroscopicity. It leads to necessity to link physico-chemical properties of emitted soot particles with soot-water interaction both for really hydrophobic and fully hydrophilic soots.

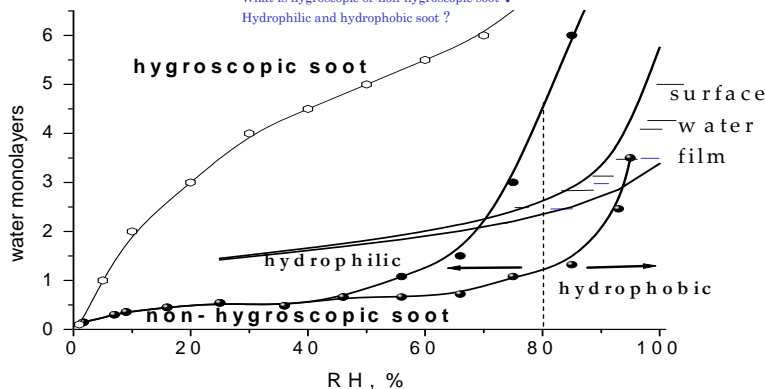
Purpose and approach

This report is devoted to the systematic analysis of the water uptake by laboratory soots proposed for atmospheric studies and the identification of water-soot interaction mechanisms in relation to surface chemistry and structure parameters.

The purpose is the definition of a *quantification measure* to separate hygroscopic and non-hygroscopic soots, and the identification of hydrophilic and hydrophobic particles between non-hygroscopic atmospheric aerosols.

CONCEPT OF QUANTIFICATION OF WATER UPTAKE

What is hygroscopic or non-hygroscopic soot?
 Hydrophilic and hydrophobic soot?



MECHANISMS OF WATER UPTAKE

Mechanism of water adsorption on hydrophilic soot

Isotherms of water film extended over surface:

Berezin et al., Russ. Chem. Bull., 47, 1879, (1998)

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

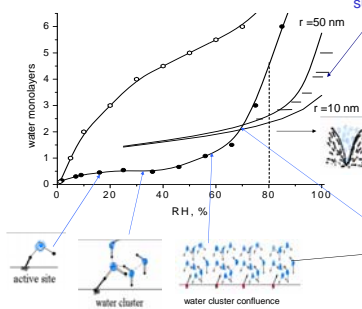
here θ is the adsorption coverage (in monolayers), calculated assuming one statistical monolayer of water estimated from an effective molecular cross-section area for the water molecule of 0.105 nm², W is the bending energy of the surface film, b is a constant defined as

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

where V and σ are the mole volume and surface tension, respectively, R is gas constant, d is a diameter of adsorbate molecule. Assuming the Kelvin equation for convex surface, W is presented as:

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

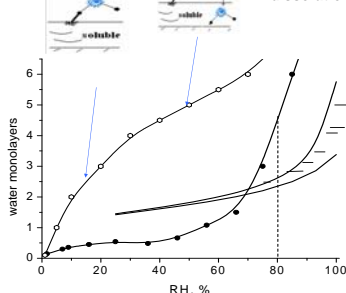
where r is the radius of the particle curvature.



water film extended over surface

Mechanism of water absorption on hygroscopic soot

dissolution



Soot is complex material composed from organic and elemental carbon with inorganic contaminations. In the limiting case of organic absence soot may be considered as black carbon. In general case two mechanisms of water interaction, namely the bulk dissolution into water soluble coverage (absorption mechanism) and the water molecule adsorption on active sites (adsorption mechanism) govern the water-soot interaction process. Comparative analysis of water uptake isotherms on soots of various composition, from black carbons to complex composites with large water-soluble fraction, allow us suggesting a *concept of quantification*. Figure demonstrates the scheme isotherm plot for this concept. The isotherm for a water film extended over the surface is suggested as a *quantification measure* which separates hygroscopic from non-hygroscopic soot. Water uptake of hygroscopic soot significantly exceeds the surface water film isotherm. If soot particles made mostly from EC and/or the organic coverage is totally water insoluble, we assume non-hygroscopic soot with isotherm less (hydrophobic soot) or approach the surface water film one (hydrophilic soot) (see Fig.).

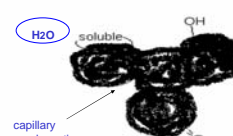
Water uptake in atmosphere

WATER UPTAKE ?



BLACK CARBON

WATER UPTAKE



Soot particles

List of key soot properties impacting water uptake

Physical properties:
 • morphology, microstructure,
 • surface area, porosity.

Chemical properties:
 • elemental composition
 • soluble and volatile fractions
 • surface functionalities
 • organic composition
 • inorganic composition
 • EC/OC ratio
 • mineral impurities

Water uptake measurements. Gravimetry.

Vacuum setup: McBein scales



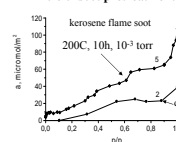
Pretreatment: soot heating 200°C, outgassing -10⁻³ torr

Excicator methodic



soot drying -10⁻³ torr

Role of soot pretreatment

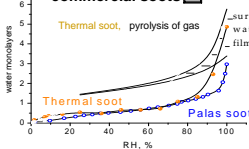


• classical pretreatment dramatically changes the surface chemistry and structure
 • original soot surface is covered by low-oxidized organics; micropores are filled by organics

WATER UPTAKE on soots: experience of original soot studies

Hydrophobic soots:

commercial soots



Laboratory-made SOOTS popular FOR ATMOSPHERIC STUDIES

artificial black carbon

Palas soot, GIG 1000 Palas generator used by Moehler, 2005 for ice nucleation studies, see in Kuznetsov et al., JAS, 2003

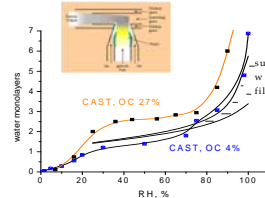
Spark discharge Palas soot

• low oxygen content,
 • low water soluble fraction, WSF ~ 0.45wt%
 • low volatility,
 • oxygen-containing active sites.

SURROGATES FOR HYDROPHOBIC INSOLUBLE SOOT IN ATMOSPHERE

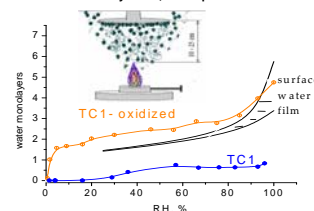
Hydrophilic soots:

Combustion Aerosol Standard Soot CAST burner



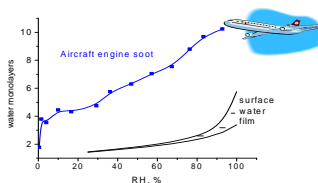
CAST soot, produced in IMK, Karlsruhe Propane burning, 27% and 4% organic carbon

Laboratory-made, oil lamp

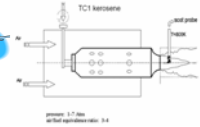


Aviation kerosene flame soot, produced MSU, Moscow TC1 aviation kerosene burning, original and oxidized see in Popovicheva et al., GRL, 2004

Hygroscopic soots:



COMBUSTION CHAMBER OF GAS TURBINE ENGINE TEST CELL SMOOKER



Aircraft engine combustor soot, produced CIAM, Moscow TC1 aviation kerosene burning, original, see in Popovicheva et al., GRL, 2004; Demirdjian et al., J. Atm.Chem., 2007

• high oxygen content in the fraction of impurities,
 • high water soluble fraction, WSF ~ 13.5 wt%, SO₂ ~ 3.5wt%
 • high volatility,
 • oxygen-containing active sites.

Water uptake measurements coupled with comprehensive soot characterization have shown that aircraft engine combustor soot and wood combustion soot are representatives of hygroscopic soots due to high water soluble fraction and multilayer water uptake. Spark discharge (Palas) soot demonstrates the features of hydrophobic black carbons because low water uptake. While TC1 kerosene flame and CAST burner soots are classified as hydrophilic between non-hygroscopic soots because water film formation on their surface before capillary condensation is happen for coalescence soot particles.

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