"Atmospheric Soot: Environmental Fate and Impact"
ASEFI 2006 Meeting Summary and
the Atmospheric Soot Network (ASN) definition

O. Popovicheva[a]*, D. Baumgardner[b], K. Gierens[c], R. Miake-Lye[d], R. Niessner[e], M. Rossi[f], M. Petters[g], J. Suzanne[h] and E. Villenave[i]*

[a] *Institute of Nuclear Physics, Moscow State University, Moscow, Russia*
[b] *Universidad Nacional Autónoma de México, Mexico*
[c] *DLR, Oberpfaffenhofen, Germany*
[d] *Aerodyne Research Inc., Billerica MA, USA*
[e] *Technical University of Munich, Munich, Germany*
[f] *EPFL, Lausanne, Switzerland*
[g] *Colorado State University, Fort Collins CO, USA*
[h] *CRMCN, University of Marseilles, CNRS UPR 7251, Campus de Lumigny, France*
[i] *University of Bordeaux, CNRS UMR 5803, Talence cedex, France*

** Corresponding authors*

Abstract

The ASEFI 2006 (Atmospheric Soot: Environmental Fate and Impact), held 18-20 October 2006 in Arcachon, France, brought together forty invited experts to discuss how to improve the quality of soot measurements in laboratory and field observations with the objective of decreasing the uncertainties in climate response to soot - a still, largely unresolved problem. One of the primary results of the meeting was the recommendation to form an international network of individuals and groups, designated the Atmospheric Soot Network (ASN), who have a mutual interest in sharing ideas, promoting research, and collaborating in projects that relate to improving the state of knowledge about soot.

1.0 **Introduction**

Carbonaceous soot in the atmosphere is a major concern with regards to its impact on health and the environment. Soot aerosols have gained considerable attention because of their influence on the earth's radiative balance, atmospheric chemical composition and cloud formation. Currently black carbon (BC) is considered one of the the most important constituencies of atmospheric particles by every major environmental agency and who have instigated programs to monitor BC concentrations wherever soot is emitted and puts the environment at risk. At present, however, there is very limited information on the characteristics of soot and how it interacts with the environment, largely because of the lack of adequate measurement techniques and methods to calibrate them. There is new technology that may alleviate the limitations and uncertainties of present instrumentation; however, the uncertainty in BC measurements at the moment is on the order of ± 30-50%. This uncertainty is somewhat related to the limitations in the techniques, but is to a greater extent the result of there being no adequate standard reference materials to calibrate the instruments or validate the measurements.

One of the major uncertainties in assessing the impact of anthropogenic aerosols on the Earth's radiation balance is the lack of information on the physical, optical and chemical properties of soot with respect to their emission sources, how they evolve with time and how they interact with their environment. Soot is a component of the atmospheric aerosol that changes its shape, size and chemical properties as it ages and interacts with radiation, and other atmospheric gases and particles. Its capacity to directly impact climate through the extinction of light is related to its optical cross section and refractive index, properties that evolve the further the soot travels from its source of emission. The indirect effect of soot on climate, i.e. the enhancement of its radiative impact via the formation of cloud particles, is related to the chemical properties of BC and these also change depending on the surrounding environment. In the past few years there have been a number of observational and theoretical studies that link soot to the formation of ice crystals in cloud. In microphysical models of cirrus clouds, for example, the climate impact of these type of cloud is significantly enhanced when BC as a heterogeneous freezing ice nuclei is included along with the more predominant homogeneous freezing processes. The quantification of this process through observational studies is advancingbut the state of scientific understanding is still poor primarily because of limited studies of the cloud condensation and ice nucleating ability of atmospheric soot aerosols.

Measurements of soot and clouds in the natural environment, while useful for characterizing the microphysical properties of clouds with in relationship to the aerosols characteristics measured at the same time, must be complemented by laboratory studies that link the properties of soot to their subsequent capacity to form the types of particles that are measured in cloud.

Hence, the assessment of soot requires a detailed evaluation of its number, surface and mass concentration, morphological characteristics, chemical composition, kinetics (reaction rates, uptake coefficient) and mechanistic data (reaction products, branching ratios) with respect to the reactions with other atmospheric constituents. Most black carbons are reducing agents suspended in an oxidizing atmosphere. This should lead to reactions and/or gaseous products of intermediate oxidation state that are not directly emitted into the atmosphere and that may take part in reactions with (oxidized) atmospheric trace gases. In addition, oxidation processes, commonly known as aging of soot, lead to adsorbed reaction products such as hydroxyl- and nitro-substituted polyaromatic hydrocarbons that are often more toxic than their nonsubstituted parent congeners.

These problems have been discussed at detail during a previous workshop “Ice, Soot and Aviation: what Impact on the Environment” (ISAIE) supported by the ESF Networking Programme INTROP (Interdisciplinary Tropospheric Research: from the Laboratory to Global Change) that was held in La Londe (France), 10-14 May 2004. A number of significant results have been obtained following this workshop within the framework of the PartEmis and APEX emission measurements projects; however, as there has been limited progress in the laboratory measurements of soot, a workshop “Atmospheric Soot: Environmental Fate and Impact” (ASEFI) was organized in Arcachon (France), 18-20 October 2006, under the supports of INTROP Programme and the French Ministry of Ecology, to elucidate the current problems of characterizing soot and to develop ideas that can address these problems

2.0 Relevance to the INTROP Programme

According to INTROP “heterogeneous chemistry on aerosols and its impact on air quality are far from being well understood and large uncertainties are associated with the climate forcing exerted by different types of atmospheric aerosols”.

One of the approaches that has been taken as part of the INTROP Program has been to study the characteristics of soot produced by aircraft engines through the use of laboratory studies that utilize ground based, test aircraft engine facilities for producing soot particles whose properties can subsequently be studied in the laboratory. This process, however, is time consuming and expensive, a limitation that has constrained scientific progress in this field. As an alternative approach, various laboratory-produced surrogates for soot have been introduced. Typically they are produced under conditions quite different from those prevailing in an aircraft engine combustor. As a consequence, current laboratory data on surrogate soots can vary widely in composition and their chemical and nucleation properties.

3.0 Objectives of ASEFI 2006

The INTROP Programme states that:

"***building a framework that is able to meet new challenges in the field of elementary chemical processes in the atmosphere requires collaboration between the best research teams that can be found throughout Europe***",

The purpose of the ASEFI 2006 Workshop was to address one aspect of "elementary chemical processes", i.e., those that involve atmospheric soot. The objectives set out in the workshop planning document were 1) to discuss how the research community can improve the quality of soot measurements in laboratory and field studies, with the objective of decreasing the uncertainties in climate response to soot, and 2) to layout a plan for developing an international organization, designated the Atmospheric Soot Network (ASN), with a clearly defined mission, objectives and strategy, that will bring together individuals and groups who have a mutual interest in sharing ideas, promoting research, and collaborating in projects that relate to improving the state of knowledge about soot..

4.0 ASEFI 2006 Working Programme and Content

The participants in the ASEFI 2006 (listed in the appendix) represented the current understanding of soot/climate interactions on all levels, from physico-chemistry on soot surfaces to soot emission impact on induced cloudiness and radiative budget. Twenty-seven speakers gave oral presentations in five thematic sessions on *Soot measurements in global environment, Aircraft engine emission experiments, Water-soot interactions: CCN/ IN, Laboratory and theoretical studies and Chemistry of soot.* The intent of the oral presentations was to summarize the current state of the knowledge in each of the thematic area and to highlight the significant scientific questions and associated uncertainties and obstacles. The main objectives of the working group (WG) discussions were to provide a clear definition of the current state of the science, to list the problems that must be addressed and prepare recommendations for actions that will lead to solving the problems. The following sections summarize the thematic presentations.

4.1 Soot Measurements in Global Environment

High levels of particles, including black carbon, have been reported by K. Velchev at sites around the Mediterranean Sea along cruise tracks during the period November 2005 – August 2006. Long term observations are limited to a few sites and observations over the sea surface are particularly scarce for assessing the effect of air pollution on Mediterranean climate. BC, derived from aethalometer measurements, have been compared to results obtained by thermal-optical analyses of filter samples collected during the cruise in order to evaluate the uncertainties in the measurements. The measured BC concentrations were compared to modeled values, obtained by the TM5 global atmospheric chemistry-transport zoom model. First results suggest that the model tends to underestimate BC concentrations over the open sea in the Eastern and Western Mediterranean in autumn/winter.

J.B. Renard presented remote sensing measurements (extinction, brightness and polarization of scattered light) of stratospheric soot aerosols originating from aircraft traffic and tropical biomass burning. Reference scattering functions of soot are required to distinguish between liquid and solid particles. The need for specific instruments that can measure aerosol properties in the stratosphere and can operate at low pressure and concentrations was stressed.

The direct and indirect methods most commonly used by the atmospheric research community for measuring soot were summarized by D. Baumgardner. This review discussed various techniques, e.g. thermo-optical, light absorption and laser induced incandescence, their advantages, disadvantages and uncertainties. The need for more accurate measurement systems and improved methods for calibrating and quantifying these accuracies were addressed.

H. Puxbaum suggested the analysis of source attributes of PM2.5 and PM10 based on six component, macro tracer concepts (three sources based on organic tracers, two sources based on inorganic tracers and diesel exhaust). BC from diesel engines, wood and coal combustion are derived from individual tracers (levoglucosan, arsenic) and the BC signal. Thus, the quality of the source attributes is crucially dependent on the analytical quality of the BC determination. This model gives remarkable agreement between the observed organic carbon and the organic carbon explained by the six sources; nearly 100% of the winter OC is explained quantitatively by the six sources whereas two thirds of the summer OC is explained with this technique. However, thermal methods for EC determination may be in error as a result of inorganic salts or wood smoke that interfere in the themo-optical analysis method.

4.2 Aircraft engine emission experiments

R. Miake-Lye reported on the composition of aerosols nearfield and downwind of aircraft gas turbine engines exhausts. Since the soot particles leave an engine at high temperature and velocity, unlike most other combustion emission sources, it makes the extraction and measurement of the particle properties very difficult. Even successful extraction and transport of these particles can be confounded by microphysical processing with the exhaust gases which may occur in the sampling probe and transport tubing. For aircraft exhaust, the contributions of condensed sulfate and organics are important indications of the manner in which gaseous emissions at the engine exit interact with soot particles to contribute to condensed material later in the exhaust plume or in the sampling system under certain conditions.

J. Suzanne and D. Ferry introduced microphysical properties of AEC soot particles produced by a combustor of D30KU,CIAM, (Russia) aircraft engine at cruise combustion conditions and of ES soot emitted from a civil aero-engine bench at SNECMA Villaroche center (France), during landing/take-off cycles. AEC soot was collected at a combustor exit at 12 cm and was found to be highly heterogeneous in respect to size, structure and composition. There is a fraction of impurities with large content of oxygen, sulfur and iron in AEC soot. ES particles collected 30 m behind the engine are mainly made of carbon, oxygen and of some traces of sulfur. E. Ruiz confirmed the ONERA's capability of conducting engine emission research as well as related environmental impact studies, using both experiments and modeling. Rolls-Royce measurements have been taken on combustion rigs and on engines using intrusive gas sampling based techniques, (filter paper, optical absorption cell, and SMPS) and the non-intrusive Laser–Induced Incandescence (LII) technique. The project directed towards the production of the First Order Approximation for particulate mass vs. smoke number was presented by J. Black, which can be used in assessing local air quality around airports.

4.3 Water-Soot Interactions : Condensation Cloud Nucleation / Ice Nucleation (CCN/IN)

Soot particles directly interfere with the flow of radiative energy in the atmosphere and by affecting cloud properties, lifetimes, and coverage. K. Gierens concentrated on 1) the *semi-direct effect* related to local heating due to absorption of radiation that causes decrease of relative humidity, evaporation of droplets, and changing cloud dynamics and on 2) *indirect effects* associated with the Twomey effect, suppression of precipitation, change of liquid water content, glaciation of mixed phase clouds, increase of precipitation rate, generation of additional clouds, certain ship tracks, contrails, contrail cirrus and uncertain non-contrail related cirrus caused by aviation aerosol. The open questions, with the largest uncertainty with respect to simulating and predicting climate, are 1) what is the net effect of soot as related to estimates of single effects, and primary effects from feedbacks?; 2) How relevant are current emission data bases, i.e. are they accurate and up-to-date?; 3) What is the ice forming ability of various kinds of soot ?

J. Cozic demonstrated the indirect soot effect with observational data for transferring BC into cloud droplets via nucleation scavenging. Experiments performed at the Alpine research station Jungfraujoch (3580 m asl) showed that the scavenged fraction of BC decreases with decreasing temperature, from 60% in liquid clouds in summer down to <10% in mixed phase clouds in winter. The BC fraction was found to be enriched in small ice particles in comparison to the total aerosol phase (~20%), indicating that a high BC content renders a particle more likely to act as ice nucleus.

4.4 Water-soot interactions: laboratory and theoretical studies

Laboratory experiments aimed at the modeling of direct radiative forcing due to soot-water interactions were reported by E. Mikhailov. Hydrophobic soot (HBS) does not exhibit any morphological differences, whereas hydrophilic soot (HLS) collapses into globules at saturation. The absorption coefficient of HLS increases markedly with RH; for water-soot droplets the maximum enhancement in adsorption is as much as a factor 3.5.

M. Petters stressed that the overall role of combustion particles in aerosol-cloud interactions remains highly uncertain. Therefore, laboratory studies were carried out to measure hygroscopic growth factors, CCN activity, and freezing probabilities (-60°C < T < -30 °C) as a function of saturation ratio and particle size for carbonaceous aerosols. The aerosol used were laboratory hydrophobic soot, resuspended aircraft engine combustor (AEC) soot, surrogates for fresh and chemically aged hydrocarbon aerosol, diluted samples from a tractor diesel engine and aerosols generated from open flame combustion of various biofuels. Only AEC and open flame biofuel aerosols showed appreciable hygroscopic growth factors, CCN activity and freezing initiated near the homogenous haze freezing limit (T ≤ -40 °C). These results agree with water uptake measurements presented by O. Popovicheva who showed that laboratory soots popular in laboratory researches, such as commercial soots spark discharge soot, kerosene flame and CAST soots, are characterized by a variety of physico-chemical properties but may be accepted only as hydrophobic surrogates of atmospheric soots. While AEC soot is highly hydrophilic, its uptake relates with phenomena of water dissolution in the soluble surface coverage.

B. Demirdjian reported on the neutron diffusion technique for examining the structure and dynamics of water on soot. Results obtained on kerosene flame and AEC soot show the soot structure and water freezing as functions of the temperature and relative humidity. However the disadvantage of this method is the large mass of soot samples (near 1 g) that limits the use natural soot and stresses the needs for laboratory-made surrogates.

To address the issue of BC activation, B. Henson suggested the use of models based upon a parameterization of laboratory data for water uptake by a number of laboratory soot. The model assumes a general modification of the Koehler equation for insoluble activation in which a term based on the activity of water adsorbed on the particle surface was introduced. P. Hoang provided detailed theoretical understanding of the water-soot interaction assuming the combined quantum calculations and classical molecular dynamics simulations for large graphite clusters with oxygen-containing groups. The influence of soot morphology on water adsorption has been investigated by means of grand canonical Monte-Carlo calculations that allowed simulation of a real adsorption experiment data.

4.5 Chemistry of soot

R. Niessner emphasized the following aspects: the ways to measure soot based on its physico-chemical properties; the fact that the soot is black and hence easy to measure by light absorption; Raman microspectrometry as an ideal tool for observing structural changes in soot undergoing oxidation. Further detailed elucidation of molecular and crystalline structures and their relation to the reactivity and Raman spectroscopic parameters is needed, e.g. by HRTEM. Examples of the size distribution and EC/OC fraction of propane soot generated by Combustion Aerosol Standart (CAST) Generator were given by E. Barthazy who also reported on the dependency of soot properties on CAST burner operating conditions.

P. Desgroux concluded that the selective detection of PAH on soot and in the gas phase, along with the soot volume fraction f_v, helps the understanding of elementary processes involved in soot formation in flames and emissions in the exhaust of combustion chambers. Studying the impact of alternative fuels on soot characteristics is performed by providing cartography and correlation of global PAHs, selective PAHs, PAHs adsorbed on soot surface, and f_v as a function of the fuel. The original experimental strategies have been developed, such as the laser desorption/laser ionisation/ mass spectrometry (LD/LI/MS) presented by C. Fosca and laser induced incandescence (LII) reported by E. Therssen. In order to provide understanding of the complex processes involved in LD/LI/MS analysis method, a 3-step program has been adopted: 1) complete characterization of the laser desorption process on pure or mixed PAH samples; 2) use of "surrogate" soot samples by adsorbing PAHs on activated charcoal surfaces; 3) analysis of combustion soot samples. LLI is successfully used for soot cartography in flames and in-situ soot volume fraction measurements in aero-engine exhausts.

M. Rossi summarized the molecular aspects of the kinetics and mechanisms of the interactions of NO_y and H_2O with soot that may be included in atmospheric modeling. Multiple pathways of reaction depending on the type of soot show the great difficulty of defining the properties of a unique model of soot as it has been found that the kinetic behavior of combustion soot towards H_2O and NO_y significantly changes with the flame parameters chosen to generate it. Y. Bedjanian discussed the kinetic data (uptake coefficients) for reactions of O_3, NO_2 and HO_2 with soot measured under varied experimental conditions (temperature range 240 – 350 K, pressure, initial concentrations of gas phase species) with different types of soot (hexane, toluene, kerosene) and for different soot sample preparation and deposition conditions (soot sampling position in the flame, flame richness). H. Budzinski focused on the reactivity of PAHs adsorbed on different types of particles, developing powerful analytical techniques to study the chemical degradation and photodegradation of PAHs by reactions with atmospheric oxidants (OH, NO_x, O_3…). This method is promising to study chemical composition, organic content and toxicity of carbonaceous particles in the atmosphere.

5.0 Working Group discussion summaries

5.1 Atmospheric measurements and emissions

5.1.1 Atmospheric/environmental interactions. Outstanding scientific questions related to the interaction of soot with the environment :

a) radiation: What are the optical cross sections and refractive indices of atmospheric soot? (direct, semi-direct effect), What is the hygroscopicity of soot? (indirect effect)

b) How does soot impact meteorology through increased heating rates in layers of soot, stabilization of the boundary layer and influence on the microclimate near surface sources),

c) What are the removal mechanisms and how do soot properties affect the rates of removal?

5.1.2 Atmospheric soot measurement requirements

With respect to required accuracies and resolution (spatial and temporal) detailed measurements of soot properties are needed for:

a) process and aerosol source studies,

b) validation of laboratory experiments,

c) satellite validation or improvement of aerosol models used in satellite retrieval algorithms,

d) climate model parameterization,

e) air quality parameterization and monitoring,

f) certification standards for compliance with Environmental Regulations,

g) industries that produce BC,

h) development of BC inventories,

i) fire propagation studies.

5.2 Water-soot interactions 5.2.1 Laboratory studies: surface water uptake including isotherms, the surface initiated freezing/deposition freezing; volume water uptake assumes dissolved matter in aqueous solution surrounding a soot core, water activity of shell solution, volume initiated freezing (homogeneous nucleation), mixed particle CCN activation.

5.2.2 Cloud/climate interactions are pure understandable: there is more scatter in soot data between different laboratory and field experiments than for other aerosol types (i.e. dust). Ice effects on climate are more uncertain than CCN.

5.3 Soot chemistry and reactivity

Products resulting from reactions of probe molecules with soot are a sensitive function of the type of soot compared to the uptake kinetics. Probe molecules used are: NO_y family (NO_2, N_2O_5, HNO_3, N_2O_5, NO_3), O_3, H_2O, small aldehydes and ketones, H_2SO_4, HNO_3, SO_2, H_2O_2, etc. Micro Raman spectrometry affords a spatially resolved map of reactivities with selected gases. Laser-induced desorption affords a sensitive means of investigating the surface composition of flame soot obtained in different diffusion flames.

Soot aerosol consists of harmful substances, such as adsorbed PAHs as well as their hydroxylated and nitro-substituted congeners which have significant higher carcinogenic potential. Especially nitration of parent PAHs adsorbed onto the EC particle core yields extremely mutagenic contaminants.

5.4 Thematic discussion report: What is soot ?

Soot means a lot of different things to different people, a unambiguous definition is therefore necessary. A general definition could be: *soot is a carbon-containing aerosol resulting from the incomplete combustion of hydrocarbon fuel of varying stoichiometry, defined by the λ-ratio of fuel to oxygen.* Soot not only addresses the properties of BC or elemental carbon (EC) fraction commonly associated with "soot" but also includes its organic fraction. The chosen combustion conditions control the soot properties to a large extent when comparison is made across a narrow type of fuels, for instance pure linear and branched liquid hydrocarbons. The comparison between grossly different types of fuel, for instance between coals of different composition, must take into account the variable fuel composition. The notion of "soot" always implies a certain fraction of EC or BC that will dominate the absorption properties of soot across the UV to the near IR spectral range. Therefore, in order to converge to a viable definition of “soot” one may arbitrarily fix a lower limit of BC/EC mass fraction of the condensed phase of a combustion plume, for instance 10%. (This is still open to debate)

5.4.1 Different types of Soot of atmospheric and human health issues

Diesel soot: the organic fraction (OC) may approaches 50 wt %, the remainder is BC or EC. The smallest size fraction (nucleation mode, 3 nm - 20 nm particle diameter) consists of oil or sulphuric acid nanodroplets from unburned or partially oxidized fuel and is colorless in the visible spectral range. The accumulation mode (50- 250 nm diameter) contains a large amount of EC and is strongly absorbing, but also contains OC. The coarse mode (submicron to several microns in diameter) contains a large amount of EC through coagulation, but also OC. Note that the ship soot is also a diesel soot but arising from heavy diesel fuel whose FSC is often quite high.

Aviation soot: it includes undefined OC fraction (depending on engine operation conditions and sampling). Particles size ranges from a few to ~ 300 nm in diameter in dependence on engine power. Soot index emission nonlinearly depends on engine power and is typically <20 mg/kg over the 4 to 70% power range and >200 mg/kg at 80 to 100% trust level.

Wood combustion soot: large OC fraction, usually including only 10 % or so EC. Lignine-derived substances are found in OC fraction. Next generation of wood burning stoves are expected to be much improved with high combustion temperatures leading to reduced smoke emission.

Biomass burning soot: similar to wood combustion. Open fires are characterized by unstable flickering flames and lead to a large OC fraction as well as important smoke emissions. *Coal combustion soot:* is NOT biomass burning and therefore should be considered separate. *Cigarette smoke is similarly generated from tobacco smoldering and leads to significant smoke formation.*

5.4.2 List of main soot characteristics:

Due to complex and variable structures of soot and because of the different needs of different research groups, the same soot sample may be characterized by many different parameters. More important metrics of soot are proposed as follows:

Microphysics properties: primary particle size distribution and morphology of agglomerates (mobility, diffusion or aerodynamic diameter, or optical cross section, chosen depending on measurement techniques),

BET surface area, porosity and microstructure (amorphous, ordered microcrystallines or graphitized)

Composition: elemental composition, surface composition in terms of surface functional groups, organic and inorganic surface coverage, water soluble fraction

Optical properties: complex index of refraction across λ-range of interest. Short wave (solar): 220 nm to 5 μm; long wavelength range (terrestrial): a few μm to a few hundred microns; emissivity (gray vs. black body radiation as a function of the type of soot); scattering or absorption cross section as a function of λ.

5.4.3 The following common techniques to measure soot properties are reported:

a) light scattering and absorption techniques, b) filter transmission, c) photoacoustic, d) spectroscopic analysis, e) laser induced incandescence, f) cavity ring down spectroscopy, g) gravimetric measurements, h) electrical low pressure impaction, i) Raman and FTIR spectroscopies, j) adjustable condensation nuclei counters (CCN and IN counters), k) tandem differential mobility analyzers, l) thermal treatment techniques (e.g. thermal optical), m) SEM, TEM, AFM microscopies, n) neutron diffusion, o) liquid extraction, gas and liquid chromatography, p) particle and laser desorption mass spectrometry and q) surface analytical techniques for elemental composition (PIXE (Proton-induced X-ray Emission), RBS (Rutherford backscattering), energy-dispersive X-ray fluorescence).

5.4.4 List of the limitations of measurement techniques:

Sampling difficulties and artifacts (losses, changes to particle properties, distinction between nanoparticle and soot aerosol); required accuracy not yet met for many applications; differentiating between compound families within the OC fraction; relevance of laboratory studies to atmospheric impact; connection of lab soot to soot in the atmosphere; lack of reference particles for calibrations and laboratory surrogates for soot; quantification by calibration methods.

5.4.5 The general problems addressed to water condensation aspect:

Need to better understand ice nucleation ability (or inability) of various soot; Need to distinguish between deposition nucleation, homogenous freezing, and heterogeneous nucleation; progress has to be made in the molecular interpretation of results in order to associate a certain surface composition or structure of soot with CCN or IN activity; intercomparison of different approaches on the same type of particle and the same measured properties to cross-validate the applicability of a measurement technique for a certain property (e.g. isotherms vs. heterogeneous nucleation theory vs. actual activation).

5.4.6 Development of models with predictive value :

a) Need of global climate models taking into account soot emission occurring either in the atmospheric boundary layer (diesel engines, stationary coal, gas and oil-based power plants) or in the free troposphere by civil and military aviation. Such models have to incorporate every important processes dealing with soot such as atmospheric reactions, aging processes and soot-cloud interactions.

b) Need to address water and ice nucleation ability of soot in model-accessible properties (critical supersaturation, critical supercooling, nucleation rates).

c) Development of new theories bridging different laboratory approaches (linking surface properties to measured nucleation rates).

d) Public health implications of soot emission: quality of life, acute and chronic effects, space-time budget of exposure, effect of soot deposition on biological membranes of cells.

e) Fundamental understanding in terms of adsorption, elementary reaction dynamics and structural parameters. “Realistic” models with a minimum complexity are required in order to adequately mimic the “real” situation. This necessitates detailed knowledge of critical properties of soot.

f) In view of complex and changing composition of soot, models must incorporate *a minimal set of microphysical processes that can distinguish EC and OC* as a first approximation in order to distinguish between a strongly EC and weakly absorbing OC fraction. As a second approach, a clear distinction between different combustion conditions should be made in view of the resulting soot composition: from a surface chemistry point of view soot (EC + OC fraction) from lean burn will have different surface active sites, usually more oxidized, compared to rich flame conditions whose soot is characterized mainly by reducing sites.

6.0 Special Session “Atmospheric Soot Network: A tool for soot laboratory studies”

Workshop organizers recommended the organization of the Atmospheric Soot Network (ASN) whose participants would be researchers with experience in soot emissions, atmospheric measurements, laboratory studies, and other of soot-related atmospheric processes. The discussion of the ASN formation took place at the **Special Session “Atmospheric Soot Network: A tool for soot laboratory studies”**

Why to create the “Atmospheric Soot Network” ? *“Natural” reasons*, such as a great variety of different sources and physico-chemical properties of original combustion soots, and

- ✓ *“artificial” reasons*, namely a limit in in-situ observations of soot-initiated processes at microscopic level in the atmosphere, expensive and time-consuming emission experiments, also no single laboratory has all measurement techniques available for full characterization of soot, and
- ✓ *“methodological reason”* coming from a large variety of laboratory-made soots with different characteristics used for atmospheric studies

all limit our current ability to predict environmental effects of soot exhausts.

6.1 ASN laboratory soot

The point of view of laboratory researchers was presented by O. Popovicheva and M. Rossi. Laboratory-made soots, popular for atmospheric studies, were reported: different commercial soots, spark discharge (Palas) soot, combustion soots produced by burning gaseous and liquid fuels in laboratory burners (diffusion and premixed flames), CAST (Combustion Aerosol STandard) soots which are all not yet fully characterized in respect to main soot characteristics

The main questions are rising:

- What kind of laboratory soot is available for atmospheric studies?
- What do we know about soot-related processes in the atmosphere and such kinds of laboratory surrogates?
- What are the properties of real atmospheric soot particles?
- There is a large variety of soots in the atmosphere because of different sources: should we simulate all kinds of soot?

- How correctly address the phenomena of soot aging?

Experts suggest the following:

1. To elaborate the methodological approach for the characterization of soot particles;
2. To characterize a set of "natural" soots of atmospheric and health importances using complementary techniques;
3. To choose the minimal number of criteria parameters identical between atmospheric soots and laboratory surrogates;
4. To produce a set of laboratory soots; such a production needs to be reproducible (no flickering (unstable) flames), simple, controlled, and produced by laboratory burners (no engines).
5. To create an international standard for soot; such standard soot should be made available to the community to make cross-group comparisons of measurement techniques possible.

One example of laboratory-made GTS soot, specially produced to perform reference measurements with hydrophobic soot, was shown by V. Tishkova. Total EC, absence of organic coverage and negligible impurities provide the high extent of chemical homogeneity and negligible water adsorption; high level of graphitization leads to a perfect structural homogeneity of the GTS surface.

6.2 Soot for Air Quality Measurements, Definition of Calibration Standard :

For calibration purposes, for comparability and reliability of the measurements, a constant output aerosol source is needed. A so-called transfer standard is required, which means a reproducible aerosol generation in terms of size range, chemical and physical qualities, mimicking the soot production process of interest. It must be available and operated with a high reproducibility under preset flow rate and application time everywhere used (for example, spark-discharge aerosol generator (GFG, Palas, Karlsruhe). M. Kasper presented flame technologies (CAST, Matter Engineering, Wohlen) and announced the main principles of CAST burner based on a laminar propane co-flow diffusion flame. The special design of the burner ensures the stability of the particle size (that can be varied over a wide range from 30 nm to 150 nm) and of the number concentration within 5% or better.

D. Baumgardner emphasized the limit of accuracy of instrumentation, the absence of means to interpret soot measurements or to evaluate the differences that are found between measurements made by different instruments. Round-robin studies in which different techniques are used to measure the same atmospheric sample have shown a large variance among the results of deriving OC/EC ratio also because no means to evaluate each measurement technique was existing. The reference material with a precisely known mixture of OC and EC is strongly required.

6.3 Proposed Mission for the ASN

The ASN can serve as an organization that can promote and coordinate a variety of activities that improve our capacity to understand the impact of soot on the environment. The following are some of the activities that could be incorporated into the ASN.

6.3.1 Collaborative Research Projects

The ASN, as a centralized resource for sharing information, would provide a forum for researchers with mutual interests to exchange ideas and information. One of the purposes of such exchanges would be to initiate research projects that could be informal, i.e. lacking detailed proposals to funding agencies but of benefit to the soot research community and those who use information on soot, or formal, whereby several institutes would write proposals to government or private agencies seeking financial support for studies related to soot.

As examples of possible informal projects, that could also be developed into more formal ones:

- measurement methodology intercomparisons (Round-Robin Tests)
- laboratory and reference soot intercomparisons (Round-Robin Tests)
- A network of international sites where soot properties are being measured on a continuing basis. These can be urban or rural sites and the measurements would be used to build a database of soot characteristics for evaluating trends in visibility, health, etc.
- Assessing soot lifetime in the troposphere by deriving rates of deposition, wet and dry. This could utilize existing precipitation chemistry stations, i.e. those that are currently used to evaluate wet deposition of inorganic ions and acid rain. These same samples could be evaluated in laboratories that do soot research in order to assess soot concentrations in precipitation
- The impact of soot on glaciers and snow
- Composition of engine –derived and flame soots: elaboration of laboratory surrogates
- Preliminary tests of particle emissions (soot) from solid fuels / coal, biomass

6.3.2 Exchange of scientific and technical personal.

There are many small-grant programs within the EU, UNEP, etc., that fund short-term visits of researchers. The ASN could serve as a central contact point whereby such programs could be identified and described as they related to soot research projects or researchers with positions open at their institutes for visiting scientists. It would not be the responsibility for ASN to fund these types of visits. One possibility, however, would be for private companies to fund such visits as “fellowships”. This is also commonly done by industry. ASN could have a “bulletin board” of such opportunities and could facilitate the development of such fellowships by promoting the benefits to industry of such financial support.

6.3.3 Coordinated Soot Data Base information

The soot data base takes a number of different forms. One data base would be a well organized list of references sorted by the different topics associated with soot, i.e. its environmental impact, measurement techniques and laboratory studies. The second type of data base would be an archive and graphical display of things like global soot inventories, soot measurements globally compiled from the literature and presented in a number of types of formats, e.g. tables, isopleths, all cross linked so that researchers and policy makers can access and the data in various ways. This data base could be used by modelers, health researchers, etc. This would be an effort requiring funding to compile and maintain it.

6.3.4 Centralized facilities

This could be a central calibration laboratory for atmospheric measurement equipment, a central laboratory to produce “tailored” soot surrogates or other facilities that have specialized equipment that is not in continuous use by a specific institute but that is needed for a certain specialization. The neutron activation equipment, for example.

6.3.5 Publicity in general.

First will be the publication of the workshop report that specifies what the mission of the ASN will be and how to find out more information.

Secondly would be to have a poster at international meetings that describe the ASN.

Third would to have a booth at the EGU/EAC/AGU/IUGG with literature about the ASN.

Fourth, all companies that are impacted by soot should be contacted directly about the ASN, i.e. soot instrumentation companies, auto/aircraft/power companies.

Conclusions of ASEFI 2006

At the end of the ASEFI 2006 Workshop, all participants have supported the organization of the international Atmospheric Soot Network, between soot producers and soot experts in atmospheric measurements, modeling and laboratory studies, with the general purpose to have some real progress in the prediction of soot impact upon atmosphere.

The objectives of the Atmospheric Soot Network are :

- to build a link between engine makers, field observers, laboratory researcher and climate modelers, to elaborate the common approach for characterization of soot exhaust from engine and laboratory combustion sources;

- to elaborate the common basis for studies of soot-related atmospheric processes and to increase the common ability to use complementary techniques;

- to produce common laboratory soot for atmospheric studies, to elaborate, test and recommend Reference Soot Materials;

- to organize inter-laboratory comparisons to increase soot quality measurements in the atmosphere and progress in laboratory studies;

- to develop cooperative projects in the field of global changing and air quality.

- to remove the lack in the knowledge of physico-chemical properties of soot particles generated by industrial and residential emissions, vehicular and aircraft emission, domestic home heating, and biomass burning;

- to predict the lifetime of soot particles as well as their fate in either an atmospheric or biological context;

- to develop a comprehensive Soot Database of laboratory - characterized soots of natural and anthropogenic sources.

The creation of a Laboratory and Reference Soot Committee, responsible for the elaboration of common actions of ASN in respect of described objectives is under elaboration. All the information about ASN is available at the following website address: http://www.asn.u-bordeaux.fr. The ASN methodic and techniques as well as a list of potential ASN participants will be soon available.

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Appendix: List of ASEFI 2006 participants, available at the following ASEFI 2006 website address: http://www.asefi2006.u-bordeaux.fr