

Quantification of water uptake by soot particles

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Abstract

Quantification of atmospheric processes including the water uptake by soot particles of various origin, emitted from different sources, requires identification of hydrophobic and hydrophilic soot. Water uptake measurements are performed on well-characterized laboratory soots available for atmospheric studies. Comparative analysis of water adsorption isotherms on soots of various compositions allows us to suggest a *concept of quantification*. Systematic analysis demonstrates two mechanisms of water/soot interaction, namely, bulk dissolution into soot-water-soluble coverage (absorption mechanism) and water molecule adsorption on surface active sites (adsorption mechanism). The formation of water film extended over the surface is suggested as a *quantification measure* which separates hygroscopic from non-hygroscopic soot. Water uptake on hygroscopic soot takes place by the absorption mechanism: it significantly exceeds the formation of many surface layers. If soot particles are made mostly from elemental carbon and/or are covered by a water-insoluble organic layer, they are classified as non-hygroscopic. Low water adsorption on some active sites following cluster formation is a typical mechanism of water interaction with hydrophobic soot. If a water film extended over the surface is formed due to the cluster confluence it is suggested that soot is hydrophilic. A few classical models are applied for parameterization of water interactions on hydrophilic and hydrophobic soots.

Keywords: water uptake, soot particles

1. Introduction

Carbonaceous (soot) aerosol emission from transport systems, industry, domestic heating and biomass burning and its indirect effect on the atmosphere is currently acknowledged as one of the largest sources of uncertainties in understanding the anthropogenic aerosol impact on climate. On the one hand, a significant role played by soot particles in the radiative balance and cloud formation is assumed due to the high soot absorption ability and a potential to act as cloud condensation nuclei (CCN) and ice nuclei (IN). As wet deposition may be the dominant mechanism for removal of fine aerosols from the atmosphere, the CCN/IN activity of soot particles defines their cloud droplet nucleation scavenging and residence time

in the atmosphere (Hendricks *et al* 2004). On the other hand, there is a lack of knowledge of water/soot interactions, mostly because of a high natural variability of combustion particle properties in respect to the source of origin, conditions of combustion and fuel. The problem is complicated by the fact that soot emitted into the atmosphere from a great variety of combustion sources undergoes the influence of a humid and reactive environment. Thus, soot aerosols, produced in urban regions, are assumed to be hydrophobic and change their hydrophobic quality due to the condensation of ambient gases and coagulation with soluble aerosols (Riemer *et al* 2004, Okada and Hitzemberger 2001). Water-soluble compounds are found on the surface of atmospheric soot (Decesari *et al* 2001) and are assumed to be responsible for CCN activity of

combustion particles (Hagen *et al* 1989, Hallett *et al* 1989, Lammel and Novakov 1995) and aerosols aged by exposure to soluble and reactive gases (Kotzick and Niessner 1999, Decesari *et al* 2002). Atmospheric black carbon is observed to be scavenged into the cloud phase to the same extent as the bulk aerosols due to aging in the atmosphere (Cozic *et al* 2007). Hydrophilic soot particles have proved to be effectively scavenged by water droplets (Mikhailov *et al* 2001) leading to significant changing of the cloud's optical properties (Chylek and Hallett 1992, Mikhailov *et al* 2006), thus addressing the soot/cloud interaction effects.

It has been recently concluded that soot particles may be an important aerosol impacting ice cloud formation in the troposphere (Haag *et al* 2003, Cantrell and Heymsfield 2005). Numerous observations and modeling studies prove that aircraft-generated soot facilitates contrail and cirrus formation (Seinfeld 1998, IPCC 1999). 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 (DeMott *et al* 1997, Jensen and Toon 1997, Gierens 2003). However, sparse documentation exists on the ice nucleation activity of soot particles measured at the contrail and cirrus level. The lack of experimental data on the hygroscopicity of original soot from aircraft engines led investigators to an assumption about the initial hydrophobicity of emitted soot and its activation by plume processing (Kärcher *et al* 1996). But recent laboratory studies of aircraft engine-generated soot proved the significant role played by surface sulfates and organic compounds in original soot hydrophilicity and CCN activity (Popovicheva *et al* 2004b, Petzold *et al* 2005). Finally, global climate models predict the significant aviation impact on cloudiness and climate assuming the high CCN/IN activity of aircraft-generated soot (Hendricks *et al* 2004, 2005) leaving the problem of its great uncertainty for future studies (Kärcher *et al* 2007).

Long-term recommended research needs include the requirements for the development of new concepts with respect to soot impacts on CCN and ice cloud formation (Wuebbles *et al* 2007). The first need is the quantification of water uptake by soot aerosols since the present atmospheric studies remain relatively empirical until a *quantification measure* of the extent of soot hydrophilicity is defined. In colloid science a wetting parameter (contact angle of a water droplet on the surface, α , defines a hydrophobic substrate if $\alpha > 90^\circ$ or a hydrophilic one if $\alpha < 90^\circ$). But from the cloud physics point of view this macroscopic parameter cannot be a criterion for identification of hydrophobic or hydrophilic soot particles since, for $\alpha \geq 90^\circ$, very high critical saturations, $S_c \gg 1\%$, are needed for CCN and IN formation (Pruppacher and Klett 1978, chapter 9). However, a literature review shows the high variability in the CCN and IN activity of different soots emitted from laboratory and original combustion sources (Hallett *et al* 1989, Hagen *et al* 1989, Diehl and Mitra 1998, DeMott *et al* 1999, Moehler *et al* 2005b, 2005a).

Moreover, in cloud physics the hygroscopicity is always associated with soluble aerosols which are active as CCN. It follows from Koehler's theory that the fraction of water-soluble compounds, ε , in the particle coverage may decrease

S_c (Pruppacher and Klett 1978): therefore ε may be proposed as a measure of soot hygroscopicity. But we should take into account that water-insoluble particles are also assumed to serve as CCN with respect to Kelvin activation if they are wettable (Pruppacher and Klett 1978, chapter 9). But it is a case of $\varepsilon \rightarrow 0$. If soot particles are insoluble but wettable, what surface characteristics do they have? The answer to this question should be found by analyzing the water interaction mechanism at the microscopic level.

In adsorption science, the high fraction of the surface area covered by adsorbed water is proposed as a criterion for hydrophilicity (Naono and Nakuman 1991). A hypothetical statistic water monolayer is assumed by Carrott (1992) as a reference for characterization of the level of the surface polarity. However, due to preferable adsorption on hydrophilic active sites and the strong adsorbate–adsorbate interaction in the water–soot system, a monolayer of continuous adsorbed water cannot be formed on the hydrophobic soot surface. A water film may originate due to the cluster formation around active sites which may eventually become connected if the number of active sites is relatively high (Vartapetyan and Voloshchuk 1995, Müller *et al* 1996, Berezin *et al* 1998). The formation of water film on the soot surface releases the wetting phenomena at the microscopic level; that may present a feature of hydrophilic soot. Additionally, it may serve as the necessary condition for the Kelvin activation of a soot particle. To quantify the conditions for water film formation a comprehensive analysis of water uptake on soot particles with various surface chemical and structural properties is needed.

This paper is devoted to the systematic comparative analysis of water uptake on laboratory soots proposed for atmospheric studies and to the identification of water–soot interaction mechanisms in relation to soot composition. The purpose is to define a *quantification measure* for the separation between hygroscopic and non-hygroscopic soots and for the identification of hydrophilic and hydrophobic particles within non-hygroscopic atmospheric aerosols. A few classical water adsorption models are applied for parameterization and quantitative comparison.

2. Theoretical part

2.1. Theories of mono- and multilayer adsorption

The adsorption behavior of a solid is generally characterized by a plot of the amount of gas adsorbed as a function of the gas pressure at constant temperature (adsorption isotherm). In the simplest Langmuir model the adsorbed film is assumed to be just one monolayer, owing to the very short range of intermolecular forces and the negligible interaction between adsorbate molecules (Brunauer *et al* 1967, Gregg and Sing 1982). The assumption that all adsorption sites on the surface are equivalent to each other leads to a famous Langmuir isotherm for the dependence of the amount of vapor adsorbed a on pressure p :

$$a = \frac{a_m K p}{(1 + K p)}, \quad (1)$$

where a_m is the monolayer coverage and K is a constant for the given temperature and adsorbing material. The BET theory

extends the Langmuir model to include multilayer adsorption and assumes that (1) each molecule adsorbed in a particular layer is a possible site for adsorption of a molecule in the next layer, (2) no horizontal interactions between adsorbed molecules, (3) the heat of adsorption is the same for all molecules in any given adsorbed layer, and (4) the heat of adsorption is equal to the latent heat of evaporation for all adsorbed layers except the first one (Brunauer *et al* 1967). The BET equation is written as

$$a = \frac{a_m C p / p_s}{(1 - p / p_s)(1 + p / p_s(C - 1))}, \quad (2)$$

where p_s is the saturation vapor pressure for vapor being adsorbed and C is a constant of adsorbent–adsorbate interaction. The BET equation (2) is very widely used for surface area estimations by determining a_m . However, usually it treats the adsorption data in the range of p/p_s , from 0.05 to 0.35, and at $C > 10$. Moreover, in the limiting case $p/p_s \rightarrow 0$ the correct equation should be reduced to the ideal gas equation and as p/p_s approaches unity the Gibbs integral should not be diverged (that is not the case for a BET equation).

Isirikyan and Kiselev (1962) considered the interaction between adsorbed molecules in the first layer. However, three parameters introduced significantly complicate using their equation. The lattice theory of Ono and Kondo is used by Aranovich (1988) for improvement of the BET theory since it allows the vertical adsorbate–adsorbate interactions to be taken into account. The two-parameter Aranovich equation

$$a = \frac{a_m C p / p_s}{(1 + C p / p_s)(1 - p / p_s)^{0.5}} \quad (3)$$

provides qualitatively corrected results in the limiting cases and successfully simulates multilayer adsorption on various solids (Aranovich and Donohue 1995), extending the range for the equation’s application up to $p/p_s \sim 0.7$ – 0.8 .

2.2. Fundamentals of water interaction with black carbon

The classical model of black carbon proposes it to be composed of misaligned graphite platelets that form a nanoporous network in which oxygenated functional groups are contained (Marsh 1989). The peculiar nature of water adsorption on black carbon is related to the relatively low dispersion energy between water molecules and graphite platelets. According to the fundamental mechanism (Dubinin 1980, Gregg and Sing 1982 chapter 5, Kiselev *et al* 1961) the initial water adsorption takes place on oxygen-containing groups which may act as primary adsorption sites; this is opposite to simple non-polar molecules, like nitrogen or benzene, which adsorb on graphite platelets forming a two-dimensional monolayer. At low relative pressures, the amount of water adsorbed is determined by the total density of primary adsorption sites (Henry’s law); this amount gives the value of a_m in equations (1)–(3). At higher relative pressures, hydrogen bonding between free and adsorbed water occurs, the primary adsorbed water molecules act as nucleation sites for further adsorption of water and the formation of three-dimensional clusters begins (Müller *et al* 1996, Collignon *et al* 2005). Both the density and geometrical

arrangement of the active sites have a pronounced effect on the value of p_c/p_s at which water clusters bridge between them (fluid–fluid cooperative effect) producing a film of bonded water molecules extended over the surface (Vartapetyan and Voloshchuk 1995, Müller *et al* 1996).

The secondary water adsorption mechanism, realized as the fluid–fluid cooperative effect, is unique for the water–carbon system, it is not considered by the BET theory. Cooperative multi-molecular sorption (CMMS) theory (Rutherford 2003) has been elaborated to account for the influence of the adsorbed molecule promoting the entry of other molecules to adjacent sites. The CMMS theory is employed to account for the type II, III, V and hybrid isotherms (in the BET classification scheme) for water–carbon systems (Rutherford 2003, Rutherford and Coons 2004).

The three-parameter Aranovich equation, instead of the two-parameter equation (3), has been developed by Aranovich (1988) to take into account the adsorbate–adsorbate interactions that are a specific feature of water/soot interaction. It was noted that equation (3) may also still be applied for the strong adsorbate–adsorbate interaction case in consideration of 15% accuracy.

The model of ‘long-winded’ fluid formation has been proposed by Berezin *et al* (1998) to describe the water cluster confluence and liquid water phase origin on carbonaceous adsorbents. It is based on the thermodynamic analysis of the multilayer water adsorption which shows the existence of the fluid film long-winded by the surface forces (Berezin 1995). This film may be formed at a relative pressure not less than the threshold one, $p/p_s = 0.178$, at $T = 293$ K. Halsey–Hill’s equation for the long-winded fluid film was used for obtaining the isotherm equation, taking into account its correction for the curvature of particles (Berezin 1995):

$$\ln(p_s/p) = b/\theta^3 - W/RT, \quad (4)$$

where θ is an adsorption coverage (in monolayers) calculated assuming one statistical monolayer of water estimated from an effective molecular cross-sectional area for the water molecule of 0.105 nm^2 , 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 the gas constant and d is the diameter of the adsorbate molecule. Assuming the Kelvin equation for a convex surface, W is presented as

$$W = 2 \frac{V\sigma}{r}, \quad (5)$$

where r is the radius of the particle curvature. Finally, for a water film extended over a convex surface we have the isotherm equation

$$\ln(p_s/p) = 4.34/\theta^3 - 1.08/r \text{ (nm)} \quad (6)$$

that may be used for inferring the estimation for p/p_s when water clusters bridge between each other, producing a large film extended over the surface of a soot particle with radius r .

2.3. Water uptake on combustion particles

Because of the incomplete combustion of fuel and the specific mechanism of particle formation, exhaust soot appears as a complex material of micro-mesoporous structure composed from elemental and organic carbon. Therefore, the understanding of water interaction with real combustion particles is still rudimentary. Only in the limiting case of the organic coverage absence the soot entity may be considered by the classical model for black carbon. If the soot coverage thickness exceeds a few monolayers and coverage matter consists (even partially) of water-soluble materials ($\epsilon > 0$) the water uptake should be treated in terms of the bulk dissolution while adsorption should be assumed for the interaction with the surface active sites and with sites inside the water-soluble coverage (volume sites). The general model of the 'dual sorption' should be useful in the case (Paul and Koros 1976) where both absorption and permeation processes of vapor in soluble material are taken into account. Then, the concentration of water molecules in the soot coverage a is a sum of the dissolved molecules and molecules absorbed on active sites, determined by Henry's law and from the Langmuir isotherm, similar to equation (1):

$$a = K_d p + \frac{a_v K p}{(1 + K p)}, \quad (7)$$

where K_d is a dissolution coefficient and a_v is the equilibrium concentration of vapor determined by volume adsorption sites (sorption capacity). The models accounting for water uptake and hygroscopic growth by soluble atmospheric aerosols are presently being elaborated (Metzger and Levievel 2007) but they assume knowledge of the solute composition. However, there is always a problem with the identification of compounds in the surface coverage of combustion particles (Fraser *et al* 1999).

Micropores between the graphite platelets inside a soot particle and mesopores in the interparticle cavities of soot agglomerates create the soot porous structure which may impact water uptake in accordance with the pore size and volume. A general theory for adsorption of self-associated molecules in micropore structures was developed by Talu and Meunier (1996). It has been found that soot micropores may impact initial water uptake (Müller *et al* 1996, Persiantseva *et al* 2004). Even if a single water molecule does not have sufficient dispersive force to adsorb inside the micropore, a cluster of a few water molecules produces sufficient forces to stay within the micropore (Do and Do 2000). Micropore filling by water may lead to swelling of the soot particles (Popovicheva *et al* 2000, 2008). Developed microporosity of active carbons changes the classical type III isotherm to the S-shaped isotherm that is well described by Dubinin and Astakhov's equation (Stoekli *et al* 1994). Capillary condensation in the mesopores at $p/p_s > 0.8$ shows a hysteresis loop (Pierce and Smith 1950).

Finally, because of the complicated chemistry and various microstructures of the original combustion particles, a universal model of the water/soot interaction is absent. But fundamentals of the classical models may help us to perform the quantitative comparison analysis and to distinguish the different mechanisms of water interaction with soot.

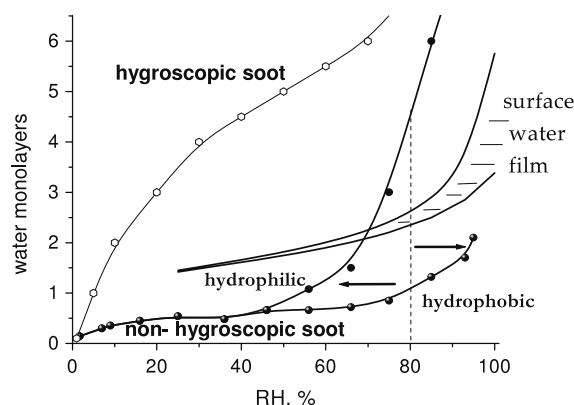


Figure 1. Scheme isotherm plot for a *concept of quantification*. The area of existence for water film on the surface is indicated, with low and high boundaries for 5 nm and 125 radius particles, respectively.

3. Concept of quantification

Identification of water uptake mechanisms and comparative analysis of isotherms for soots of various compositions, from pure elemental carbon to complex composites with large water-soluble coverage, allows us to make a quantification of water uptake. Figure 1 presents the scheme isotherm plot for demonstration of a *concept of quantification*. For clear atmospheric applications the dependence on the relative humidity $RH = p/p_s * 100\%$ is presented. The isotherms of the surface water film (4) are plotted for the radii of soot primary particles of 5 and 125 nm (low and high boundaries of marked area, respectively). They are suggested as a *quantification measure* which separates hygroscopic from non-hygroscopic soot. If the soot water-soluble fraction is quite large we may assume hygroscopic soot whose isotherm is higher than the one for the surface water film on particles of corresponding size. If soot particles are made mostly from elemental carbon and/or the organic coverage has low water solubility we may propose non-hygroscopic soot whose isotherm is less than or maybe just approaching the isotherm for the surface water film (see figure 1).

The number density of active sites on the surface may be a parameter for the definition of hydrophilic and hydrophobic soots within non-hygroscopic ones. The high value of a_m on the surface of hydrophilic soot leads to water cluster confluence and the formation of a water film extended over the total soot surface. Therefore, the water adsorption isotherm for hydrophilic soot should approach the isotherm (4) for the surface water film (see figure 1). To draw conclusions about the hydrophilicity of primary soot particles the surface water film should be formed at a relative humidity less than 80%, as typically the capillary condensation of water in interparticle cavities and polymolecular adsorption happens at RH higher than 80% (Gregg and Sing 1982). But the isotherm of hydrophobic soot never approaches the isotherm for the surface water film due to the low value of a_m (see figure 1); hydrophobic soot particles may be only partly covered by water molecules.

4. Experimental part

4.1. Laboratory approach

Because of the difficulties with *in situ* measurements of the water interaction with airborne soot particles, the laboratory approach is widely utilized. Various laboratory-produced soot surrogates have been introduced for atmospheric studies. Commercially available soots, namely FW1 (Lammel and Novakov 1995) and Lamp soot (DeMott *et al* 1999), were used for CCN and IN studies. Palas soot generated by spark discharge between graphite electrodes has recently become popular among researchers because of the high reproducibility of the Palas GFG 1000 generator (Kotzick and Niessner 1999, Kuznetsov *et al* 2003a, 2003b, Moehler *et al* 2005b). Combustion particles produced by burning various fuels in different burners have been proposed for hydration and wetting studies (Chughtai *et al* 1999, Alcalá-Jornod and Rossi 2004, Persiantseva *et al* 2004, Zuberi *et al* 2005) and for ice nucleation research (Moehler *et al* 2005a, Diehl and Mitra 1998). In particular, the CAST soot produced by the Combustion Aerosol STandard burner is currently a subject of intensive studies (Moehler *et al* 2005a, Salgado and Rossi 2002), as the CAST generator allows the production of soot under controlled combustion conditions. But it is obvious that one of the best soot surrogates for upper troposphere research is soot produced by a combustor of a typical gas-turbine engine operating at cruise conditions (Popovicheva *et al* 2003a, 2003b, 2004b, Gysel *et al* 2003).

4.2. Set of soots for study

To perform the quantitative comparison analysis of water uptake and demonstrate the concept of quantification a *set of soots* with a large variety of compositions and structural properties is proposed in this study. It includes spark discharge Palas soot analyzed previously in Kuznetsov *et al* (2003a), (2003b), commercial thermal soot produced by pyrolysis of natural gas (Electrougly Ltd) presented in Popovicheva *et al* (2008) and laboratory-made TC1 kerosene soot produced by burning TC1 aviation kerosene in a usual oil lamp described in Popovicheva *et al* (2008). To examine the hydrophilic properties of CAST soot two samples were specially generated at IMK, Karlsruhe by burning propane at controlled flows of propane and synthetic air, namely at a C/O ratio of 0.29 and 0.4, as described in Moehler *et al* (2005a). We will call them CAST-4 and CAST-27, respectively, in correlation with the OC content found in these samples (defined below). To have the best surrogate for atmospheric applications, original aircraft engine combustor (AEC) soot produced at typical cruise combustion conditions at the background facilities (Popovicheva *et al* 2008) is included in the set of soots. Additionally, combustor soot produced by burning propane/butane fuel in a gas-turbine engine combustor (Popovicheva *et al* 2003a) is taken to be available for comparison.

4.3. Physico-chemical properties

The mean diameter of primary particles found previously by TEM analysis is presented in table 1 for general characterization. The agglomerates of CAST-4 soot particles emitted from the CAST burner for a C/O ratio of 0.29 have a count mean diameter (CMD) of about 300 nm with a sigma of 1.7. The particles of CAST-27 soot for a C/O ratio of 0.40 have a tri-model size distribution with CMD1 30 nm (sigma: 1.28) and CMD2 68 nm (sigma: 1.32) for nucleated particles and CMD3 151 nm (sigma: 1.56) for soot mode particles (Saathoff 2005). The values for CMDs are also presented in table 1. Particles of AEC soot were found to be highly heterogeneous in respect to both the size and composition (Popovicheva *et al* 2004b, 2004a, Demirdjian *et al* 2007). Therefore we separated them into two fractions: a main fraction of particle diameters 30–50 nm and a fraction of impurities with various structures of different sizes.

The specific surface area of soots is determined by the N₂ thermodesorption method with an accuracy of 5–7% (Popovicheva *et al* 2000). The elemental composition is obtained by x-ray energy-dispersive spectroscopy (XREDS) with sensitivity near 0.3 wt%, see for details Demirdjian *et al* (2007). The water-soluble mass fraction (WSF) of soot is determined after ultrasonic treatment in distilled water, filtration and evaporation. The low accuracy of this routine method for low mass, 50%, does not allow for measuring WSF for soot samples with masses less than 100 mg. Oxygen content as well as the water-soluble mass fraction is assumed to correlate with the water adsorption ability of carbonaceous adsorbents (Gregg and Sing 1982). The results of the analyses are presented in table 1. For AEC soot we should note two fractions: a main fraction consisting essentially of carbon with oxygen ~1.6 wt% and a fraction of impurities with a large amount of sulfur (up to 2 wt%), iron (up to 30 wt%) and potassium (up to 1.25 wt%).

The organic carbon (OC) with respect to total carbon (TC) content in TC1, AEC, and CAST-4 and CAST-27 soots is measured by a standard thermographic VDI 2465 method described by Moehler *et al* (2005a). Additionally, the soot volatile fraction is obtained by weighing the sample after heating at 537 K for 30 min in air; this fraction was proposed by Ohta and Okita (1984) as a good estimation of OC in soot. Because of the significant discrepancies in the organic carbon content obtained by different thermal and thermo-optic methods (Schmid 2001), it is reasonable to use this method for OC estimation. The results obtained in both measurements are presented in table 1. For AEC soot the difference is found to be still 15%.

With the purpose of identifying the functional groups responsible for the presence of active sites on the soot surface, infrared spectra were recorded for Palas soot (Kuznetsov *et al* 2003b), TC1 kerosene and combustor soots (Popovicheva *et al* 2003b). Fourier transform infrared (FTIR) spectroscopy was applied for measuring spectra of AEC soot in Popovicheva *et al* (2004b). A large variety of –CH and –CH₂ groups in aromatics and aliphatics as well as oxygen-containing functional groups such as –C=O carbonyl, carboxyl and –OH hydroxyl were found. The functional groups may create

Table 1. Physico-chemical characteristics of the *set of soots*.

Soot name	Mean diameter (nm)	Surface area (m ² g ⁻¹)	Composition (wt%)	WSF (wt%)	OC content (%)	Functional groups
Palas	6.6	308	C 100	0	~0 ^c	C=O carbonyl; -COOH carboxyl; C-O in aromatics; -OH phenolic, hydroxyl CH, CH ₂ -aliphatic
Thermal	246	10	O 0.4	0.5	0.6 ^c	Carbonyl; carboxyl; aliphatic
TC1 kerosene	57	49	C 95 O 5	0.9	2.1 ± 1.4 ^d 4 ^c	-CH in polyaromatics; carbonyl; carboxyl phenolic; hydroxyl
CAST-4	300	46	nd ^a	nd	4 ± 4 ^d	Carbonyl
CAST-27	32; 90;140	21	nd	nd	27 ± 7 ^d	Polyaromatics; carbonyl; carboxyl; hydroxyl
AEC	^b	6	C ^b O, S, Fe, K	13.5	20 ± 1.5 ^d 17 ^c	HSO ₄ ⁻ ion; organic sulfate; C=O aromatic; aliphatic; phenolic; polyaromatic
Combustor	30-50	54	C 95 O 5	2.0	nd	Polyaromatics; carboxyl; hydroxyl

^a nd non-determined.

^b Two fractions are found in AEC soot, see for details Demirdjian *et al* (2007).

^{c,d} Determined by volatility and thermographic method, respectively.

hydrogen bonds of different strengths impacting the soot hygroscopicity (Curthoius *et al* 1974). Additionally, the peaks of HSO₄⁻ ions and organic sulfates were found in the spectra of AEC soot that indicate the presence of really hydrophilic compounds on the surface of this soot.

In this work the FTIR analysis is additionally performed for CAST-4, CAST-27 and thermal soots on an Infracum FT-801 spectrometer in the range from 4000 to 400 at 4 cm⁻¹ resolution. The FTIR spectra of CAST soots for 4% and 27% of OC content are plotted in figure 2. Soot samples are mixed with KBr powder and pressed into pellets with the ratio CAST-4 : KBr = 1 : 174 and CAST-27 : KBr = 1 : 300. Different functional groups such as polyaromatics at 836 and 880 cm⁻¹, carbonyl at 1400 cm⁻¹, carboxyl at 1485, 1604 and 1629 cm⁻¹, and hydroxyl at 3201 and 3402 cm⁻¹ are observed for CAST soot containing a large amount of organics, and only the carbonyl group at 1489 cm⁻¹ is prominent on the surfaces having low organic coverage.

4.4. Water uptake measurements

Water uptake by soot, *a*, as a function of the relative humidity (RH) is measured in mmole per gram of soot by a gravimetric method proposed by Kantro *et al* (1967). To preserve the original surface chemical features we limit the sample cleaning by drying in air at a water vapor pressure of 2 × 10⁻⁵ Torr and do not use a baking treatment. The level of cleaning is controlled by repeatedly weighing the soot sample until a constant weight is attained. The accuracy of water uptake measurements is near 0.05 mmol g⁻¹. To build the absolute adsorption isotherm for comparative analysis we recalculate the *a* value into the amount of statistic monolayers (ML) assuming the measured surface area, *S* (m² g⁻¹), for a given soot. One monolayer is estimated as 1 ML ≈ *a* · 60/*S*, assuming a cross-sectional area of a water molecule of 0.105 nm².

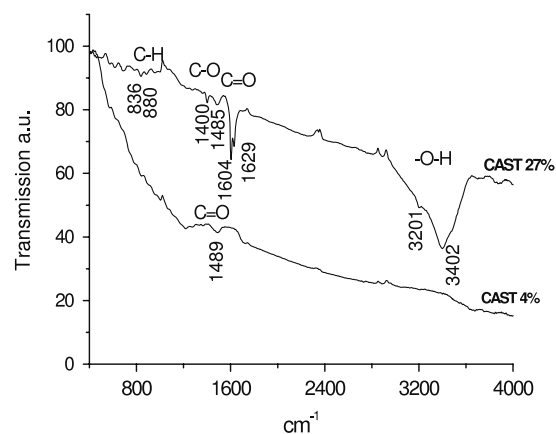


Figure 2. FTIR spectra of CAST soots with 4% and 27% of organic carbon. The peaks of intensive absorption bands, corresponding to surface functional groups, are indicated.

5. Quantification of water uptake

5.1. Hydrophobic soot

Spark discharge Palas soot is found to consist totally of elemental carbon with a negligible amount of water-soluble material on the surface but still having some functional groups responsible for the interaction with water. The absolute isotherm of water adsorption on Palas soot is presented in figure 3. The mean diameter of Palas soot particles was found to be 6.6 nm; therefore, for classification of their water uptake ability we should draw the isotherm of the surface water film for soot primary particles with radius near 5 nm on the same plot (see figure 3). As was found, the isotherm for Palas soot is always lower than the lower boundary of the marked area for existence of the water surface film. Therefore, we conclude that the initial water adsorption on active sites of Palas soot may probably stimulate the water cluster growth but cannot

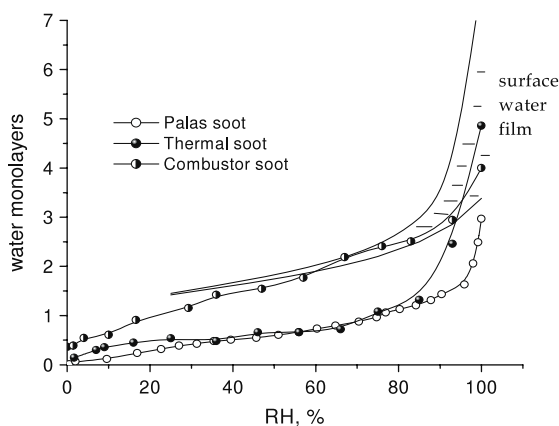


Figure 3. Isotherms of water adsorption on hydrophobic Palas and thermal soots, and on hydrophilic combustor soot. The curves are to guide the eye. The area of existence for water film on the surface is indicated, similar to figure 1.

lead to the cluster confluence and the formation of the water film extended over the total soot surface. This is a feature of hydrophobic soot with respect to the concept of quantification.

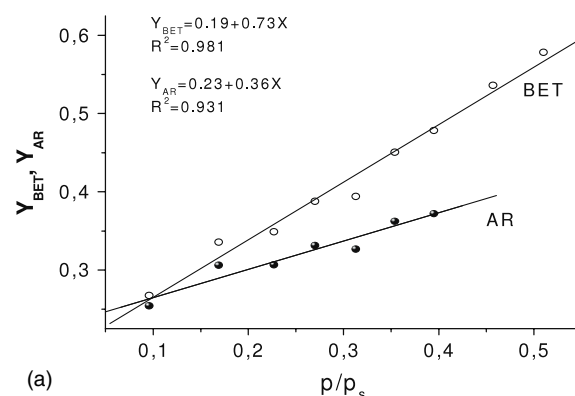
For the quantitative description of the water–soot interaction mechanism as well as for parameterization of water uptake the application of classical adsorption equations to experimental data is fruitful. For these purposes the BET (2) and Aranovich (3) equations are frequently used in a linear form:

$$Y_{\text{BET}} = \frac{p/p_s}{a(1 - p/p_s)} = \frac{1}{a_m C} + \frac{C - 1}{a_m C} p/p_s, \quad (8)$$

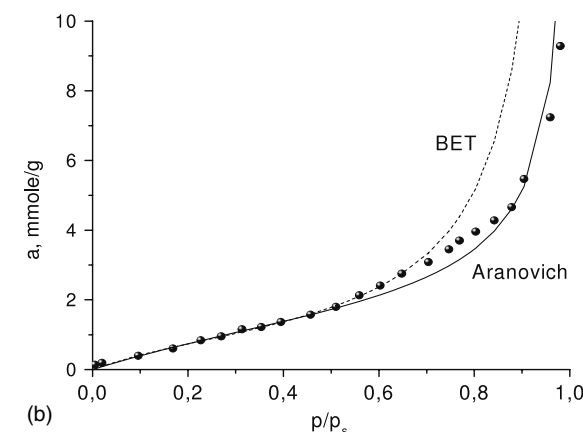
$$Y_{\text{AR}} = \frac{p/p_s}{a(1 - p/p_s)^{0.5}} = \frac{1}{a_m C} + \frac{p/p_s}{a_m}. \quad (9)$$

Figure 4(a) gives the plots of the water adsorption isotherm for Palas soot in linear forms (8) and (9), respectively. The solid lines show the linear fit of experimental points denoted by symbols in the range where the highest correlation R^2 is found. The slope and R^2 value from a linear fit are presented in figure 4(a). The parameters a_m and C found from the linear fits as well as the range for the good application of the BET and Aranovich theories are summarized in table 2. The range for the BET equation application is found to be up to 0.5 which is even higher than the range generally accepted for the BET theory (up to 0.35). The estimation of the amount of water molecules in a monolayer, a_m , allows the calculation of the surface area covered by water, $S_{\text{H}_2\text{O}}$, presented in table 2. As one can see, both theories give values of $S_{\text{H}_2\text{O}}$ less than the surface area measured by N_2 adsorption—this is a typical feature of hydrophobic soot.

Figure 4(b) shows the experimental data for water uptake of Palas soot and the isotherms obtained from various equations with parameters a_m and C presented in table 2. We may infer that within experimental accuracy the Aranovich equation gives a better representation of the experimental data over the entire p/p_s range than the BET equation in accordance with a more developed consideration of adsorbate–adsorbate interactions in the Aranovich theory. Probably



(a)



(b)

Figure 4. (a) Data points and water adsorption isotherm for Palas soot in a linear form of the BET equation (8) and Aranovich (AR) equation (9). (b) Adsorption isotherms of Palas soot: experimental data and fitting curves obtained from the BET and Aranovich equations.

the vertical interactions taken into account in Aranovich's theory may more comprehensively address the water cluster formation.

Additionally, the Langmuir isotherm was calculated from equation (1) using a similar linearization procedure as described above for the BET and Aranovich isotherms. We found that the Langmuir equation does not describe the water adsorption on Palas soot at p/p_s higher than 0.1. Therefore, there is no longer any justification for using the Langmuir theory for the description of water/soot interaction. This is why the attempt of Kärcher *et al* (1996) to apply the Langmuir equation for water uptake on hydrophobic aircraft-generated soot failed.

Gas pyrolysis thermal soot is characterized by the low oxygen content and WSF (see table 1). Functional surface groups are found on its surface (see table 1) but, either because of their small amount or low strength, we observe low water adsorption on thermal soot similar to Palas soot up to $\text{RH} \approx 80\%$ (see figure 3). The increase in the adsorption observed at higher RH may take place due to polymolecular adsorption in the mesopores. The water film is never extended over the hydrophobic thermal soot surface as the isotherm does not approach the surface water film isotherm for particles of 250 nm diameter (the higher boundary of the marked area in figure 3). The parameters a_m and C found from a linear fit of

Table 2. Parameters for fitting of experimental data by the BET and Aranovich (AR) equations.

Parameter	Palas soot		Thermal soot		Combustor soot		TC1 soot		AEC soot	
	BET	AR	BET	AR	BET	AR	BET	AR	BET	AR
R^2	0.981	0.931	0.995	0.996	0.985	0.989	0.995	0.985	0.997	0.994
a_m (mmol g ⁻¹)	1.08	2.77	0.06	0.08	0.81	1.42	1.44	1.59	2.02	2.46
C	4.84	1.58	62.1	25.8	65.7	7.9	104	49.8	49.14	31.2
Range of application, up to	0.7	0.5	0.5	0.7	0.6	0.76	0.4	0.7	0.4	0.5
S_{H_2O} (m ² g ⁻¹)	65	167	3.6	4.6	49	86	86.5	96	122	148

experimental data by the BET (8) and Aranovich (9) equations are presented in table 2.

5.2. Hydrophilic soot

Oxygen content and water-soluble fraction are found to be higher for combustor soot produced by burning gaseous fuel in a combustor of a gas-turbine engine in comparison with those for hydrophobic soots (see table 1). Accordingly, the isotherm of combustor soot may be perfectly treated with respect to the concept of quantification as a characteristic of hydrophilic soot, see figure 3. It starts increasing at very low RH due to a significantly higher amount of active sites on its surface than on the surface of Palas or thermal soots. The water cluster confluence may be predicted at $RH \geq 60\%$ where the isotherm approaches the water film formation for particles with 15–25 nm diameters (the size for combustor soot particles). However, due to the relatively small amount of water-soluble surface compounds and, therefore, relatively low water uptake, even in the best case of formation of the water film on the surface, all Palas, thermal and combustor soots belong to a class of non-hygroscopic soots, as is marked on the scheme in figure 1.

Figure 5 shows the experimental data for water uptake on combustor soot and fitting isotherms obtained from the BET and Aranovich equations. Equation (8) gives a good representation of the experimental data only up to 0.6 while it appears that the Aranovich model is valid in the range of p/p_s even greater than 0.7. This finding proves that the secondary water adsorption mechanism on soot realized as the fluid–fluid cooperative effect is hardly considered by the BET theory.

Further, formal quantification may be done for water uptake on TC1 kerosene flame soot; it should be classified as really hydrophilic or, even, slightly hygroscopic soot with respect to the concept since its isotherm lies higher than the upper boundary of the marked area in figure 6. However, there is one suspicious fact that the WSF of TC1 soot is noticeably less than the WSF of combustor soot (see table 1). Probably, there is one other mechanism impacting water uptake that is different from water solubility of the soot coverage. In the case of TC1 soot, it is the high (in comparison with other soots) microporosity which, as was proved in Popovicheva *et al* (2008), may increase the water adsorption. Formal treatment of experimental data by the BET and Aranovich equations (see figure 7) demonstrates better applicability of the last equation and only a restricted range (up to $p/p_s \sim 0.3$) for the first one. Therefore, we conclude that, for soot with higher hydrophilicity, the BET theory is less applicable.

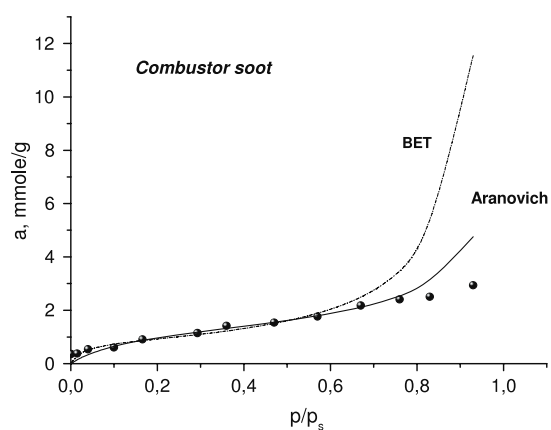


Figure 5. Adsorption isotherms of combustor soot: experimental data and fitting curves obtained from the BET and Aranovich equations.

Special attention should be paid to water uptake of CAST soot since it can be produced in the laboratory with various controlled amounts of organics on the surface (Moehler *et al* 2005a, Salgado and Rossi 2002). In Moehler *et al* (2005a) it was concluded that the increase in the OC content of soot markedly suppresses the ice nucleation ability of particles. This result led the authors of Kärcher *et al* (2007) to the conclusion that the increase in the OC content makes the flame soot particles more hydrophobic. Our measurements of water uptake prove the increase of water adsorption with the increase in organic content (see figure 6). How the OC content correlates with WSF in each soot remains unclear because only low mass soot samples were available for the WSF analysis. But the FTIR spectra (see figure 2) clearly indicate more pronounced features of oxygen-containing groups on the surface with 27% of organics in correlation with the isotherm for CAST-27 being higher than the isotherm for CAST-4.

The isotherm for CAST-4 soot with a mean particle diameter of 300 nm does not approach the higher boundary of the area for existence of a water film indicated in figure 6. Therefore, we should classify CAST-4 as hydrophobic soot. In contrast, a significant increase in the water adsorption for CAST-27 soot is observed at $RH \leq 20\%$ (see figure 6); it happens even before the threshold for water film formation (see section 2.2 above). In this case we are definitely sure about the hydrophilic nature of the CAST-27 soot surface and should consider the hygroscopic character of water uptake with respect to the concept of quantification illustrated by figure 1.

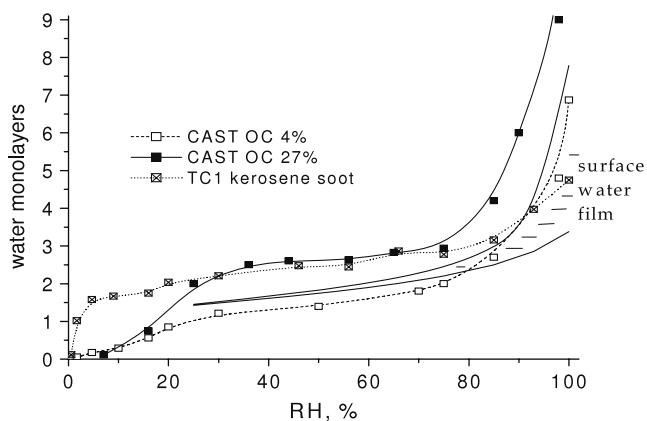


Figure 6. Isotherms of water adsorption of TC1 kerosene flame soot, and on CAST-4 and CAST-27 soots with 4% and 27% of OC content, respectively. The curves are to guide the eye.

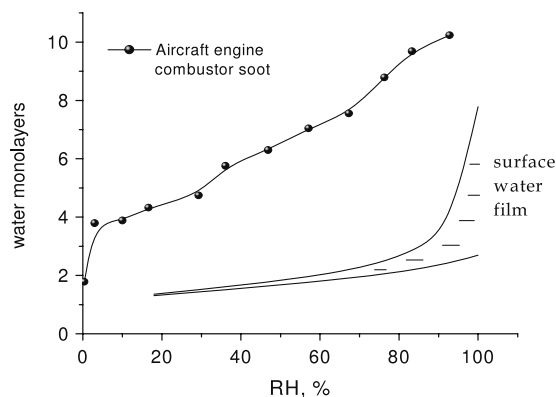


Figure 8. Isotherm of water absorption on hygroscopic aircraft engine combustor AEC soot. The isotherm for water film on the surface of particles of 250 nm diameter is indicated. The curve is to guide the eye.

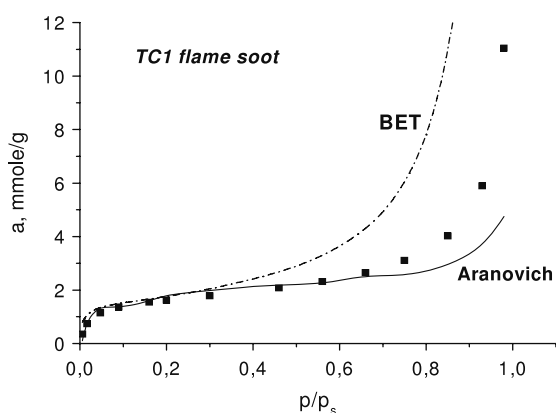


Figure 7. Adsorption isotherms of TC1 kerosene flame soot: experimental data and fitting curves obtained from the BET and Aranovich equations.

But in the range of initial RH (less than 10%) both isotherms of CAST soots exhibit negligible uptake, even lower than on hydrophobic Palas and thermal soots. Such behavior relates to the presence of hydrophobic organics on the surface of CAST soots which are to be replaced by water molecules before the following significant adsorption begins (Brunauer 1945). It is worth noting that TC1 kerosene flame soot has less OC on the surface than CAST soots, only near 2 wt% (see table 1). This demonstrates the significant uptake already at the initial RH, around 5%, and similar adsorption on CAST-27 soot in the RH range from 30 to 80% (see figure 6), probably due to the similar oxidation level of condensable organic compounds on its surface. Such a complex mechanism of water uptake on CAST soots with large organic coverage is outside consideration in the BET and Aranovich theories; therefore, these equations describe the experimental data poorly for values of $p/p_s \geq 0.2$.

5.3. Hygroscopic soot

Finally, aircraft engine combustor AEC soot produced by burning TC1 kerosene in a combustor of a gas-turbine engine

has a really high organic carbon content, ≈ 20 wt%, as well as high water-soluble fraction, ≈ 13.5 wt%, including 3.5 wt% of sulfates. The water uptake by AEC soot is presented in figure 8. Significant increase up to 10 monolayers does not leave any doubt about the dominant mechanism of water uptake being the dissolution of water into the soluble soot coverage and the formation of a thick solution film surrounding the soot particles. The role of sulfates in hygroscopicity may be dominant. Thus, AEC soot is the best candidate for being the original hygroscopic soot with respect to the concept of quantification.

The dual sorption theory is proposed above (section 2.3) for modeling water uptake on hygroscopic soot. The isotherm obtained using equation (7) by the least-squares fitting is shown in figure 9 with the following values of parameters: $a_v = 2.1 \text{ mmol g}^{-1}$, $K = 15 \text{ Torr}^{-1}$, and $K_d = 0.15 \text{ mmol g}^{-1} \text{ Torr}^{-1}$; it treats measurements well up to 70%RH. The formal application of the BET and Aranovich theories (see table 2) gives very high values of surface areas covered by water, tens of times more than the surface area measured by N_2 adsorption. This finding confirms the absorption mechanism of water uptake on hygroscopic AEC soot, while these classic theories are preferentially applied for adsorption on non-hygroscopic (hydrophobic/hydrophilic) soots.

6. Conclusions

Soot is a complex material composed of 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. Comparative analysis of water uptake on soots of various compositions, from elemental carbon to complex composites with large water-soluble fractions, allows us to suggest a *concept of quantification*. The isotherm for a water film extended over the surface is proposed as a *quantification*

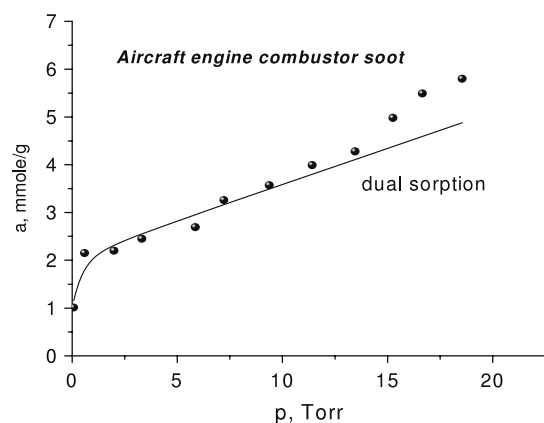


Figure 9. Adsorption isotherms of AEC soot: experimental data and curve obtained by least-squares fitting based on the equation of dual sorption.

measure which separates hygroscopic from non-hygroscopic soot. Water uptake on hygroscopic soot significantly exceeds the surface water film formation and may reach tens of water monolayers. If soot particles are made mostly from elemental carbon and/or the organic coverage is totally water insoluble, we assume non-hygroscopic soot with water uptake less than (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 representative of hygroscopic soots due to its high water-soluble fraction leading to a multilayer water uptake. Spark discharge Palas soot is hydrophobic black carbon because of its chemically pure surface which supports only low water adsorption due to a few active sites. Meanwhile laboratory-produced TC1 kerosene flame and CAST burner soots may be classified as hydrophilic within non-hygroscopic soots because of the presence of some water-soluble compounds and functionalities on their surface, leading to 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 there is no single model which could be universally applied for water uptake on soot with an arbitrary extent of hydrophilicity.

The concept of quantification of water uptake by soot particles developed in this study is useful for relating the isotherm data and the cloud condensation soot activity (CCN data). It may allow definition of which combustion soot may be activated with respect to overcoming the Kelvin barrier. The formation of the water film extended over the hydrophilic surface is assumed to be needed for wetting that soot particle which becomes activated at water supersaturations in respect to the Kelvin theory. Whether the condition is achieved may be concluded from the adsorption data. In the case of hydrophobic soot, the low adsorption just on a few active sites is not indicative of CCN activation; such kinds of soot

will require really high supersaturations to become activated. Further measurements to prove this conclusion are required.

We believe that the concept of quantification of water uptake will be also useful for understanding ice nucleation on soot particles since water–soot interaction is the first step before freezing in any atmospheric system, whether in the cooling plume or the background atmosphere. The amount of adsorbed water on soot particles and the fraction of frozen water may depend on temperature (Popovicheva *et al* 2004a, Ferry *et al* 2002). But if surface water remains unfrozen at low temperatures the mechanism of water uptake and water distribution over the surface may be concluded from the concept of quantification.

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